

Heats of Dissolution of Several Imidazolium-Based Ionic Liquids
into Low Dielectric Media

A Senior Honors Thesis

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We the undersigned have read this thesis and recommend the Award of Honors in Chemistry to Nathan Scharf upon completion of all requirements of graduation.

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Abstract:

Ionic liquids (ILs) are salts that are liquid at or near room temperature. They have unique properties since they are completely composed of ions and therefore have many potential applications. This thesis research focuses on the properties of ILs in low polarity solvent, chloroform (CHCl_3). The motivation for this research was to further confirm the presence of particularly stable, long-lived ion pairs for several different imidazolium-based ILs dissolved in chloroform, as evidenced in prior research by the presence of two resonance sets in ^1H NMR spectra.¹ Specifically, it was shown that the variation of experimental conditions such as temperature and concentration changed the relative intensities of the two sets of resonances in the ^1H NMR spectrum for the particular IL 1-ethyl-3-methylimidazolium bis(triflyl)amide ($[\text{C}_2\text{mim}][\text{NTf}_2]$), indicating an equilibrium between freely dissolved ions and ion pairs. From this discovery, it became relevant and of interest to measure the heats of dissolution of $[\text{C}_2\text{mim}][\text{NTf}_2]$, which are useful to assess the thermodynamic stability of the ion pair formation. For comparison, the heats of dissolution were also obtained for the structurally similar ILs 1-hexyl-3-methylimidazolium bis(triflyl)amide ($[\text{C}_6\text{mim}][\text{NTf}_2]$) and 1-hexyl-3-methylimidazolium tris(triflyl)methide ($[\text{C}_6\text{mim}][\text{MeTf}_3]$). These ILs serve as comparisons for the effect of imidazolium chain length and anion.

An RC1 calorimeter was used to obtain the heats of dissolution measurements of three imidazolium-based ILs using adiabatic controls. The dissolution of $[\text{C}_2\text{mim}][\text{NTf}_2]$, $[\text{C}_6\text{mim}][\text{NTf}_2]$, and $[\text{C}_6\text{mim}][\text{MeTf}_3]$ were observed to be exothermic, releasing a small amount of heat into the solution, varying from -2.5 kJ/mol for $[\text{C}_6\text{mim}][\text{MeTf}_3]$ up to -5.5 kJ/mol for $[\text{C}_2\text{mim}][\text{NTf}_2]$. To assess the reliability and accuracy of the measurements, the effect of different potential contaminants were examined, dissolved gas and solvent stabilizers

(amylenes). It was determined that these potential contaminants did not affect the heats of dissolution. Heats of dissolution measurements were found to be lower for [C₂mim][NTf₂] when dissolving into 96:4 CHCl₃:acetone solvent as compared to pure CHCl₃. Using Hess' Law, the change in enthalpy for the equilibrium between the freely dissolved ions and ion pairs in CHCl₃ was determined to be between -1.0 and -2.1 kJ/mol IL for each of the temperatures investigated in this study, the largest change in enthalpy being at the lower temperatures.

1. Introduction

1.1. History of Ionic Liquids:

Ionic liquids (ILs) have been a promising and rapidly growing area of research. The term ‘ionic liquid’ is that of relatively recent history. The current, working definition of an ionic liquid is a salt that has a melting temperature below the boiling point of water.² Despite the recent growth of ILs and their potential uses, the history of ILs dates back to the early 19th century to when the first room temperature IL (RTIL) was prepared.³ Prior to the term ionic liquids, the term ‘molten salts’ was and still is used, referring to an ionic compound in its liquid state. However, many salts require extreme conditions to become a liquid. For example, sodium chloride, table salt, has a melting point of 801°C.⁴ When comparing RTILs to molten salts, there is a large difference in melting points between these two types of liquid salts, and they have much different applications. Therefore, it only made sense for these particular liquid salts to have their own name, and the phrase ‘ionic liquids’ has been coined. IL research has continually grown and ILs have been studied and applied to a large range of purposes.

Initial interest in ILs sparked after an important discovery made from the analysis of a separated phase of a Friedel–Crafts reaction catalyzed by the Lewis acid AlCl_3 . The component of this phase was identified to be an IL with a cyclohexadienyl cation and a heptachlorodialuminate anion, Figure 1.² The cyclohexadienyl cation was a long-presumed intermediate of the Friedel-Crafts reaction. The incipient discovery in the Friedel-Crafts alkylation led to the research of using ILs containing Lewis acids as a solvent due to their catalytic properties.

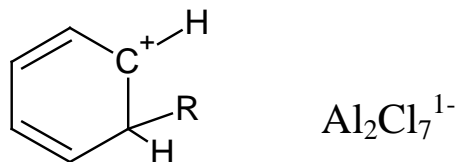


Figure 1. Cyclohexadienyl cation. The long presumed intermediate of a Friedel–Crafts reaction was determined to be an IL when coupled with the heptachloroaluminate anion.

The problem with chloroaluminate ILs is that they are water reactive, limiting their potential applications. This eventually led to research to find water stable ILs. Research at the Air Force Academy by Zawortko and Fuller led to an array of water stable ILs that could be prepared outside of a glove box.^{5,6} These ILs were imidazolium-based with a wide array of water stable anions of various sizes.

This research opened up the field of using ILs as a medium for chemical synthesis, especially for reactions where the IL can serve as a catalyst. Since then, the properties and applications of ILs are continually being studied, and IL research has been rapidly growing over the last decade. Figure 2 shows how the field has grown since the turn of the century and that it is continually growing, as is the research of ILs for novel applications. Current and potential future applications are further discussed in section 1.2.

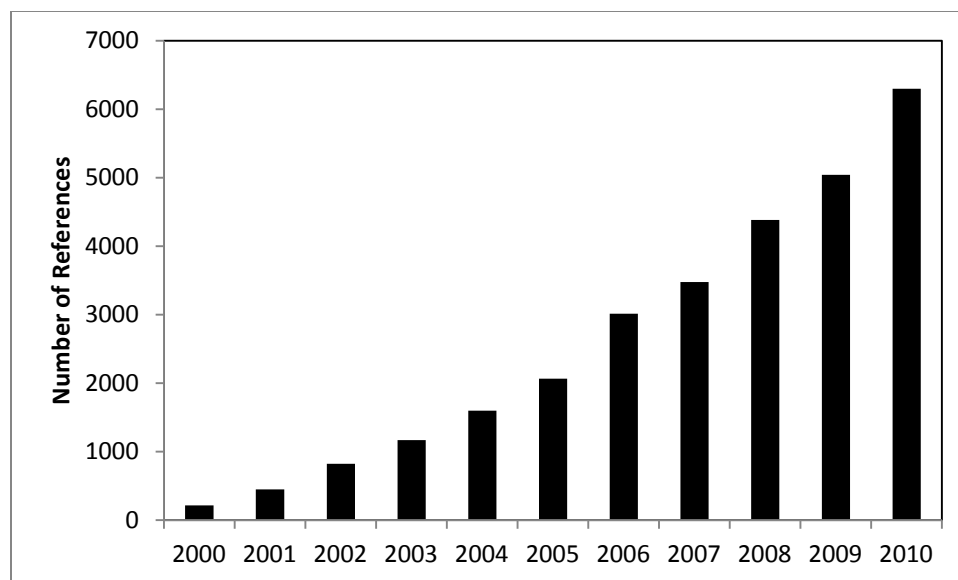


Figure 2. Number of references in SciFinder for the search “ionic liquids” for the years 2000 – 2010. There were 217 references for the year 2000, and 6,297 references for 2010 alone.

1.2. Uses of Ionic Liquids:

ILs, and more specifically, RTILs, are of great interest because of their potential for a broad range of applications. An initial interest of several ILs was as electrolytes in batteries.^{7,8} ILs have the potential to be much more efficient and longer lasting than the electrolytes currently used in batteries. This is due in part to their low volatility and their large electrochemical window. These and other properties of ILs are further discussed in section 1.3.

A large application of ILs is as a solvent in organic synthesis. As mentioned in section 1.1, some ILs have catalytic properties, such as being Lewis Acids for Friedel-Crafts reactions. ILs have also been used as a unique solvent in microwave-assisted reactions.⁹ Many organic solvents are limited in use for microwave reactions due to their relatively low boiling points, making them difficult for use under atmospheric conditions. Research also indicates that using ILs as the solvent for Diels-Alder reactions can increase the rate of product formation by more than 10-fold as well as the endo:exo selectivity.^{10,11}

As for other potential applications that won't be specifically discussed, ILs are being investigated for commercial use in gas storage and transport¹², and also for their potential as extraction solvents in chromatography^{13,14,15}. A 2007 Nature article has proposed the use of low temperature ILs as the fluid base of lunar telescopes for silver deposition.¹⁶ For those interested, there are numerous reviews summarizing the many current and potential applications of ILs. For example, Babu et al. summarize advances in the extraction and separation of rare-earth metals using ILs.¹⁷ Natelson et al. outline many of the chemical properties relevant to electrochemistry.¹⁸ A review by Bica et al. outlines Lewis acidic ILs, specifically chloroferrates, that act as a catalytic solvent system.¹⁹

1.3. Properties of Ionic Liquids:

In order to understand the properties of ILs, it is important to compare them to ionic compounds that are not ILs. An ionic compound is formed by the combination of positive and negative ions.²⁰ These ions are held together by the electrostatic force between the oppositely charged species. These compounds are inherently non-volatile because they are only composed of ions, making the transition to the gas phase unlikely. Most ionic compounds are very stable and are naturally found as a solid at room temperature, and they will only melt once a high enough temperature is reached.

In contrast, ILs are stable in the liquid phase at or near room temperature. The melting point of an IL is an important property because it determines the potential applications. Other properties such as viscosity, acidity, and conductivity can be adjusted by altering the cation and anion combination.^{21,22} An important question stemming from the discovery of ILs is “why are these ionic compounds liquid at low temperatures?”, or “why is the liquid state

thermodynamically favorable compared to the solid state?" Krossing et al. demonstrated that the conversion from solid to liquid of these particular compounds leads to small lattice enthalpies and large entropy changes are involved, favoring the melting of the ionic compounds.²³ In other words, in order for melting to occur, a large enough entropy change is needed to overcome the enthalpy loss from breaking the crystal lattice. This is the same reason any solid melts, but the reason for the comparably low melting points of ILs is attributed to the large size and conformational flexibility of the ions, something that most other ionic compounds lack.²³ With that said, changing the size and flexibility will therefore change the melting points and other physicochemical properties of the ILs. One subset of IL research involves understanding and formulating the effects of structural changes on the physical properties of the IL.²⁴

Since ILs are non-volatile, unlike other common organic solvents, they could potentially be used as an alternative to current organic solvents used. Before ILs are used prominently for commercial use and in laboratories, it is important to understand as many properties of ILs as possible. As previously mentioned, the viscosity, density, and melting temperatures of various ILs have been studied extensively^{5,21,25} and a significant amount of property data of ILs have been obtained.

However, there is only a limited amount of information about the physical properties of ILs and their effects as a solute. Most salts are not soluble in organic solvents such as CHCl_3 . As a result, there is minimal prior knowledge in this field. It is true that many of the applications of ILs is to serve as an alternative to organic solvents. However, typical organic synthesis methods using traditional solvents are required to synthesize the ILs. Therefore, there is certainly going to be interactions between the IL and the organic solvent during the synthesis process. From unpublished data obtained in the Hoffmann group, several RTILs were observed

to have two distinct ^1H NMR resonance sets. Further work by Tubbs and Hoffmann attributed this observation to the presence of ion pairing in solution, which is further discussed in section 1.4.¹

1.4. Chemicals In Solution:

When a chemical is dissolved into a solvent, the solvent molecules will interact with the species dissolved. Some molecules that dissolve will dissociate into charged species, while others that do not contain ionic bonding will not dissociate. The charged species that form from the dissociation of ionic compounds are not necessarily completely separated from their charged counterparts. While in a solution, the solvent and solute molecules are in equilibrium with each other. In a solution of one ionic compound, the most abundant species are the contact ion pairs (CA), the freely dissolved ions (C^+ and A^-), and solvent separated ion pairs ($\text{C}^+||\text{A}^-$).²⁶ The equilibrium among these species is outlined in Figure 3.

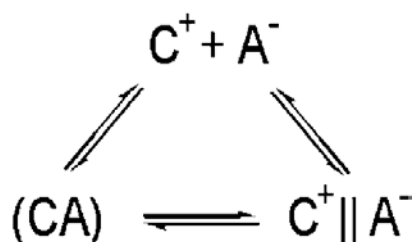


Figure 3. Equilibrium between the ionic species present in an ionic solution containing one dissolved species that forms one cation and one anion upon dissolution.

Not all ionic solutions are limited to these species due to the possibility of complex formation with the solvent (hydroxide complexes, etc). However, in the solutions of interest, complex formation with the solvent is not involved. The particular equilibrium of interest is the equilibrium between the contact ion paired species (CA) and the freely dissolved ions C^+ and A^- .

In order to understand this equilibrium, it is essential to understand what affects the equilibrium between freely dissolved ions and contact ion pairs. Ion paired species in a solution are not a new discovery and the conditions that affect this equilibrium are well understood. In our studies it was not experimentally possible to differentiate between the contact ion pair and the solvent separated ion pair, so the equilibrium in Figure 3 is simplified to the equilibrium between the freely dissolved ions and contact ion pairs:



The predominant factors that affect the equilibrium in equation (1) are temperature, ion concentration, solvent dielectric, and the size of the ions.

Since the temperature is simply a measure of the kinetic energy of a system, changes in temperature will have a predictable effect on the equilibrium. As the temperature increases, the ions in solution will have more energy, which will allow for the breakage of the ionic bonds between the ions. This increase in energy therefore causes the equilibrium to shift towards the freely dissolved species, so higher temperatures favor the freely dissolved ions. The effect of ion concentration on this equilibrium is a matter of probability. In order for ion pairing to occur in a solution, the molecules must come into contact with each other. The strength of these ion pairs should be independent of the ion concentration. However, an increase in the concentration itself should cause a shift in equilibrium toward the formation of ion pairs in solution.

The dielectric of the solution, a factor that is predominantly dependent of the solvent used affects the equilibrium of ions in a solution. The dielectric constant, ϵ , of a solvent is used as a quantitative measure of the polarity of that solvent. The dielectric constant is also known as the relative permittivity, which is a ratio of the electrical energy stored in the particle relative to that of free space (i.e. vacuum).²⁷ The larger the dielectric constant of a solvent the more polar the

solvent is. For comparison, chloroform is a low polarity organic solvent, where $\epsilon = 4.8069$ while for acetone, a polar solvent, $\epsilon = 21.01$.⁴ A polar solvent will contain stronger dipoles than a less polar or non-polar solvent. When in contact with the ions or ion pairs, these dipoles will shift the equilibrium of ionic compounds toward the dissociated ions, which interact favorably with the dipoles of the polar solvent. Therefore, a higher dielectric medium shifts the equilibrium towards the presence of charged species, causing the ion pairs to dissociate more. Adding solutes to a solvent can change the dielectric of the solution. However, in this study dilute concentrations (0.03*m*) of IL are used, and the contribution of the IL to the overall solution dielectric constant is negligible.¹

The size of the ion is an important factor in the equilibrium between the species, because the relative sizes of the cation and anion will affect how well they interact with each other, and how they could interact with the solvent. Since the interactions between the cation and anion are what lie at the heart of the formation of ion pairs, the size and conformation of the ions play an important role in understanding the equilibrium between species present in an ionic solution. This aspect is important to consider when comparing different ionic compounds to one another. The initial research focus was on [C₂mim][NTf₂], which is discussed in detail in section 1.6.1, and the ILs [C₆mim][NTf₂] and [C₆mim][MeTf₃] served as a comparison.

1.5. Imidazolium-Based Ionic Liquids:

Imidazolium-based ILs are of interest in current research because of the high degree of variability of the chemical properties. The variability is achieved by changing the alkyl chains that are attached to the nitrogen atoms on the imidazolium ring, as shown in Figure 4.

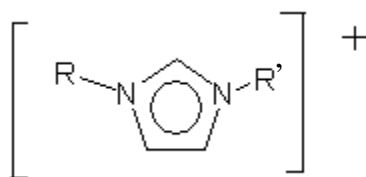


Figure 4. Imidazolium cation used for many types of ionic liquids. The variable alkyl chains are denoted by R and R'.

The positive charge of the cation is delocalized throughout the imidazolium ring. Also, the hydrogen atom attached to the carbon adjacent to both nitrogen atoms of the imidazolium ring can participate in hydrogen bonding. This is an important factor when understanding the varying physical properties observed for the imidazolium-based ILs. It is also important to consider hydrogen bonding when studying imidazolium-based ILs in solution. R' = CH₃ for all of the ILs in this study while R is either an ethyl (C₂) substituent or a hexyl (C₆) substituent.

Aside from the variability of the alkyl chains, the anion of the IL also has a substantial effect on the physical properties of the IL, which results in even more variability since there are a very large amount of anions that could be paired to the imidazolium-based cation. ILs with two different anions were studied in this thesis research. The bis(trifluoromethylsulfonyl)amide ion ([NTf₂]), as shown in Figure 5, is the anion for two of the three ILs investigated in this study. The negative charge of the anion has a large degree of delocalization due to the multiple resonance structures involved with the sulfonyl groups. The anion of one of the ILs studied is the tris(trifluoromethylsulfonyl)methide ([MeTf₃]) anion, shown in Figure 5.

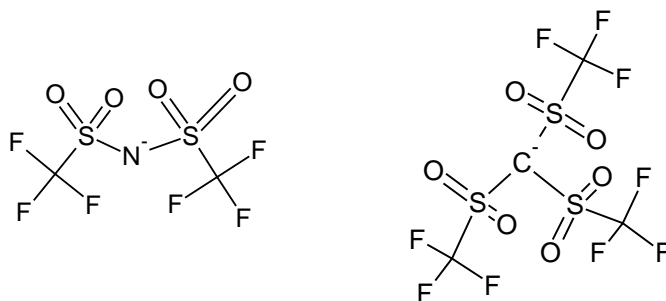


Figure 5. Bis(trifluoromethylsulfonyl)amide (left) and tris(trifluoromethylsulfonyl)methide (right) anions of the ILs studied.

1.6. Ion Pairing of 1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)amide:

Based on the work by Tubbs and Hoffmann, long-lived ion pairs of the IL $[\text{C}_2\text{mim}][\text{NTf}_2]$ are observable using ^1H NMR spectroscopy.¹ Tubbs and Hoffmann determined the effect of the dielectric constant, temperature, and concentration on the mole fraction of the freely dissolved cation, x_{C^+} , from ^1H NMR spectra of dilute concentrations of the IL in chloroform. Initial interest was of the IL studied by Tubbs and Hoffmann, $[\text{C}_2\text{mim}][\text{NTf}_2]$. Tubbs and Hoffmann's work that led to the thesis research is briefly described.

Tubbs and Hoffmann observed two distinct sets of resonances in the ^1H NMR spectrum for $[\text{C}_2\text{mim}][\text{NTf}_2]$ in chloroform-d (CDCl_3). When varying the dielectric the relative peak areas of the two resonance sets varied accordingly, as seen in Figure 6.¹

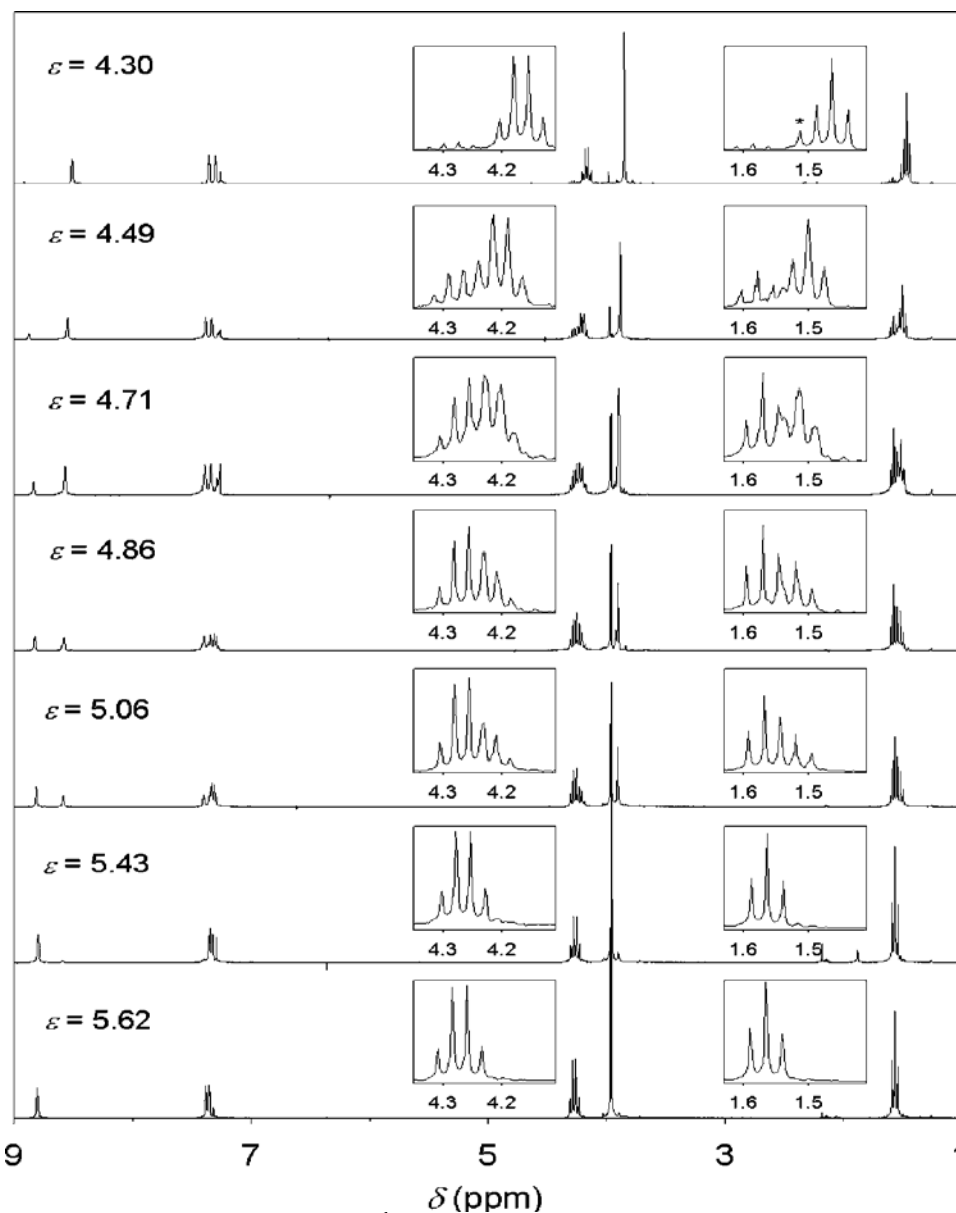


Figure 6. A series of ^1H NMR spectra at 25°C of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide in solvents of varying dielectric constants, ϵ .¹

Through various investigations, the most conceivable explanation for this observation was the presence of ion pairs that were long-lived enough to be observable by NMR spectroscopy. A closer look at Figure 6 displays the effect of the solvent polarity on the equilibrium between the freely dissolved and ion paired species. In the more polar solvent, $\epsilon = 5.62$, only the freely dissolved species are present, while in the less polar solvent, $\epsilon = 4.30$, the

ion paired species is predominant. By varying the concentrations of ions in solution, Tubbs and Hoffmann supported the hypothesis of long-lived ion pairing as the cause of the two resonance sets. Table 1 contains the concentrations of the solutions prepared by Tubbs and Hoffmann, whose spectra are shown in Figure 6. Carbon tetrachloride (CCl₄) was added to reduce the polarity of the solution, while acetone-d₆ (C₃D₆O) was added in small concentrations to increase the polarity of the solvent. Since only one resonance set was observed for a mixed solvent of 96:4 CDCl₃:C₃D₆O by volume, this was the ratio used for experiments in this calorimetric study of mixed solvents to completely dissociate the ion pairs. The dielectric values for the solution were obtained by Tubbs and Hoffmann using CRC values for the pure compounds and a fit as described by Wang and Anderko.^{4,28}

Table 1. ¹H NMR Sample Details

Volume (mL)			molality (mol·kg ⁻¹)	Dielectric, ε
CDCl ₃	CCl ₄	C ₃ D ₆ O		
0.80	0.20	0	0.0281	4.30
0.90	0.10	0	0.0283	4.49
1.00	0	0	0.0285	4.71
0.99	0	0.01	0.0286	4.86
0.98	0	0.02	0.0287	5.06
0.96	0	0.04	0.0290	5.43
0.95	0	0.05	0.0291	5.62

As prior stated, the initial interest of this thesis research was to better understand the ion pairing of [C₂mim][NTf₂] in low-dielectric media using calorimetry. For comparison, this research also includes calorimetry measurements for two other imidazolium-based ILs: [C₆mim][NTf₂] and [C₆mim][MeTf₃]. [c6mim][NTf₂] is structurally similar to [C₂mim][NTf₂], however [C₆mim][NTf₂] does not contain two ¹H NMR resonance sets. The only difference between [C₂mim][NTf₂] and [C₆mim][NTf₂] is the length of the 1-alkyl chain of the imidazolium cation (hexyl versus ethyl). The IL [C₆mim][MeTf₃] contains an anion with a carbon center, and

two ^1H NMR resonance sets were observed for this particular IL as was for $[\text{C}_2\text{mim}][\text{NTf}_2]$. The imidazolium ILs $[\text{C}_6\text{mim}][\text{NTf}_2]$ and $[\text{C}_6\text{mim}][\text{MeTf}_3]$ were chosen because they serve as two comparisons for structural differences: one varying the alkyl group on the cation, and the other having a different anion. These two ILs were also used because two resonance sets were not observed in $[\text{C}_6\text{mim}][\text{NTf}_2]$, while two resonance sets were observed for $[\text{C}_6\text{mim}][\text{MeTf}_3]$.

In order to assess the thermodynamic equilibrium of ion pair formation, a reaction calorimeter with adiabatic control measured the heats of solution of the IL into CHCl_3 . Differential Scanning Calorimetry (DSC) measured the specific heat capacities of the resulting solutions. The fundamentals behind DSC are outlined in section 1.7.2, and the specific heats obtained are reported in section 3.2. Gas Chromatography-Mass Spectrometry (GC-MS) was used to analyze the purity of the CHCl_3 solvent. The principles of GC-MS are described in section 1.8, and the data obtained is presented in section 2.5. The mass percent of water in the ILs and CHCl_3 was measured with Karl Fischer titrations (section 1.9). The water impurities obtained are listed in section 3.3.

1.7. Calorimetry:

Calorimetry is an experimental determination of the enthalpy changes of a chemical reaction or process.²⁰ There are numerous types of calorimeters to determine enthalpy changes, and different conditions can be used to obtain the desired information. Some calorimeters are able to operate via adiabatic control, where no energy is transferred as heat between the system and the surroundings. Therefore, adiabatic heating is a thermodynamic process where the heat lost to or absorbed from the surroundings is zero.²⁹ This allows for temperature changes to be directly correlated to the changes in enthalpy of the observed process. Equation (2) correlates

the heat, q , absorbed or released during a process to the mass and temperature of the substance, where m is the mass, C_p is the specific heat of the substance, and ΔT is the change in temperature of the process.

$$q = mC_p\Delta T \quad (2)$$

The specific heat of a substance is the amount of heat that needs to be absorbed by one gram of the substance in order to raise the temperature by one Kelvin. Measuring the heat is necessary in order to directly obtain any type of enthalpy value, for our study, the enthalpy of dissolution. Enthalpy is defined as the total heat content of a system, and the enthalpy of solvation is defined as the enthalpy change associated with the binding of solvent molecules to ions or molecules in solution.²⁰ The change in enthalpy is equal to the amount of heat transferred, q , at constant pressure per mole of substance. In order to precisely obtain various enthalpy measurements, different types of calorimeters have been developed, utilizing various heat flow measurements.³⁰ The specific type of calorimeter we used for measurements for the solvation of ILs into CHCl_3 is a reaction calorimeter with adiabatic control. Reaction calorimeters are particularly useful for obtaining enthalpy changes of reactions or processes that can be contained within a reaction vessel. Section 1.7.1 describes the fundamentals behind the reaction calorimeter and section 1.7.2 describes specific heat measurements using a differential scanning calorimeter (DSC).

1.7.1. Reaction Calorimetry:

A reaction calorimeter contains the solution of interest within a reaction vessel. This reaction vessel is encompassed by a cooling/heating jacket, which maintains the temperature of the reaction vessel. A liquid continuously passes through the cooling/heating jacket to maintain

the temperature of the jacket (T_J). Most reaction calorimeters tend to have two possible modes for obtaining enthalpy data, isothermal mode and adiabatic mode. For isothermal mode, the amount of heat added to this cooling/heating liquid varies to maintain an isotherm. The difference in heat required to maintain T_J reflects the amount of heat involved in the process occurring within the reaction vessel.

In adiabatic mode, the mode of interest, T_J is set so that it maintains the reaction vessel at the specified temperature as long as there are no other heat contributions. Any heat transfers within the reaction vessel will not affect the heat contribution from the cooling/heating jacket. Therefore, the heat transfers of interest will be contained within the vessel and can be measured by the changes in temperature of the reaction vessel (T_R). Since the temperature of the jacket is set to maintain a specific temperature of the reaction vessel, changes in T_R will cause small heat transfers between T_R and T_J . This systematic error is corrected for within the optimization parameters and analysis of the temperature measurements, both of which are described in more detail in the sections 2.1 and 3.1, respectively.

1.7.2. Differential Scanning Calorimetry:

Differential scanning calorimetry (DSC) is a thermometric method to identify various thermal properties of a substance. It is a differential measurement method because the instrument simultaneously measures the temperatures of the sample of interest and a container of same weight with a reference material with a well-known heat capacity, C_p . A different amount of energy is required to maintain the same heat rate for the two containers. This difference in heat delivered is a measure of the heat capacity for the sample of interest. There are two types of DSCs; heat flux DSC and power compensation DSC. The DSC utilized for this study was a heat

flux DSC. Heat flux DSC is different from other types of calorimeters in that the measurement utilizes heat flow rates instead of an absolute amount of heat. The heat flux DSC is a type of heat-exchanging calorimeter, where the primary measurement signal is a temperature difference between a reference and the reference containing the compound of interest. For the data collected, a disk-type heat flux DSC was used, and aluminum disks were used as the reference. As the reference and sample disks are heated concurrently, a differential signal is generated based on the different heat flow rates. The measured heat flow rate is determined based on the measurement of the difference in temperature, ΔT , between the two samples. The temperature is obtained as an electrical voltage. The DSC has an internal calibration to convert the measured ΔT to the heat flow rate. The calibration must be frequently checked by the user. The heat flow is used to obtain the heat capacity of the sample based on the known heat capacity of the reference. The inherent uncertainties of heat measurements for a properly calibrated DSC amounts to less than 5%.³¹

1.8. Gas Chromatography-Mass Spectrometry:

A gas chromatography-mass spectrometer (GC-MS) is an instrument that combines the capabilities of a gas chromatograph and a mass spectrometer. The GC-MS instrument is able to identify the chemicals present in a sample and their relative amounts. The GC unit chromatographically separates species in solution and determines their relative amounts, while the MS unit is able to identify the chemicals. The fundamental principles behind both of these instruments are explained separately in the ensuing subsections 1.8.1 and 1.8.2.

1.8.1. Gas Chromatography:

Chromatography is a technique widely implemented to separate different compounds from one another. In any type of chromatography the sample of interest is dissolved in a mobile phase, for GC this mobile phase is a non-interacting gas such as helium. This mobile phase is forced through a stationary phase which is fixed in place on a column. When the sample is injected into a GC instrument, it interacts with the stationary phase of the column establishing a dynamic equilibrium between solute in the mobile phase and in the stationary phase. The specific type of equilibrium depends on the type of chromatography (affinity, ion-exchange, etc). In gas chromatography, the equilibrium is a partition of the solute between the mobile gas phase and adsorption onto the stationary solid phase. The different compounds in the sample will spend different amounts of time in the mobile phase based on their individual equilibrium constants with the stationary phase. The less a solute interacts with the stationary phase, the longer it is in the mobile phase, and the faster it moves through the column. Once the sample passes through the column it reaches a detector, which then produces a peak with an area proportional to the amount of the compound that passed through the detector. The time it takes to pass through the column is known as the retention time. Compounds will have different retention times based on the column. Therefore, different columns can be used to accommodate for the separation of the chemicals that are of interest.³²

1.8.2. Mass Spectrometry:

Mass spectrometry, as briefly mentioned in section 1.8, is able to identify the chemicals present in a sample. This is accomplished by ionizing the molecules and then separating these molecular ions based on their mass-to-charge ratios (m/z). An electron beam is used to ionize

the molecule, which results in smaller cations, radicals, and neutral molecules. The neutral molecules and negative ions are separated out, leaving only the positively charged ions. These ions pass through a magnet, which separates the ions based on their m/z . The ions then enter a collector which records the relative number of fragments with a particular m/z , producing a mass spectrum as seen in Figure 7 for chloroform.

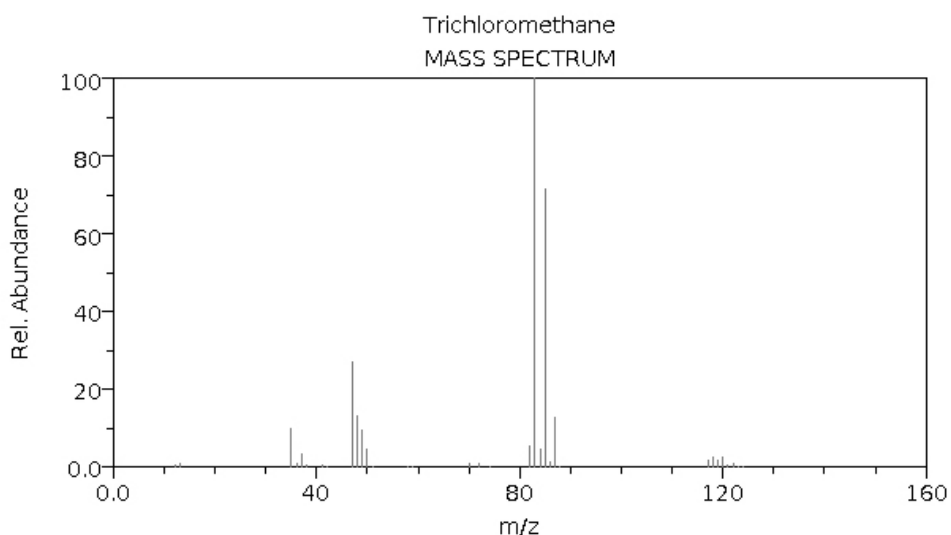


Figure 7. Mass spectrum of trichloromethane (chloroform) obtained from the NIST online database.³³

Since the charge of the fragments is usually +1, the m/z is essentially a measure of the molecular mass of the fragment.³⁴ The relative abundances of the different fragments are based on the stability of the fragments formed when bonds within the molecule are broken due to the electron ionization. In other words, the most stable fragments form when the weakest bond is broken. The different m/z values and their relative abundances allows for a mass spectrum to identify the chemical. The largest m/z value usually reflects the molecular weight of the compound. For example, for chloroform, chlorine has two isotopes with atomic weights of 35 and 37. The relative abundance of the Cl-35 and Cl-37 isotopes are approximately 76% and 24%, respectively. Due to the isotopes of chlorine, there are several different fragment peaks in

Figure 7. The peaks near an m/z of 120 result from the multiple possible combinations from the three chlorines having one of the two isotopes. For chloroform with all Cl-35, the m/z is 116, while for chloroform with only Cl-37, the m/z is 122. The most abundant fragment of chloroform is the fragment that results from breaking a C-Cl bond, leaving a carbocation and chloride ion. The two isotopes of chlorine can be seen at m/z below 40, and the relative abundances of the two isotopes could be calculated based on their relative intensities.

1.9. Karl Fischer Titration:

The ILs of interest are rather hygroscopic, and large water impurities could result in significant errors in the calorimetry measurements. Karl Fischer (KF) titrations were implemented to quantitatively determine the water impurities of the ILs studied. There are two different types of KF titrations: a volumetric titration and a potentiometric titration. A KF potentiometric titration was used for these studies. The chemistry behind the KF titration is similar to that of any titration: it involves a reaction between an analyte, water in this case, and a titrant that will react with the analyte. The titrant is added until all of the analyte is reacted, and the endpoint is reached. The titrant in this case is the $ROSO_2^-$ complex. Equations (3) and (4) are the reactions that occur between the titrant and the analyte.³⁵



As seen in equations (3) and (4), the presence of alcohol (ROH) is necessary to form the complex $ROSO_2^-$ which reacts with H_2O present in the sample and I_2 .

A typical KF titration contains two sets of Pt electrodes. One set is for the I_2 generation, while the other set is to detect the end point. For I_2 generation, the anode solution contains the

chemicals required for the reactions in equations (3) and (4) to occur: an alcohol, a base, SO_2 , and I^- . The cathode solution contains chemicals that can be reduced at the cathode. In order for the oxidation-reduction chemistry of SO_2 and I_2 to occur, there must be an ion-permeable membrane between the anode and cathode solutions.

The potentiometric KF titration endpoint is determined using bipotentiometric end-point detection probes. These probes measure the voltage at a constant current, and once the equivalence point is reached, an excess of I_2 causes an abrupt voltage drop, indicating the endpoint of the titration.³⁵ Reproducibility of water content measurements using the potentiometric KF titration is 0.5% or better.³⁶

2. Methods:

A Mettler-Toledo RC1e Reaction Calorimeter was used to monitor the heats of dissolution of various ILs into chloroform (CHCl_3 , Merck). The calorimeter was in adiabatic control to obtain precise temperature measurements for the dissolution of the IL into the solvent. The calorimeter controls were optimized for the injection of IL into CHCl_3 . The reaction calorimeter was controlled by RC1 iControl 4.0 software. A labeled schematic of relevant parts of the RC1 Calorimeter is provided in Figure 8. The reaction vessel was thoroughly cleaned by hand between each experiment using acetone and Kimwipes.

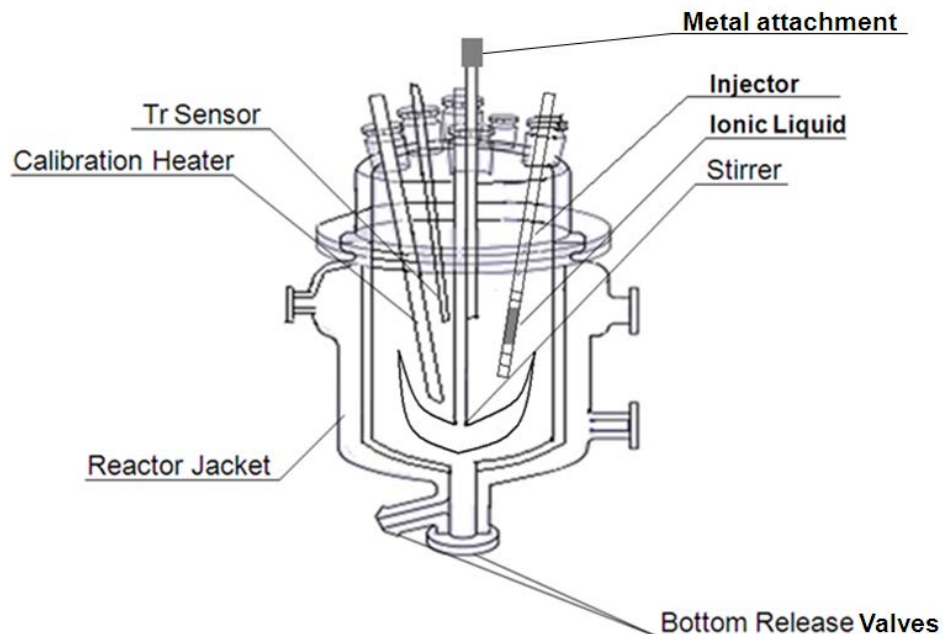


Figure 8. A schematic of the RC1 Reaction calorimeter vessel. An anchor stirrer was used for the experiments. The reactor had a 1.0 liter capacity. A volume of 300mL CHCl_3 was used for each experiment.

2.1. Optimizing RC1 Calorimeter Software:

The chemical properties listed in Table 2 of the chemicals studied were inputted into the software. The values for CHCl_3 were obtained from CRC Handbook of Chemistry and Physics.⁴ The density and specific heat values for $[\text{C}_2\text{mim}][\text{NTf}_2]$ were obtained from Bonhôte et al. and Walizewski et al., respectively.^{25,37} With the RC1 Calorimeter completely assembled (For Assembly/Disassembly, see Appendix A), 300mL CHCl_3 was added to the reaction calorimeter to obtain the necessary optimization parameters for adiabatic control of a CHCl_3 solution. The vendors of the different chemicals studied (ILs and CHCl_3) are listed in Table 2.

A computer-controlled experiment was conducted so that the “P (amplification)” and “I (Reset time)” values could be determined for the chloroform solvent. These parameters are used for heating and cooling the contents of the container to the specified temperature with an appropriate response time.

Table 2. Chemical properties for Chemicals Studied*

Name	Chloroform	[C ₂ mim][NTf ₂]	[C ₆ mim][NTf ₂]	[C ₆ mim][MeTf ₃]
Formula	CHCl ₃	C ₈ H ₁₁ N ₃ O ₄ S ₂ F ₆	C ₁₂ H ₁₉ N ₃ O ₄ S ₂ F ₆	C ₁₃ H ₁₉ N ₂ O ₆ S ₃ F ₉
Boiling Pt (°C)	61			
Mol. Weight (g/mol)	119.38	391.31	447.42	566.48
Density (g/mL)	1.489	1.52		
Spec. Heat (J/g/K)	1.6135	1.291		
Vendor	Merck, 99.8% (HPLC grade)	IoLiTec	Merck	Merck

*For mixed solvent studies, HPLC grade, 99.8% purity acetone was used (Merck, LiChrosolv)

The P and I parameters were determined for the chloroform solvent using the RC1 iControl software and an Excel Spreadsheet (Table 3) provided by the Mettler-Toledo software, the optimum P and I values were found to be P = 5.2, and I = 133 seconds. The user entries in the spreadsheet shown in Table 3 were obtained from a heating and cooling experimental run. After testing the P and I values by iteratively heating the CHCl₃ in the calorimeter and observing the resulting temperature profile, the P value was adjusted to 4.5 for better temperature control and quicker temperature changes.

Table 3. Spreadsheet to Calculate P and I for chloroform

		heating	cooling	
User entries	Experiment time at change of T _J set point (s)	4537	8193	
	T _R value at start (°C)	23.2579	33.1031	
	Experiment time at inflection point (s)	4623	8271	
	T _R value at inflection point (°C)	25.115	31.534	
	T _R slope (dT _R /dt) at inflection point (K/s)	0.036621	-0.038678	
	T _R value after 1 h (°C)	33.1013	23.2402	
Intermediate Values	C (°C)	21.97	34.55	
	Θ, Theta (s)	35.29	37.43	
	T, Tau (s)	268.79	255.00	
Results		Average		
	P, amplification	5.48	4.90	5.19
	I, Reset time (s)	129.16	137.00	133.08

After obtaining the P and I values for CHCl_3 , the parameter “slope” was determined for adiabatic control. The slope affects the amount of heat that passes through the reaction vessel in order to maintain a constant temperature. Depending on the contents of the vessel, the slope needs to be adjusted to ensure that enough heat, and not too much, is used to maintain the desired temperature. This parameter was determined simply by testing different values for the slope to determine what slope maintained a constant temperature in adiabatic mode. The slope was determined to be -0.15, with an “offset” of 0.25°C . The offset is a correction so that the selected temperature of the solution on the software is the actual temperature of the solution in adiabatic mode.

2.2. Determining Loss of Chloroform Due to Condensation:

With all of the necessary operating parameters determined, a known amount of CHCl_3 was added to the reactor. In order to determine how much CHCl_3 condenses on the walls of the reaction vessel upon heating to higher temperatures, a series of trials were conducted at 25°C for which CHCl_3 was massed, added to, removed from the reaction vessel and re-massed. This was done several times until there was a consistent mass loss. This consistent mass loss is due to evaporation of the solvent during the filling and emptying, and is unpreventable under the measurement conditions used. The temperature of 25°C was used as a reference for comparing the amount of condensation that would form at higher temperatures. This is based on the assumption that there is a negligible amount of condensation at 25°C . Figure 9 shows the mass losses with each successive measurement at 25°C .

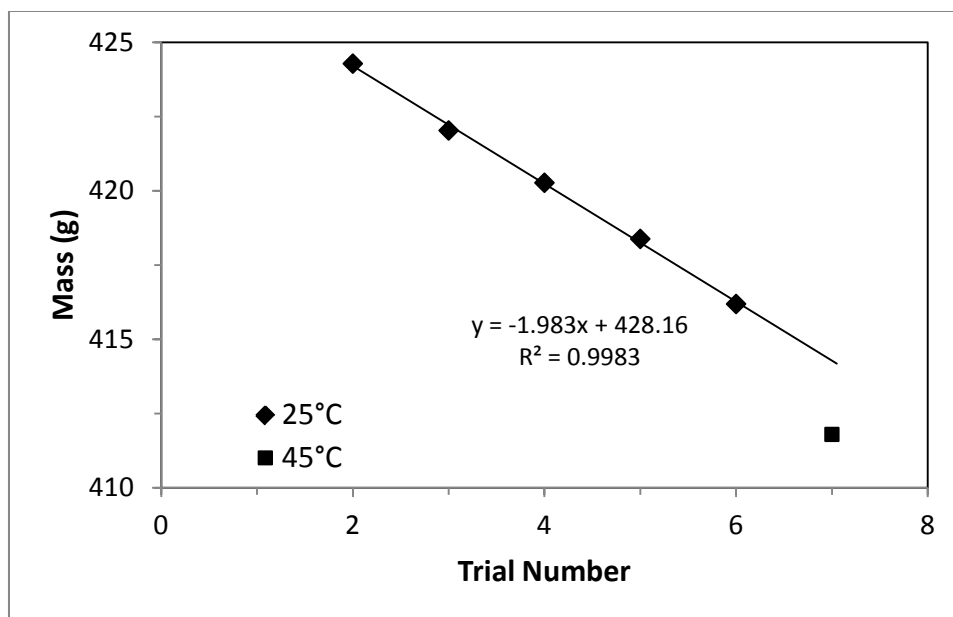


Figure 9. Masses of successive filling and emptying of reaction vessel at 25°C. The trend line was used to obtain the mass loss due to condensation at 45°C (2.48g, 0.0208mol) based on a deviation from this fit and the mass collected at 45°C.

The slope of Figure 9 predicted the expected mass for removal #7 of CHCl_3 at 25°C. The temperature of the reactor containing the CHCl_3 was increased to 45°C, and after the temperature was constant for 10 minutes the CHCl_3 was removed and remassed. This actual mass was compared to the expected mass to determine the loss of CHCl_3 due to condensation on the inside walls of the reactor. The mass loss due to condensation at 45°C was determined to be 2.48 ± 0.16 grams. The same procedure was done for 35°C and the mass loss due to condensation at 35°C was 1.88 ± 0.19 grams. The uncertainties were obtained from the linear regression.

2.3. Injecting Ionic Liquid into the Reactor:

A custom made glass piece with a ground glass joint to connect to the reactor was used to inject IL into the reactor. A schematic of the injector is shown in Figure 10. Teflon pistons with Viton O-rings were used to contain the IL inside the injector so the IL was submerged in the

solvent (CHCl_3) but not exposed to it. Using Teflon and Viton was necessary because other common plastic materials such as Buna-n are incompatible with CHCl_3 .

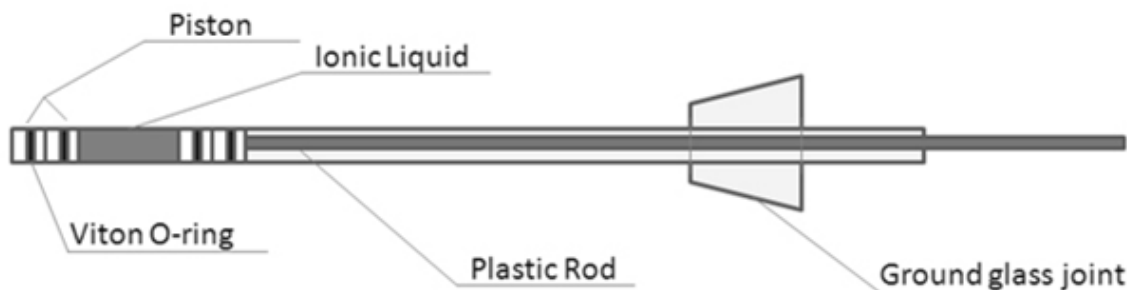


Figure 10. Schematic of the injector that delivered the IL into the CHCl_3 using four pistons to ensure precise delivery and minimize solution loss.

To prevent any possible contamination and to ensure that all the IL was transferred into the solution, four pistons were used; two above the IL and two below the IL. A plastic rod was used to gently push the pistons and IL out of the injector, making sure not to contaminate the upper part of the glass injector with solution. A volume of 0.8mL of IL was added and measured by mass ($\pm 0.0001\text{g}$). Once the injector had the IL contained within pistons, it was placed in a ground-glass fitting on the calorimeter. When the instrument was under adiabatic control and the temperature was constant, three of the pistons were injected using the plastic rod. The stirrer was on and spinning at 150 rpm when the instrument was equilibrating the temperature and during injections.

Since the injector is submerged in the solution, there was some residual solution on the injector once removed. In order to minimize and account for this mass loss the following two precautions were taken. When injecting the pistons, the last piston in the injector was not injected into the solution to prevent the solution from entering the injector, minimizing the amount of solution lost when removing the injector. To account for the mass loss, the injector was massed after removal and re-massed after cleaning to determine the amount of solution lost.

Multiple injections were performed into the solution at an isotherm to obtain heat of dissolution measurements as a function of concentration. The IL was injected into the solution until there was a separation of phases. It was known that this separation occurred near $0.03m$ for $[\text{C}_2\text{mim}][\text{NTf}_2]$.¹ The separation was indicated by a visible cloudy solution and beading of liquid at the bottom of the container. The other ILs tested, $[\text{C}_6\text{mim}][\text{NTf}_2]$ and $[\text{C}_6\text{mim}][\text{MeTf}_3]$ did not show any separation at the concentrations studied.

2.4. Saturating Solution with Gas:

Plastic tubing that was non-reactive with CHCl_3 was connected to 99.999% pure nitrogen gas. The tubing was submerged into a beaker containing CHCl_3 and the solution was bubbled with the nitrogen for 10 minutes to saturate the CHCl_3 with nitrogen gas. After saturation, the CHCl_3 was massed and added to the reactor to obtain heat of dissolution measurements as described in section 2.3.

2.5. Removing Amylene Stabilizer:

Amylenes are unsaturated five-carbon hydrocarbons, which are added to the chloroform by the manufacturer to remove any residual HCl via electrophilic addition to the amylenes (methylbutene). The residual HCl is produced from decomposition of the chloroform. The amylenes stabilizer was removed from CHCl_3 using a procedure from the patent literature.³⁸ Laboratory grade 96% sulfuric acid was used to purify the CHCl_3 of the amylenes. A 1:70 volume ratio of sulfuric acid to CHCl_3 was used. The CHCl_3 and sulfuric acid was added to a separatory funnel, which was shaken for 10 minutes, venting occasionally. The sulfuric acid was separated out from the CHCl_3 and the CHCl_3 was dried using sodium sulfate. The CHCl_3 was

distilled on a rotary evaporator. The resulting solution was analyzed using gas chromatography/mass spectroscopy. The GC-MS results in Figure 11 show that the amylene stabilizers, the methylbutenes, which are present in the untreated chloroform were successfully removed after the purification process. Only negligible amounts of 1,2-dichloroethane and 1,2-dichloroethene remained. The purified CHCl_3 was then used the same way as unpurified CHCl_3 for injections of IL as described in section 2.3.

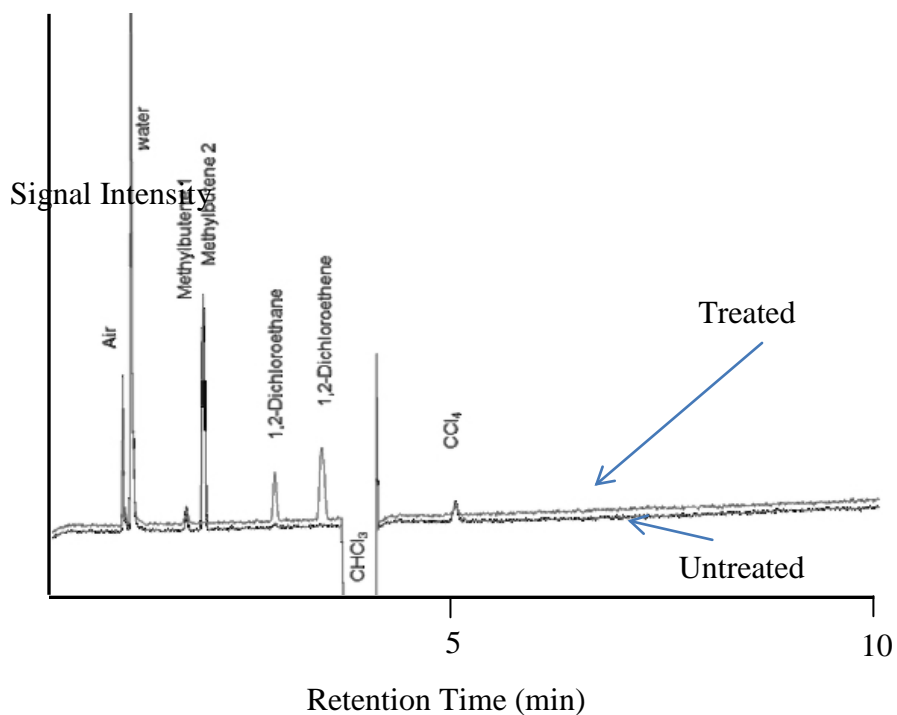


Figure 11. GC-MS comparison of the untreated and treated CHCl_3 . Methylbutene1 and methylbutene2 were successfully removed from the treatment.

3. Results and Discussion:

3.1. Equal Area Method for Obtaining Change in Temperature:

The reaction calorimeter software recorded the temperature of the reactor to $\pm 0.001^\circ\text{C}$ every two seconds. Since the heat change from dissolution is not instantaneous, the equal area

method was used to accurately determine the change in temperature of the solution from the dissolution of the IL. Figure 12 shows how this method was applied for one exemplary temperature versus time plot obtained after injection of 0.8mL of [C₂mim][NTf₂] at 25°C.

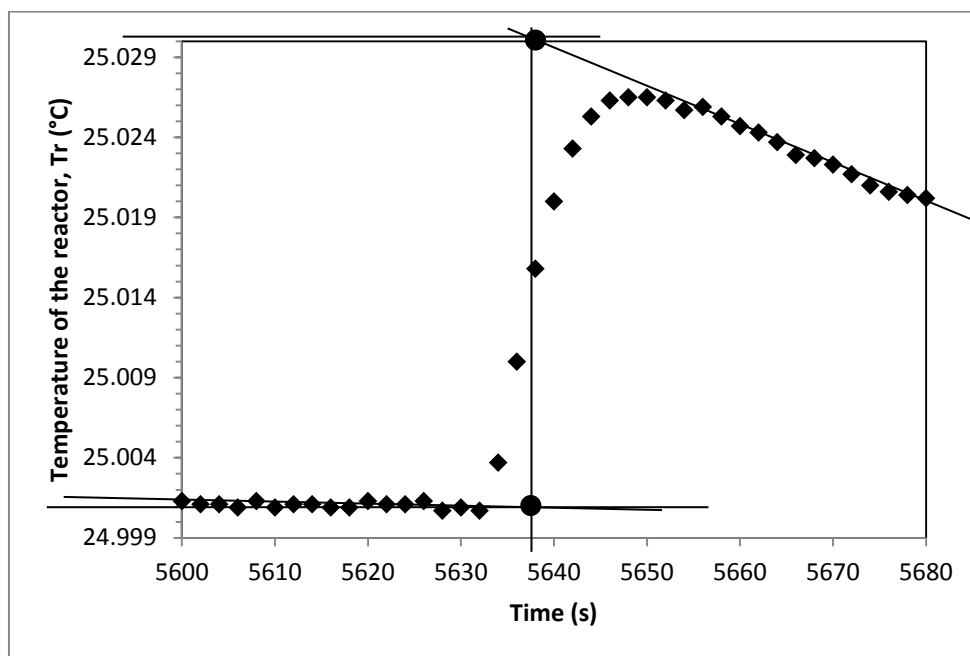


Figure 12. Temperature versus time of a 0.8mL injection of [C₂mim][NTf₂] into CHCl₃ at 25°C. The change in temperature is 0.029°C.

With the change in temperature, ΔT , the heat, q , can be determined using equation (2), where m is the mass of IL injected and C_p is the specific heat obtained from DSC data (described in section 3.2).

3.2. Specific Heats:

The specific heats of the ILs studied were obtained using DSC. Figure 13 contains the raw data obtained from the DSC for the three ILs studied. There are artefacts present in the region of 33°C – 35°C that appear in every DSC scan. Since the heat capacity trends are linear

as a function of temperature, the specific heats, C_p , of these ILs were therefore fitted to linear functions to produce equations (5) through (7).

$$[\text{C}_2\text{mim}][\text{NTf}_2] \quad C_p(\text{J/g/K}) = 0.000746T(\text{K}) + 1.2822 \quad (5)$$

$$[\text{C}_6\text{mim}][\text{NTf}_2] \quad C_p(\text{J/g/K}) = 0.00140T(\text{K}) + 1.3805 \quad (6)$$

$$[\text{C}_6\text{mim}][\text{MeTf}_3] \quad C_p(\text{J/g/K}) = 0.00143T(\text{K}) + 1.2576 \quad (7)$$

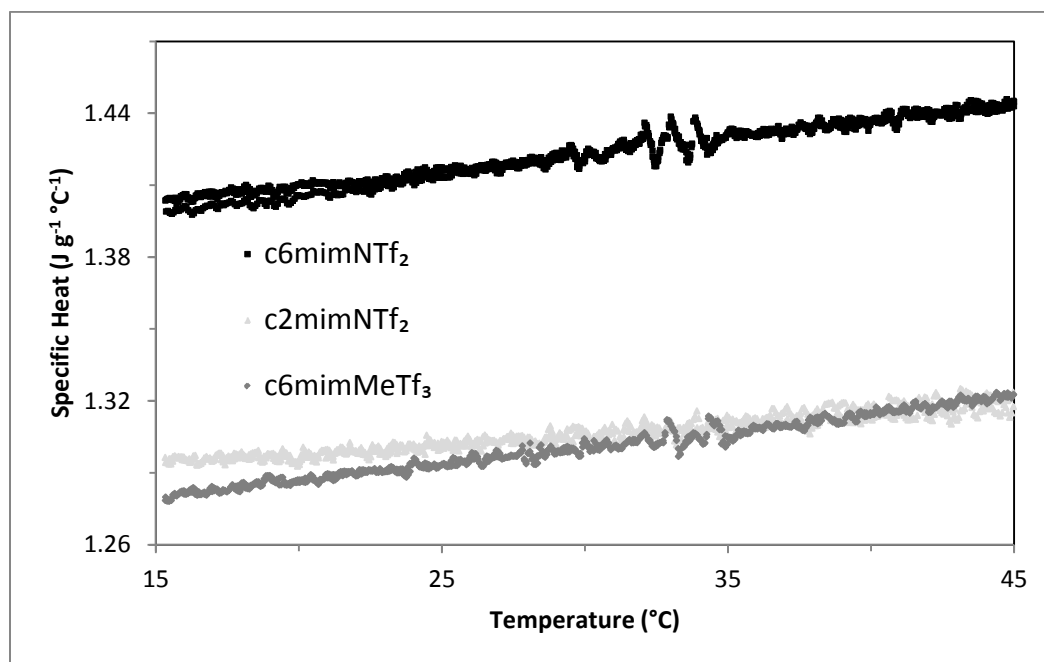


Figure 13. DSC heat capacity data for the IL $[\text{C}_2\text{mim}][\text{NTf}_2]$ as a function of temperature. The deviations from the trend near 34°C were inherent with the instrument used and the heat capacity measurements consistently contained these deviations for all measurements.

From these fit equations, the specific heat values were obtained for the temperatures of interest for each IL and are listed in Table 4. The solvents CHCl_3 and acetone are both well-studied chemicals, and the specific heats of these chemicals listed in Table 4 were obtained from the literature as follows. CRC Handbook values were used for the solvents at 25°C .⁴

Table 4. Specific Heats for ILs, chloroform, and acetone ($\text{J g}^{-1} \text{K}^{-1}$)

Temperature ($^{\circ}\text{C}$)	$[\text{C}_2\text{mim}][\text{NTf}_2]$	$[\text{C}_6\text{mim}][\text{NTf}_2]$	$[\text{C}_6\text{mim}][\text{MeTf}_3]$	CHCl_3	Acetone
15	1.293	1.402	1.279	0.947	2.137
25	1.301	1.416	1.293	0.957	2.175
35	1.308	1.430	1.308	0.960	2.192
45	1.316	1.444	1.322	0.966	2.220

Fit equations were used to obtain the specific heats at the other temperatures for CHCl_3 and acetone since their specific heat capacities are linear over the temperatures of interest.

$$\text{CHCl}_3 \quad C_p(T)(\text{Jg}^{-1}\text{K}^{-1}) = 6.28 \cdot 10^{-4}T(\text{K}) + 0.9378 \quad (8)$$

$$\text{Acetone} \quad C_p(T)(\text{Jg}^{-1}\text{K}^{-1}) = 2.775 \cdot 10^{-3}T(\text{K}) + 1.337 \quad (9)$$

Equation (8) for chloroform was obtained from Atkins and Paula.³⁹ Equation 9 for the specific heat of acetone, is published on the National Institute of Standards and Technology (NIST) website and based on experimental data from Malhotra and Woolf for temperatures between 278.15 and 323.15K.^{33,40}

In order to accurately determine the heat involved in the dissociation of the IL, the variable components of the solution must be considered with each successive addition. In order to account for the solution changing in composition, a new mass of CHCl_3 and IL was determined for each injection based on the amount of solution loss after removing the injector from the prior run, as described in section 2.3, and the amount of IL injected. Since the mole fraction of IL increases with each successive addition, a new specific heat value, C_p , was obtained for each injection. At sufficiently dilute concentrations, as in this study, the properties of the solution will not deviate significantly from an ideal liquid-liquid solution. Therefore, equation (10) was used to determine the heat capacities of the solutions, $C_{p,\text{soln}}$, where n is the number of components, x_i is the mole fraction of component i , and $C_{p,i}$ is the heat capacity of

component i . Only two components were present when injecting IL into pure CHCl_3 , and three components were present when using a mixed solvent of 96:4 CHCl_3 :acetone.

$$C_{p,soln} = \sum_{i \rightarrow n} x_i C_{p,i} \quad (10)$$

3.3. Impurity Analysis:

Before performing any injections of ILs, just the pistons were inserted into the injector and were injected into the CHCl_3 solution. This was performed to determine whether the frictional heat from injecting the pistons along had any possible effects on the temperature changes observed. There was no observable change in temperature from the injection of pistons only. Therefore, there is no detectible error resulting from the friction of forcing the pistons out of the injection tube into the solution.

Figure 14 displays the heats of dissolution of $[\text{C}_2\text{mim}][\text{NTf}_2]$ into CHCl_3 at temperatures of 15, 25, 35, and 45°C. There is no significant difference between the values obtained when dissolving IL into CHCl_3 if the amylene stabilizer or dissolved gases are present in the solution. Due to these results, the heat values for all three experiments were averaged to obtain more reliable values for the heats of dissolution of $[\text{C}_2\text{mim}][\text{NTf}_2]$. The heats of dissolution for a mixed solvent are discussed in section 3.5.2. There was a relatively large amount of deviations and uncertainty for the replicate measurements. This is due to the small temperature changes upon dissolution (~ 0.03 °C). It was noticed that the first injection of an experiment, IL into pure CHCl_3 , resulted in systematically lower heat measurements. However, without a sufficient amount of data, these apparent systematic differences cannot be considered significantly different, so they were included when obtaining average heats.

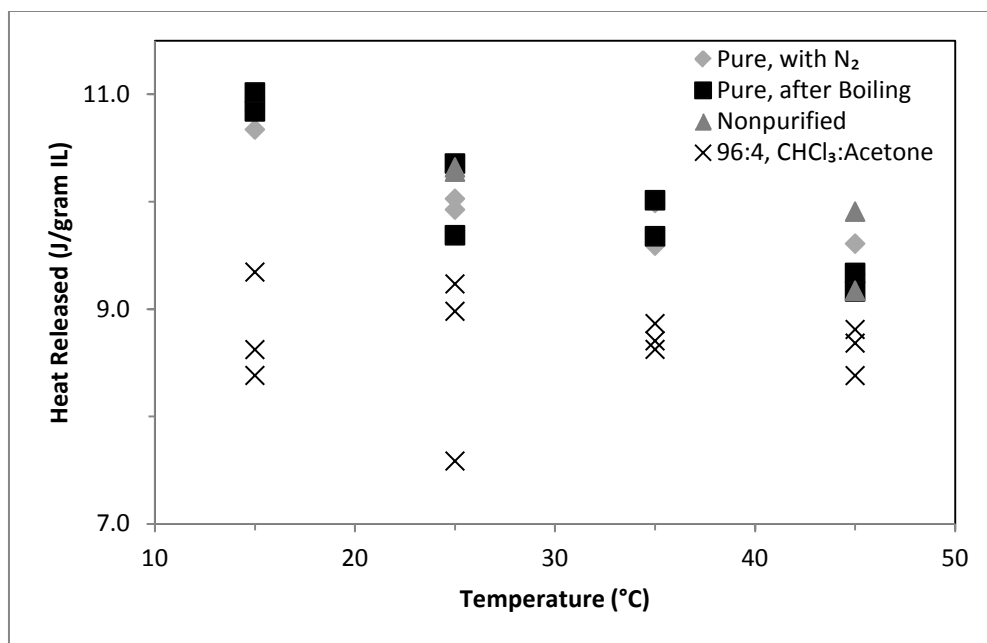


Figure 14. Heats of dissolution of $[\text{C}_2\text{mim}][\text{NTf}_2]$ into low dielectric solvents (pure CHCl_3 or 96:4 CHCl_3 :acetone) at varying temperatures. The averages of these points are in Figure 16.

In addition to these impurity tests, the Karl Fischer (KF) titration data was used to assess the water impurity of the ILs used. The results from the KF titration are summarized in Table 5.

Table 5. Karl Fischer Water Impurity Analysis*

Sample	Mass Percent H_2O
$[\text{C}_2\text{mim}][\text{NTf}_2]$	0.12
$[\text{C}_6\text{mim}][\text{NTf}_2]$	0.35**
$[\text{C}_6\text{mim}][\text{MeTf}_3]$	0.17
CHCl_3	0.02

*KF samples were prepared at the beginning and end of using a batch, highest impurity obtained is reported.

**0.35% H_2O in $[\text{C}_6\text{mim}][\text{NTf}_2]$ was the measured percent for the first sample taken from the bottle.

The largest water content was 0.35% by mass, which is higher than typical for the study of most ILs. However, this was the amount of water measured for a sample taken directly from a new bottle of the IL. Therefore, it was determined whether the amount of water present in

[C₆mim][NTf₂] resulted in a significant change in the total amount of water in the IL-CHCl₃ system. A typical injection of [C₆mim][NTf₂] is 1.1 grams. With a percent water of 0.35%, this is an injection of approximately 0.0038 grams of water. The amount of chloroform for a typical experiment was 420 grams; containing 0.084 grams of water present based on the KF data for CHCl₃ in Table 5. Therefore, injecting the IL into chloroform would increase the mass percent of water to a total of 0.021% water by mass in the resulting solution, compared 0.02% for pure chloroform. Due to this negligible change in the total water of the system, it is a valid conclusion that the 0.35% water in [C₆mim][NTf₂] does not have an effect on the results.

3.4. Concentration Dependence of Heats of Dissolution:

The equilibrium between freely dissolved ions and ion pairs in Figure 3 is often dependent on the concentration of the solution, and Tubbs and Hoffmann show a concentration dependency on the relative amounts of ion paired and freely dissolved species.¹ Due to this, a concentration dependency was originally expected for the heats of dissolution. Figure 15 shows the heats obtained for the different injections of 0.8mL of [C₂mim][NTf₂] into CHCl₃ as a function of concentration for the injections at the temperatures studied.

The data indicates that the heats of dissolution are concentration independent, which was not our original expectation. Since the heats of dissolution are concentration independent, it is possible that there are competing effects between the heats absorbed during the breakage of ion pairings and the heats released when the solvent interacts with the ions and/or the ion pairs in solution. It is known that heat is used up to break ion pairs and form the free ions, which according to Tubbs and Hoffmann, approximately 40% of the [C₂mim][NTf₂] is freely dissolved at the highest concentrations tested at 25°C. Since the heats of dissolution are overall

exothermic, these ‘competing effects’ would have to be overall exothermic. This would indicate that the ion – dipole interactions release more heat than is required to break the interactions of the contact ion pairs and the dipole – dipole interactions of the solvent molecules.

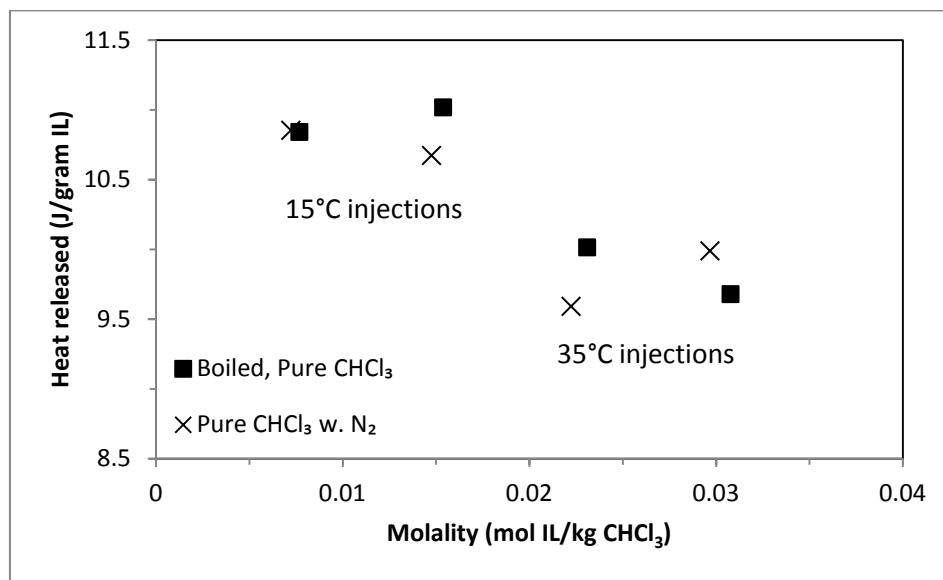


Figure 15. Heats of dissolution of [C₂mim][NTf₂] as a function of concentration at two different temperatures. The concentrations are the resulting molalities after IL addition.

3.5. Mixed Solvent Studies:

As seen by Tubbs and Hoffmann’s work, varying the dielectric of the solvent varies the relative amount of ion pairs in solution.¹ Their studies allowed for the mole fractions of the ion paired species and freely dissociated ions to be obtained based on the relative peak intensities of the ¹H NMR signals (Figure 6). With a mixed solvent, the effects of acetone must now be considered for all the calculations. The heat capacity is calculated as described in section 3.2, now with three components. Since condensation occurs at higher temperatures, section 3.5.1 determines if the actual amounts of chloroform and acetone in solution vary significantly due to

the condensation that occurs. The effects of the solvent dielectric on the heats of dissolution are discussed in section 3.5.2.

3.5.1. Condensation of Binary Mixture:

With a mixed solvent, condensation will still occur on the walls of the reaction vessel. However, the condensate is no longer a pure solvent so it is important to consider if this will have a significant effect on the subsequent calculations. At the low concentrations of acetone used (96:4 CHCl₃:acetone) it is a valid assumption that the binary mixture of chloroform and acetone deviates little from an ideal solution. Therefore, Raoult's law, equation (11), can be used to obtain the partial pressures, P_j , of the two components from the mole fractions, x_j , and the vapor pressures, P_j^* , and predict the relative amounts that condense for the two components in the mixture. It is assumed that there is still minimal condensation at 25°C and that the same amount of molecules condense on the walls of the vessel at higher temperatures as determined in section 2.2.

$$P_j = x_j P_j^* \quad (11)$$

The vapor pressures of CHCl₃ and acetone were determined using equation (12), known as the Antoine Equation. The Antoine coefficients used were calculated and published on the NIST website from literature vapor pressure values and are listed in Table 6.^{41,42} The vapor pressures calculated for CHCl₃ and acetone are in Table 7.

$$\log_{10} P(\text{bar}) = A - \frac{B}{T(K)+C} \quad (12)$$

Table 6. Antoine Coefficients

Coefficient	Component	
	CHCl ₃	Acetone
A	4.20772	4.42448
B	1233.129	1312.253
C	-40.953	-32.445

Table 7. Vapor Pressures for Binary Mixture (bar)

Temperature (°C)	Component	
	CHCl ₃	Acetone
35	0.391	0.462
45	0.574	0.678

From the vapor pressures and the known amounts of each compound, the partial pressures for each compound were calculated using equation (11). The total vapor pressure, P_{tot} , was determined with equation (13) using the mole fractions, x_i , and the vapor pressures, P_i , where i is each component of the solution, CHCl₃ and acetone.

$$P_{tot} = \sum_{i \rightarrow n} x_i P_i^* \quad (13)$$

The mole fractions of the vapor phase, y_i , were calculated using Dalton's law, equation (14) from the total vapor pressure of the two component system.²⁹

$$y_i = \frac{x_i P_i^*}{P_{tot}} \quad (14)$$

Under the assumption that the amount of condensation is constant at a given temperature for the system being studied, the amount of each component that forms condensation can be directly calculated from the mole fractions, x_i , based on the measured masses. The corrected mole fractions were compared to the values obtained from the masses (± 0.01 g) while neglecting partial pressures. The differences between these mole fractions were within the uncertainty of the mole fractions, neglecting condensation, as calculated by mass. At 45°C, x_i was 0.0442 while the corrected value was 0.0444. This results in a difference of only 0.46%. For CHCl₃ the percent difference between corrected and uncorrected x_i is even less, since the relative amount of

CHCl_3 is much higher. Since there is no significant difference in the concentrations from the partial pressures, the original concentration of mixed solvent added was used for calculations.

3.5.2. Effect of Solvent Dielectric:

Amounts of 0.8mL of $[\text{C}_2\text{mim}][\text{NTf}_2]$ were incrementally injected into a 96:4 CHCl_3 :acetone solution. Based on the data in Figure 6 from Tubbs and Hoffmann, this solution ($\epsilon = 5.43$) only contains the freely dissolved ions. This means that when the IL is injected into the solvent, the ion pairs will completely dissociate to their ions. The data obtained from the injections as a function of temperature is shown in Figure 16. The measured heats are listed in Table 8 of Section 3.7.

There is a significant decrease for the heats released when injecting IL into a CHCl_3 :acetone mixed solvent as compared to the heats released in pure CHCl_3 . The data obtained supports the hypothesis of ion pairing for a couple of different reasons. First, since the NMR data contained only one resonance set for the CHCl_3 :acetone solvent, it is presumed that there are no ion pairs upon dissolution into the mixed solvent. This is because it is expected that all of the IL would dissociate to the freely dissolved ions. If no ion pairs are present in the CHCl_3 :acetone solvent as indicated in the NMR data, the added IL will need to completely breakup into fully dissociated ions in solution. This results in lower heats of dissolution because the dissolution of IL to form fully dissociated ions is lower than that for the dissolution of contact ion pairs.

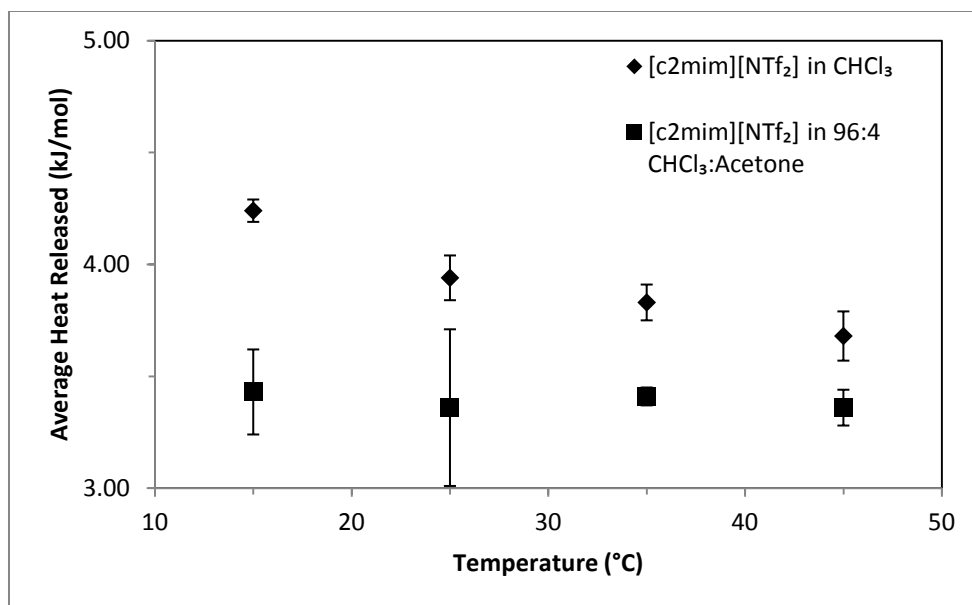


Figure 16. Average heats released (from Figure 14) for [C₂mim][NTf₂] into pure CHCl₃ and into a 96:4 mixture of CHCl₃:Acetone. The measured heats are per amount (moles) of IL injected.

Also, there is no apparent concentration dependence on the heats of dissolution into the mixed solvent. This is in agreement with no ion pairing present since the ions should be fully dissociated at the temperatures and concentrations of interest due to the dielectric of the mixed solvent. If there are no contact ion pairs in the mixed solvent then the temperature would only depend on the solvation of the freely dissolved ions into the mixed solvent. The equilibrium remains on the freely dissolved ion side for all temperatures of interest.

3.6. Temperature Dependence:

Since there was no apparent effect from potential impurities within the solution, the heats of dissolution into CHCl₃ at each temperature (Figure 14) were averaged and the heats were fitted as a function of temperature, giving equation (15), where H is the heat in J per gram of IL injected and T is the temperature in degrees Celsius.

$$H(J/g) = -0.0456T + 11.414 \quad (15)$$

There is a linear dependence of the heats of dissolution with temperature, where the most heat is released at lower temperatures. The dissolution of IL into CHCl_3 is an exothermic process, indicated by an increase in the temperature of the solution. Since it is an exothermic process, overall energy must be released from the interactions that occur, resulting in an overall increase in the temperature of solution. Therefore, the solvent must interact favorably with the injected IL. There are a couple of possible reasons that would cause this temperature dependency. The presence of ion pairs in solution is one possible explanation for the observations. Since it requires energy to break the ionic bonds between the cation and anion of the IL, one can consider the effects of temperature on the separation of ion pairs, since liquid IL prior to injection contains contact ion pairs. At higher temperatures, it is well known that ionic compounds are more likely to dissociate within a solution. Therefore, as temperature increases, the equilibrium in equation (1) will shift towards the freely dissolved ions and more energy will be consumed in the process of breaking up a larger number of ion pairs than at lower temperatures. This causes an overall decrease in the observed heats released upon solvation since energy was required to separate the ions.

Another explanation involves interactions between the ions and the solvent. It is possible that at higher temperatures the ions in solution are stabilized with less solvent molecules. If there are less solvent molecules stabilizing the ions then less energy would be released from the fewer interactions between the ions and the solvent molecules. Section 3.7 evaluates the heat of dissolution measurements with respect to enthalpy values for both freely dissolved ions and ion pairs.

3.7. Changes in Enthalpy for Ion Pair Formation:

The equilibrium between freely dissolved ions and ion paired species shown in equation (1) is the main focus of this study, however since pure IL was injected into the chloroform solvent, it is important to remember that the IL undergoes a change from pure liquid to IL dissolved in chloroform. Visual observations can be made when there is a phase separation between an organic phase and a liquid IL phase. The solution became cloudy only when x_{IL} exceeded a threshold concentration that was observed to be temperature dependent. At higher temperatures, more IL dissolves in the solution. Since the phase separation was visually observable as cloudiness, all injected IL dissolved into the CHCl_3 at concentrations below the visual phase separation. However, varying amounts of the freely dissolved ions and contact ion pairs can be formed upon injection at a particular temperature. Figure 17 shows the changes in enthalpy that occur upon dissolution of pure IL into the chloroform solvent. Since enthalpy is a state function, Hess' Law can be used to determine changes in enthalpy for the equilibrium in equation (1) based on the enthalpy values obtained from dissolution of liquid IL, CA_l , into pure chloroform and CHCl_3 :acetone solvents.

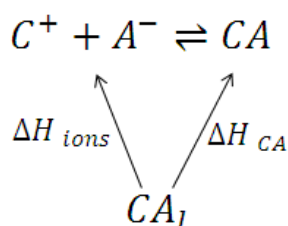


Figure 17. Diagram of changes in enthalpy for the dissolution of an IL into CHCl_3 .

Using Hess' law as applied to Figure 17, equation (16) was obtained for the change in enthalpy of the equilibrium of interest, the conversion of freely dissolved ions to contact ion pairs at dilute concentrations.

$$\Delta H_{ions \rightarrow CA} = \Delta H_{CA} - \Delta H_{ions} \quad (16)$$

The measured enthalpy values, $\Delta H_{measured}$, is the sum of the contributions from the dissolution to ions and to contact ion pairs, as shown in equation (17).

$$\Delta H_{measured} = \Delta H_{CA} + \Delta H_{ions} \quad (17)$$

Since the 96:4 CHCl_3 :acetone solvent system results in fully dissociated ions upon dissolution, as in equation (18),



the heats measured for injections into mixed solvent can be used to determine the change in enthalpy for complete dissolution of ions, $\Delta H_{dissolution}$. Since only 4% of the mixed solvent is acetone, it is a reasonable assumption that the change in enthalpy obtained from injections into a mixed solvent (-3399J/mol IL) can be used synonymously for dissolution into CHCl_3 . Equations 16 and 17 are combined to obtain an expression (eqn 19) for the change in enthalpy of the equilibrium between freely dissolved ions and contact ion pairs, containing only variables that can be obtained directly from the heat measurements.

$$\Delta H_{ions \rightarrow CA} = \Delta H_{measured} - 2\Delta H_{ions} \quad (19)$$

The enthalpy measurements obtained are due to the combined enthalpies from dissolution to freely dissolved ions and to contact ion pairs, as seen in equation (20). Based on the heat measurements into CHCl_3 , the total change in enthalpy, $\Delta H_{measured}$, for the dissolution at each temperature was calculated and listed in Table 8.

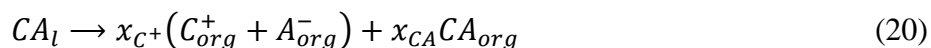


Table 8. Changes in Enthalpy for Dissolution of [C₂mim][NTf₂] into Chloroform

Temperature (K)	Dielectric (ϵ)*	ΔH_{ions} (kJ mol ⁻¹)**	$\Delta H_{measured}$ (kJ mol ⁻¹)	ΔH_{CA} (kJ mol ⁻¹)	$\Delta H, C^+ + A^- \rightarrow CA$ (kJ mol ⁻¹)
288.14	4.89	-1.09	-4.24	-3.15	-2.06
298.14	4.71	-1.13	-3.95	-2.82	-1.68
308.14	4.53	-1.20	-3.84	-2.64	-1.44
318.14	4.37	-1.29	-3.68	-2.38	-1.08

*Dielectric values for CHCl₃ were obtained from the CRC Handbook of Chemistry and Physics.⁴

**Enthalpy values were obtained from the enthalpy values for the dissolution into 96:4 CHCl₃:acetone injections and the mole fractions of dissociated ions, x_{C^+} . The mole fractions were determined by Tubbs and Hoffmann¹, as described in the text.

The enthalpy contributions of fully dissociated ions for injections into CHCl₃ were calculated using $\Delta H_{dissolution}$ obtained from injections into the mixed solvent. To obtain these contributions from the fully dissociated ions at each temperature, the mole fractions of the fully dissociated ions were obtained for each temperature using equation (21), which was obtained by Tubbs and Hoffmann for [C₂mim][NTf₂] into chloroform, where $\epsilon(T)$ is the solvent dielectric.¹

$$x_{C^+} = 0.720\epsilon(T) - 7.4002 + 0.01456T \quad (21)$$

The mole fractions obtained were multiplied by $\Delta H_{dissociation}$ to obtain the contributions from dissociated ions, ΔH_{ions} . For clarity, $\Delta H_{dissolution}$ is the enthalpy change involved for dissolution forming only freely dissolved ions, while ΔH_{ions} is the enthalpy contribution from dissolution to freely dissolved ions, even if complete dissociation does not occur. Therefore, if $\Delta H_{ions} = \Delta H_{dissolution}$ then complete dissociation occurred. The values obtained for ΔH_{ions} and the dielectric values used to obtain x_{C^+} are listed in Table 8.

3.8. Excess Enthalpy:

An excess quantity is the difference between the ideal value and the value obtained for a particular quantity. For thermodynamic quantities relating to mixtures, such as the binary

mixture in this study, there would be no heat transfers when mixing two substances for an ideal solution. This is not the case for most binary mixtures. When dissolving one substance into another, heat is frequently released or absorbed during this process, indicating a deviation from ideal behavior. The heat exchange upon dissolution can be correlated to the excess enthalpy of the dissolution, or the deviation in enthalpy from ideal behavior. Excess enthalpy values were obtained as a function of concentration at each temperature up to the solubility limit for $[\text{C}_2\text{mim}][\text{NTf}_2]$ in chloroform (0.03*m*). The excess enthalpies for the concentrations studied are shown in Figure 18 as a function of concentration of IL.

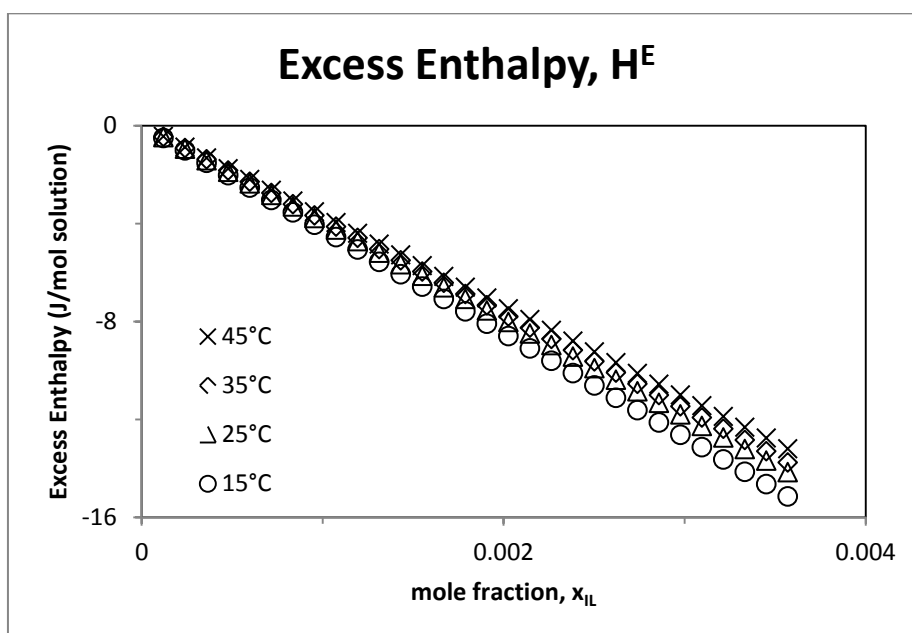


Figure 18. Excess enthalpy values for the dissolution of $[\text{C}_2\text{mim}][\text{NTf}_2]$ into chloroform at varying temperatures for mole fractions up to 0.0036 at all temperatures tested in this study.

To determine the excess enthalpies, the measured enthalpy, $\Delta H_{\text{measured}}$ (J/mol IL), was multiplied by the amount of IL (moles) at a given mole fraction to obtain the heat released at that concentration. The excess enthalpy, H^E , was obtained by determining the heat released at a

given concentration per mole of solution present. The excess enthalpies are negative, indicating that heat was released from the process, as indicated by an increase in temperature of the solution. Since the excess quantities are negative, the enthalpy change associated with the interactions between the IL and CHCl_3 is greater than the enthalpy change associated with the intermolecular interactions lost for the IL and CHCl_3 separately.

3.9. Different Imidazolium-Based ILs:

Two other imidazolium-based ILs were studied for comparison with the results obtained for $[\text{C}_2\text{mim}][\text{NTf}_2]$. As described in section 1.6, $[\text{c}_6\text{mim}][\text{NTf}_2]$ was observed to only have one resonance set, while $[\text{c}_6\text{mim}][\text{MeTf}_3]$ was observed to have two distinct resonance sets. The heat of dissolution data, Figure 19, supports the proposed equilibrium between the freely dissolved and ion paired species for the ILs tested. The heats of dissolution were measured in triplicate at each temperature for $[\text{C}_6\text{mim}][\text{NTf}_2]$ and $[\text{C}_6\text{mim}][\text{MeTf}_3]$. The heats and error bars in Figure 19 are the average values and one standard deviation from the mean, respectively. As observed for $[\text{C}_2\text{mim}][\text{NTf}_2]$, there was no apparent effect from the concentration on the heats of dissolution for the other two ILs studied.

Based on the data in Figure 19, the IL $[\text{C}_6\text{mim}][\text{MeTf}_3]$ has much smaller heats of dissolution than $[\text{C}_2\text{mim}][\text{NTf}_2]$ and $[\text{C}_6\text{mim}][\text{NTf}_2]$. These heat differences are likely due to the interactions of the anion within the solution. Since the $[\text{C}_6\text{mim}][\text{MeTf}_3]$ contained an intense second resonance set compared to $[\text{c}_2\text{mim}][\text{NTf}_2]$ in unpublished ^1H NMR data, it is possible that the lower heat of dissolution is due to stronger ion pairing for $[\text{c}_6\text{mim}][\text{MeTf}_3]$.

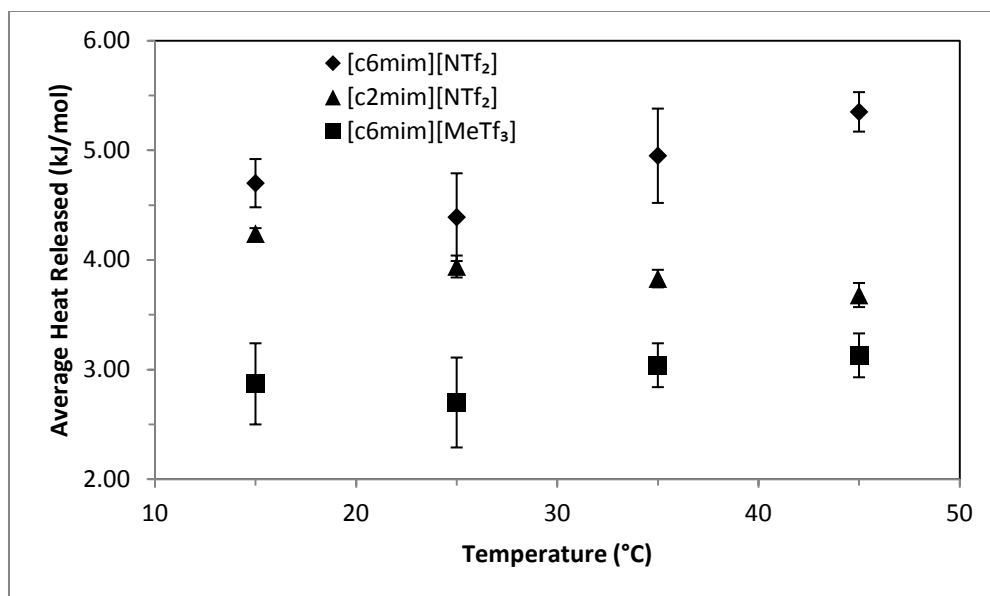


Figure 19. Heats of dissolution of all the ILs studied into pure CHCl_3 as a function of temperature. The measured heats are the heats released per gram of IL that was injected.

It is not fully known why $[\text{C}_6\text{mim}][\text{MeTf}_3]$ would have stronger ion pairing than $[\text{C}_2\text{mim}][\text{NTf}_2]$ since the $[\text{MeTf}_3]$ has a bulkier base. However, the triflyls are an integral piece of both anions, and it is very possible that the sulfonyl groups of these anions are integral in the ion-pairing interactions. Therefore, the additional triflyl of $[\text{MeTf}_3]$ may in fact improve the ion-pairing capabilities of $[\text{C}_6\text{mim}][\text{NTf}_2]$. When the ion pairs are broken from the dissolution into CHCl_3 , it is expected that more energy is required to break apart the $[\text{C}_6\text{mim}][\text{MeTf}_3]$ ion pairs for $[\text{C}_2\text{mim}][\text{NTf}_2]$. This is one possible explanation for the low heat of dissolution observed for $[\text{C}_6\text{mim}][\text{MeTf}_3]$. Another potential explanation of the low heats of dissolution is that the methide anion doesn't interact as favorably with the solvent as the bis(triflyl)amide, which would also explain the lower heats of dissolution. If this were true, we would expect a higher propensity of aggregate formation for $[\text{C}_6\text{mim}][\text{MeTf}_3]$ beyond the formation of contact ion pairs. If this were the case, it would not be expected to observe two distinct, stable, ^1H NMR resonance sets. In order to study the possibility of aggregate formation, diffusion measurements

of [C₆mim][MeTf₃] at varying concentrations in CHCl₃ would allow for using the Stokes-Einstein relation, determining the average radius of the particles in solution. The radii obtained from diffusion measurements could then be compared to the expected values of a contact ion pair and the individual ions.

From the heat data obtained for [C₆mim][NTf₂], shown in Figure 19, the heats of dissolution increase with temperature beyond 25°C, which is different than the trend found for [C₂mim][NTf₂]. Also, the heat values are larger than the values obtained for [C₂mim][NTf₂] which is in agreement with the single resonance set observed for [C₆mim][NTf₂]. The single resonance set would indicate weaker ion pairing, therefore less energy would be absorbed from solution to break the ion pairs, resulting in more exothermic heats of dissolution, as is observed. Since it is unknown whether a 96:4 CHCl₃:acetone causes complete dissociation of the ILs [C₆mim][NTf₂] and [C₆mim][MeTf₃] mixed solvent studies were not done. More studies with these ILs are needed in order to further correlate the enthalpy values obtained to the equilibrium between contact ion pairs and freely dissolved ions.

4. Conclusions:

Specific heat values were obtained for the three imidazolium-based ILs studied as a function of temperature. Calorimetric measurements were used in conjunction with specific heats to study the heats of dissolution as a function of temperature and concentration. Impurity analyses showed that the impurities present had no significant effect on the heat of dissolution measurements. For [C₂mim][NTf₂] in CHCl₃, an increase in the temperature of the solution caused a decrease in the measured heats of dissolution. This was attributed to an increase in the amount of heat absorbed in order to break the long-lived ion pairs that were observed in prior

research. The heats of dissolution as a function of temperature are concentration independent for all three ILs tested. This indicates that the breaking of ion pairs during dissolution is not the only significant contribution to the overall heats of dissolution measured. In a mixed solvent of CHCl_3 :acetone (96:4), the heats of dissolution were significantly less exothermic and were temperature independent, indicating full dissociation. This finding allowed for the use of Hess' law to calculate the enthalpy change involved in the equilibrium between ion paired species and freely dissolved species at each temperature studied.

The related imidazolium-based ILs $[\text{C}_6\text{mim}][\text{NTf}_2]$ and $[\text{C}_6\text{mim}][\text{MeTf}_3]$ were also studied in CHCl_3 since they were chemicals of interest due to their chemical similarities to $[\text{C}_2\text{mim}][\text{NTf}_2]$. Initial measurements on $[\text{C}_6\text{mim}][\text{NTf}_2]$ into CHCl_3 indicate a temperature dependence, however more studies with this IL are necessary to confirm that the heats are directly proportional to the temperature. Initial studies with $[\text{C}_6\text{mim}][\text{MeTf}_3]$ indicate that the heats of dissolution into CHCl_3 are temperature independent at the temperatures studied. The heats of dissolution for $[\text{C}_6\text{mim}][\text{MeTf}_3]$ were significantly lower than for the bis(triflyl)amide ILs. This was attributed to the bulkier anion, $[\text{MeTf}_3]$.

Both $[\text{C}_6\text{mim}][\text{NTf}_2]$ and $[\text{C}_6\text{mim}][\text{MeTf}_3]$ have higher solubility in CHCl_3 than $[\text{C}_2\text{mim}][\text{NTf}_2]$, so studies at higher concentrations can be done with these similar ILs. In order to further understand the interactions occurring in low dielectric solutions for $[\text{C}_6\text{mim}][\text{NTf}_2]$ and $[\text{C}_6\text{mim}][\text{MeTf}_3]$ more studies need to be done. Self-diffusion measurements as a function of concentration for both ILs would give further insight into the equilibrium of ion pairing and the possibility of aggregation.

5. Appendix:

Disassembly and reassembly instructions of the Reaction Calorimeter

1. Make sure the stirrer is turned off and not spinning. If the stirrer is on, it can be turned off using the iControl 4.0 software or using the switch on the RC1 calorimeter.*
2. Remove the plastic casing around the reaction vessel by loosening the four bolts then sliding off the casing.
3. Disconnect the calibration heater and Tr sensor from the top of the RC1 calorimeter instrument. Then, remove all the electrodes and probes from the ground glass openings on the top of the reaction vessel.
4. Loosen the metal attachment that connects the stirrer to the instrument using the proper wrench.
5. Tighten the black ring that is around the stirrer at the center of the lid to prevent the stirrer from sliding up or down.
6. Unscrew the metal rod from the stirrer. The part to unscrew is just above where the glass stirrer ends.
7. Further loosen the part attaching the metal rod and the instrument enough so you can completely remove the metal rod.
8. Remove the metal attachment from the stirrer.
9. Unscrew and remove all of/the fly nuts that keep the metal ring in place.
10. Slowly remove the metal ring, which has to be done at an angle because the reactor lid is non-concentric.
11. Slightly move the lid to one side, remove one half of the wooden ring, then slide the lid to remove the other piece.
12. Carefully remove the lid, holding the stirrer in place to ensure that it does not slide out, and gently place it down to the side.**
12. The assembly for this instrument is identical to the disassembly in reverse order. Instead of removing parts, unscrewing fly nuts, and loosening parts; you will put on the parts, screw the fly nuts, and tighten parts.

*When needing to flush out the chloroform or pistons, you simply have to twist the plug at the bottom of the reactor. The lower knob of this plug will open the flush valve so that the liquid can pour out. To remove the Teflon pistons that came from the injection tube when injecting IL you have to twist the upper valve of this same plug, so that the whole plug can be removed from the reactor and the little piston pieces can fall out.

**To remove the stirrer, slowly open the black ring at the center of the lid while the lid is sitting sideways and slowly remove the stirrer.

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