UNDERSTANDING THE EFFECTS OF MOLECULAR ADDITIONS
IN ENERGETIC IONIC LIQUIDS

by

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ABSTRACT

Ionic liquids (ILs) have been utilized in a multitude of areas breaking past the traditional thoughts of ILs only useful as conventional solvents. Recently researchers have been constantly attempting to push and break past the current boundaries of how we think about and exploit ILs as energetic materials. Ionic liquids provide a modular platform that can be changed at the molecular level to take advantage of targeted physical and chemical properties to form energetic materials suitable for use by the Air Force Office of Scientific Research (AFOSR). This work sought to utilize this modular platform to target physical and energetic deficiencies in the ILs through subjecting the ILs to the addition of molecular aromatics. The driving force for the aromatic selection also allowed for tunability of energetic properties within the IL-aromatic mixture.

First, an investigation of the interactions among aromatics and ionic liquids, leading to the formation of liquid clathrates, for the targeted modification of the IL platform’s physical and chemical properties. ILs’ liquid clathrate forming ability is utilized to target the ILs’ inherent deficient physical properties in regards to being considered as an energetic material. In this work, the ILs’ high viscosity was targeted while maintaining the other inherent attractive properties of the IL (density, melting point, and hypergolicity). Liquid clathrate formation is a powerful tool in viscosity reduction as the IL-aromatic intermolecular interactions help to reduce the ion-ion intramolecular interactions in the IL. The aromatics being used to form the liquid
clathrates also traditionally have good space filling abilities in a crystal lattice lending to the density of the liquid clathrate being very close to the original parent IL. Secondly, the molecular level interactions between the ions and the aromatic in the complexed liquid clathrate form can be utilized to tailor the hypergolic reactivity of the material. Theoretical calculations and modeling are used in conjunction with a plethora of experimental spectroscopy and hypergolicity measurements to shed some light on the crucial properties for hypergolic ignition. This work shows the donation of electron density from the dicyanamide ([DCA\(^-\)]) anion, which is what initiates the hypergolic decomposition pathway with white fuming nitric acid (WFNA), to the aromatic imidazolium cation in the presence of an aromatic in the complexed liquid clathrate form and provides a theoretical and experimental platform to modify these liquid clathrates for future energetic materials.
# LIST OF ABBREVIATIONS AND SYMBOLS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>AFOSR</td>
<td>Air Force Office of Scientific Research</td>
</tr>
<tr>
<td>AFRL</td>
<td>Air Force Research Laboratory</td>
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<tr>
<td>API</td>
<td>Active Pharmaceutical Ingredient</td>
</tr>
<tr>
<td>AzAz</td>
<td>Azolium Azolate</td>
</tr>
<tr>
<td>[BMIM][DCA]</td>
<td>1-Butyl-3-Methyl-Imidazolium Dicyanamide</td>
</tr>
<tr>
<td>[BMIM][Cl]</td>
<td>1-Butyl-3-Methyl-Imidazolium chloride</td>
</tr>
<tr>
<td>BnzNH2</td>
<td>Benzylamine</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeters</td>
</tr>
<tr>
<td>cP</td>
<td>Centipoise</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl Sulfoxide</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>EIL(s)</td>
<td>Energetic Ionic Liquid(s)</td>
</tr>
<tr>
<td>[EMIM][OAc]</td>
<td>1-Ethyl-3-Methyl-Imidazolium Acetate</td>
</tr>
<tr>
<td>fps</td>
<td>Frames Per Second</td>
</tr>
<tr>
<td>g</td>
<td>Grams</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>IL(s)</td>
<td>Ionic Liquid(s)</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared Spectroscopy</td>
</tr>
<tr>
<td>[MAT][DCA]</td>
<td>1-Methyl-4-Amino-1,2,4-Triazolium Dicyanamide</td>
</tr>
<tr>
<td>MHz</td>
<td>Megahertz</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>[MMIM][PF₆]</td>
<td>1,3-Dimethyl-Dmidazolium Hexafluorophosphate</td>
</tr>
<tr>
<td>ms</td>
<td>Milliseconds</td>
</tr>
<tr>
<td>μL</td>
<td>Microliter</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>1,3-Dimethylbenzene; <em>Meta</em>-xylene</td>
</tr>
<tr>
<td>[NCA]</td>
<td>Nitrocyanamide</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>1,2-Dimethylbenzene; <em>Ortho</em>-xylene</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>1,4-Dimethylbenzene; <em>Para</em>-xylene</td>
</tr>
<tr>
<td>TMS</td>
<td>Tetramethylsilane</td>
</tr>
<tr>
<td>WFNA</td>
<td>White Fuming Nitric Acid</td>
</tr>
<tr>
<td>χ</td>
<td>Mole fraction (mol\textsubscript{aromatic}/mol\textsubscript{total}) defined as the number of moles in question (e.g. mol\textsubscript{aromatic}) divided by the total number of moles in the system (mol\textsubscript{total})</td>
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ACKNOWLEDGEMENTS

First and foremost, I would like to thank my research advisor, Dr. Robin D. Rogers, for his guidance, support, and, most of all, his patience during my time at The University of Alabama. I learned a great amount not only about how to conduct myself professionally as a chemist, but how to conduct myself personally in my everyday life. He always preached that the key to success in chemistry, as in all things, is self-accountability and self-motivation and this is one of the most valuable lessons that I will take away from my time in graduate school. Ever confident in himself and his opinions, he taught me to stand firm in what I believe and go after what I want with voraciousness and push myself to be a better chemist. Finally, he taught me that chemistry could be fun and that I should enjoy everything that I venture into and I truly thank him for that.

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CHAPTER 1
INTRODUCTION

Ionic liquids (ILs), defined as salts with melting points below 100 °C, have garnered much attention in the scientific community in recent years.\textsuperscript{1-6} This class of salts possesses many unique properties, including the weak intermolecular interactions required for the salts to remain liquid below 100 °C. Traditionally, ILs have been considered ‘designer solvents’ due to the ability of both the cation and anion to be independently modified structurally to target specific properties. This solvation property can be seen in the utilization of the IL 1-butyl-3-methyl-imidazolium chloride ([BMIM][Cl]) for the dissolution of cellulose\textsuperscript{1} and also in the use of novel Brønsted acidic ILs for the purpose of dual solvent catalysts.\textsuperscript{2} This foundation of ILs as designer solvents and their unique properties such as low to negligible vapor pressure, high heats of formation, high thermal stability, and low viscosities served as a platform for future research in the area.\textsuperscript{3,4,5} This led to research in the area of active pharmaceutical ingredients (API) with the idea that these attractive physical and chemical properties could be incorporated into the API molecule itself to combat a variety of pitfalls typical APIs face such as low solubility and polymorphism.\textsuperscript{6,7}

This platform of attractive physical and chemical properties exhibited by ILs led researchers to consider these unique materials as potential candidates for energetic materials and energetic ionic liquids (EILs) were born.\textsuperscript{8} This exploration into the use of ILs as potential energetic materials led to the synthesis of a new class of ILs named
‘azolium azolates’ (AzAz).\textsuperscript{8,9} These azolium azolates differed from previous generations of EILs in that the ILs incorporated an azolium core in the ions. This inclusion of these azolate ions into the IL brought about physical and chemical properties that differed from the previous generations of EILs. Design of both the cation and anion allowed for molecular level control of the IL and compartmentalized tunability of the physical and chemical properties. Researchers not only found promise in this class of EILs that possessed a high nitrogen content, but EILs were next found to show promise in the ability to be hypergolic (spontaneous ignition of a fuel upon contact with an oxidizer).\textsuperscript{4} After this initial finding, much effort and research was invested in exploring this new class of hypergolic ILs and discovering the advantages and pitfalls of the structural properties.

Throughout all of this, our group has had a major interest in this field of EILs as well through investigating synthetic design.\textsuperscript{8,10} This initial synthetic work in our group formed the basis of the AzAz platform and proved as crucial work in developing this generation of EILs and moving forward. Our group’s next scientific push was into exploring the physical and chemical properties and the effect of modular design on these properties. This exploration of modular design was accomplished through synthetic modification of the ion cores as well as the ion functionalities. Throughout that work it was shown that controlling the type of aromatic core of the ion and manipulating the functionalities attached to the ions can lead to major physical and chemical property changes.\textsuperscript{9} With this understanding of how synthetic modification affect physiochemical properties, we sought to understand how a similar synthetic modification could affect the energetic properties of the EILs.\textsuperscript{11} That work looked at the effect of a permanent cation
through methylation compared to a protonated cation on structurally similar cations. The result of this work showed that protonated EILs exhibited extreme flammability compared to the methylated analogs, which exhibited very low flammability. However, in our continuing study of EILs, we have observed that EILs have several deficient properties, such as relatively high viscosities and low densities, which would need improving without negatively influencing other necessary properties for EILs to be utilized to replace current energetic materials. With this in mind, our group has attempted to develop strategies in order to improve the EIL platform and deficiencies. Our first attempt at an improvement strategy was utilizing EILs in the solubility and stabilization of metal nanoparticles. This stabilization of boron nanoparticles in the EILs not only increased the density of the materials, but also improved the quality of the ignition without hampering the ignition delay.3 We also looked at targeting other physical properties in order to improve upon the EIL platform and we did this by stabilizing graphene sheets in EILs to ‘lubricate’ the IL and decrease the viscosity.12 This resulting viscosity decrease led to a hypergolic ignition at extremely low temperatures (< 0 °C), which had not been previously reported in the literature. With this in mind, the work reported here sought to use the liquid clathrate strategy to improve upon the current generation of EILs.

Atwood first proposed liquid clathrates as semi-ordered liquids containing complex salt hosts and aromatic hydrocarbon guests,13,18 suggesting that they are formed by associative interactions between aromatics and salt ions to form localized cage structures. Atwood described the first examples between highly reactive air-sensitive alkylaluminum salts and aromatics14-19 with the field expanding to a range of organic
salts, typically with halide-containing anions, being shown to support liquid clathrate formation in contact with aromatic solvents. Zaworotko et al. suggested that formation of liquid clathrates depended primarily on the physical properties of the organic salt and the resulting intermolecular interactions between the organic salt and aromatic. With this knowledge of liquid clathrates, we sought to use the model as a platform in addressing some of the inherent deficiencies of the current platform of EILs by adding aromatic based fuels to decrease the viscosity of these EILs without further decreasing the density of the system and observed not only liquid clathrate behavior, but discovered a unique crystallization phenomenon that we believe, along with strong evidence from the experimental spectroscopy showing a consistent donation of electron density from the anion to the cation when complexed in liquid clathrate form, strongly supports Atwood’s original hypothesis on the nature of liquid clathrates. Further investigation with hypergolicity measurements have shown a significant increase in ignition delay with the increase in donation of electron density from the anion to the cation when complexed in liquid clathrate form. This is supported experimentally with spectroscopy and theoretically with computer modeling to confirm the electron density donation to shed some light to what is occurring at a molecular level in these systems.

This work has utilized ILs to investigate the unique ion-aromatic interactions that allow for liquid clathrate formation to address some of the inherent deficient physical properties of the current EIL platform. In depth spectroscopy has shown a significant donation of electron density from the anion to the cation in the presence of an aromatic when complexed in liquid clathrate form. This donation of electron density increases with the amount of aromatic present in the liquid clathrate. Theoretical modeling done
by Dr. Steven Chambreau of Air Force Research Laboratory has shown an increase in the electron density centered on the imidazolium cation of the IL in the liquid clathrate compared to the majority of the electron density being centered around the anion in the neat IL. These theoretical and experimental observations work in tandem to explain the increase in ignition delay and provides a solid knowledge platform in which to aid in the design of future ILs and liquid clathrates.
CHAPTER 2
GENERAL EXPERIMENTAL PROTOCOLS

2.1 Nuclear Magnetic Resonance Spectroscopy

Nuclear Magnetic Resonance (NMR) spectra were recording utilizing a Bruker Avance Spectrometer Bruker/Magnex UltraShield 500 MHz magnet (Madison, WI) or a Bruker Spectrospin DRX 400 MHz UltrashieldTM spectrometer (Madison, WI). $^1$H (500 MHz) and $^{13}$C (125 MHz) spectra were collected using DMSO-$d_6$ as the solvent with TMS as the internal standard and shifts reported in $\delta$ (ppm). The materials were sampled neat through a technique utilizing a coaxial insert contacting the neat sample. The coaxial tube containing the sample was flame sealed and placed inside an NMR tube containing the DMSO-$d_6$ which was used as an external lock.

2.2 Infrared Spectroscopy

Infrared (IR) spectra were collected using a Bruker ALPHA-FTIR by direct measurement via attenuated total reflectance on a diamond crystal. Samples were dried previous to measurement, sampled with a pipette placing one droplet of the neat sample on the diamond. The samples was scanned twenty times at four seconds per scan rate.
2.3 **Differential Scanning Calorimetry**

DSC scans were conducted on a Mettler Toledo DSC 1 calorimeter (Columbus, OH) cooled with a water chiller and calibrated to the melting point of indium, water, and octane. Sample sizes ranged between 10 and 15 mg and were placed in fresh aluminum pans (ME-00026763, hermetic sealing pans, Mettler Toledo, Columbus, OH) crimped closed and massed using an Excellence Level, XS Series Analytical Balance (Mettler Toledo, Columbus, OH). The cell of the DSC was flushed with dry nitrogen to prevent condensation and crystallization from ambient moisture upon cooling of the sample. The following protocol was used on all samples unless otherwise stated: an initial cooling rate of 1 °C min\(^{-1}\) to -70 °C followed by 10 min isotherm. A heating rate of 1 °C min\(^{-1}\) to 20 °C, with the cycle repeated two times.

2.4 **Viscosity and Density**

Viscosity measurements were recorded utilizing a Cambridge Viscosity VISCOlab 3000 (Houston, TX) that was temperature controlled to 40 °C with an internal heating apparatus. In all cases unless otherwise noted, 1 mL of sample was used for viscosity measurements with 10 measurements recorded and averaged. The instrument was cleaned thoroughly in between measurements to ensure no carryover contamination.

Density measurements were recorded utilizing an Anton-Paar DMA 500 density meter (Ashland, VA) that was temperature controlled to 40 °C with an internal heating apparatus. In all cases unless otherwise noted, 1 mL of samples was used for density measurements. The instrument was cleaned thoroughly in between measurements to ensure no carryover contamination.
2.5 Hypergolicity

Hypergolic ignition test were conducted using a Redlake MotionPro HS-4 at 1000 frames per second. The microsyringe containing the sample was placed at exactly 2 cm from the tip of the microsyringe to the top of the cuvette containing the oxidizer to promote reproducibility. 10 μL of fuel sample and 500 μL of oxidizer were used in all cases unless otherwise states. Ignition delay times were measured from the time the fuel initially hit the oxidizer, time zero, until the time flame ignition was observed, time final. Time zero subtracted from time final yields ignition delay in milliseconds.
CHAPTER 3
MOLECULAR INTERACTIONS OF AROMATICS AND IONIC LIQUIDS
LEADING TO LIQUID CLATHRATE BEHAVIOR

3.1 Introduction

Atwood first observed the liquid clathrate phenomena early in the 1970s with the formation of air-sensitive alkylaluminum liquid clathrates such as $\text{K}[\text{Al}_2(\text{CH}_3)_6\text{NO}_3]\cdot7.0\ \text{C}_6\text{H}_6$, $\text{Rb}[\text{Al}_2(\text{CH}_3)_6\text{NO}_3]\cdot9.4\ \text{C}_6\text{H}_6$, and $\text{Cs}[\text{Al}_2(\text{CH}_3)_6\text{NO}_3]\cdot12.0\ \text{C}_6\text{H}_6$.

From the liquid clathrate $\text{K}[\text{Al}_2(\text{CH}_3)_6\text{NO}_3]\cdot7.0\ \text{C}_6\text{H}_6$, a crystal solid clathrate was brought forth with the composition of $\text{K}[\text{Al}(\text{CH}_3)_3\text{NO}_3]\cdot\text{C}_6\text{H}_6$ through the addition of dibenzo-18-crown-6 at a one to one equivalent. This initial work by Atwood was only the beginning of a great deal of work by a number of researchers into the liquid clathrate phenomenon.

Zaworotko et al. postulated that formation of liquid clathrates depended primarily on the physical properties of the organic salt and the resulting intermolecular interactions between the organic salt and aromatic. This implication would shift the liquid clathrate formation dependency onto the organic salt, which would make the interactions brought about by the aromatic in the system completely irrelevant in terms of liquid clathrate formation. Holbrey et al. demonstrated the range of salts supporting liquid clathrate formation included ILs. In Holbrey’s work, a range of ILs were investigated for liquid clathrate formation with classical aromatics that have been previously shown to support
this behavior (benzene, toluene, and xylenes). These liquid clathrates were observed to be air- and water-stable liquids proving to be vastly different than the pyrophoric air- and water-sensitive alkylaluminum liquid clathrates that had been reported earlier. These salts differed from other salts exhibiting liquid clathrate behavior in that they are hydrophobic and also contain weakly coordinating, non-reactive anions. In one such case that was studied, [MMIM][PF$_6$]-benzene, not only was a liquid clathrate formed but also a solid state inclusion compound was crystallized from the liquid clathrate with the liquid clathrate and the solid state inclusion compound formed at a different salt : organic ratio. Neutron scattering data from this work also indicated clathrate formation in the liquid of [MMIM][PF$_6$]•2.0 benzene through the strong interactions of the cation methyl groups with the π-system of the benzene, where benzene molecules are surrounded by anion-cation cages. One major thing to take away from the x-ray crystallography presented in Holbrey’s work is the interaction between the [PF$_6$]$^-$ anions and the π-system of the cation. The zigzag nature of the crystal packing lends to this interaction between the anion and the cation π-system and will be an important precedence for the work reported herein.

In recent years, there has been a major push to replace current state of the art energetic materials such as hydrazine.$^{3,22}$ These state of the art energetic materials have concerns due to characteristics such as carcinogenicity,$^{22}$ shock and impact sensitivity,$^{23}$ and high volatility,$^{22}$ which can lead to environmental hazards. ILs have been looked at as suitable replacements for these high hazard state of the art energetic materials due to the ILs’ inherent favorable properties such as low to negligible vapor pressure, high heats of formation, high thermal stability, and low viscosities.$^{3,4,22}$ Although EILs have
satisfied most of the performance requirements set forth to be an energetic material, they still have some inherent deficiencies that need to be addressed such as viscosity and density. These inherent pitfalls of the ILs present a need for a molecular additive that will allow for certain problematic properties to be addressed and corrected while not interfering with the favorable properties of the IL such as low sensitivity and low melting point.

With this in mind, this chapter reports the utilization of liquid clathrates as a strategy to consistently and reproducibly address some of the problematic characteristics of EILs without interfering with the favorable characteristics of the IL. Introducing an aromatic to the EIL and formation of a liquid clathrate will lower the viscosity while maintaining the relative density required of a suitable energetic material.

3.2 Experimental

3.2.1 Chemicals

Benzene, toluene, o-xylene, m-xylene, p-xylene, 1,2,5-trimethyl-pyrrole, 2,5-dimethyl-furan, tetrahydrofuran, 1-methyl-pyrrole, 2,5-dimethyl-pyrrole, aniline, benzylamine, and nitrobenzene were purchased from Sigma Aldrich (St. Louis, MO) and used as received. [BMIM][DCA] and [EMIM][OAc] were purchased from IoLiTec. High vacuum drying for 48 hours was performed on the ILs, otherwise they were used as received. DMSO-d6 was purchased from Cambridge Isotope Laboratories (Andover, MA) and used as received.
3.2.2 Formation of liquid clathrates

Liquid clathrate screening experiments were carried out to investigate the liquid clathrate forming ability of a variety of molecular aromatic liquids with the IL, [BMIM][DCA]. [BMIM][DCA] was chosen as a model for EILs due to its hypergolicity (spontaneous ignition upon contact of a fuel with an oxidizer) and favorable physical properties, such as low melting point (\(\sim -10 \, ^\circ C\)).\(^{25,26}\) A range of aromatic and non-aromatic liquids (Figure 3.1) were chosen to study liquid clathrate formation with EILs (e.g., benzene, toluene, xylenes) based on previous observations of liquid clathrate formation with ILs. Additional liquids, aniline, benzylamine, nitrobenzene, tetrahydrofuran, 2,5-dimethyl-furan, 1-methyl-pyrrole, 2,5-dimethyl-pyrrole, and 1,2,5-trimethyl-pyrrole were chosen to study a range of hydrogen bonding and \(\pi\) character.
Figure 3.1 Molecular liquids mixed with [BMIM][DCA]: liquid clathrate formers on the left and liquids completely miscible with the IL on the right.
The initial test for liquid clathrate formation was conducted by mixing [BMIM][DCA] with the liquids in Figure 3.1 in a 1:10 molar ratio followed by vigorous stirring. If a liquid clathrate formed it would do so immediately forming a complete biphase upon mixing; however, these systems were allowed to stir for 12 h to ensure equilibration of phases under ambient conditions and complete mixing. Liquid clathrates were observed for the seven solvents on the left of Figure 3.1, while the remainder were miscible in all proportions studied.

Liquid clathrate formation was characterized by the formation of a biphasic system with an IL-rich lower phase of reproducible composition (by $^1$H NMR) and an upper phase free of IL (Figure 3.2). The addition of aromatic to the IL led to much lower viscosities and noticeable volume increases with the largest volume increase noted for benzene. The noted visual volume increase followed the aromatic content of each mixture: benzene > toluene > $o$-xylene ≈ $p$-xylene ≈ $m$-xylene. The aromatic content of the liquid clathrate phase is somewhat lower than that found in the organoaluminum liquid clathrate systems reported by the Atwood group,$^{15-19}$ but largely comparable with the IL-aromatic liquid clathrate systems observed and reported previously.$^{21,27}$
Figure 3.2  Formation of a liquid clathrate with [BMIM][DCA] and benzene.
3.2.3 Aromatic Content and Characterization of the Liquid Clathrates

All liquid clathrate formers were analyzed for maximum aromatic content with $^1$H NMR. The excess aromatic present as the top layer after equilibration was decanted away leaving only the liquid clathrate. A coaxial NMR tube setup was utilized in order to be able to observe the direct ion-aromatic interactions in the liquid clathrate. Determination of the maximum aromatic content in the liquid clathrate was accomplished through integration comparisons of a known peak of the IL and a known peak of the aromatic. In this way, the content is represented as a molar ratio of the two constituents of the liquid clathrate. Comparison of the liquid clathrate mixture, the neat IL, and the neat aromatic were also compared to determine electronic interactions that exist in the liquid clathrate system.

Infrared was used to observe bond energy differences in the liquid clathrate systems compared to the neat IL and neat aromatics in order to deduce any chemical or physical interactions that are occurring in the liquid clathrate. In one instance, a liquid clathrate former and non former were compared at similar aromatic contents to observe differences in the nature of the effects on the aromatic resulting from the aromatic-ion interactions in the liquid clathrate. This was executed by forming a liquid clathrate and determining the aromatic content. Once the aromatic content of the liquid clathrate is determined, a solution of IL and completely miscible aromatic can be mixed at a similar IL-aromatic ratio as that of the liquid clathrate. In this way, the concentration effects are taken out of consideration when observing the effects in the IR, and differences can be narrowed to resulting from being complexed into liquid clathrate form.
Routine physical property measurements of the liquid clathrates compared to the neat IL and aromatics were used to reveal and deduce unique interactions in the liquid clathrate formers compared to the non liquid clathrate formers. Physical properties measured and compared were viscosity, density, and thermal behavior observed through differential scanning calorimetry. DSC was also utilized to observe unique thermal behavior that was only noted for liquid clathrate formers.

3.3 Results and Discussion

3.3.1 Formation of Liquid Clathrates

Screening experiments were designed to determine which molecular liquids supported liquid clathrate formation. Due to prior work showing liquid clathrate formation of ILs with traditional aromatics, such as benzene, toluene, and xylenes, these aromatics were initially used as a platform for which to design experiments and gain an in-depth understanding of the nature of the ion-aromatic interactions in the liquid clathrates. This platform could then be used to expand the aromatic selection in an array of aromatics that would help to improve deficient physical and energetic properties of the ILs. [BMIM][DCA], the specific IL chosen for the initial model due to its hypergolic nature and low melting point, exhibited liquid clathrate formation with benzene, toluene, all xylenes, 1,2,5-trimethyl-pyrrole, and 2,5-dimethyl-furan. In contrast, molecular liquids that were miscible in all proportions studied were aniline, benzylamine, nitrobenzene, tetrahydrofuran, 1-methyl-pyrrole, and 2,5-dimethyl-pyrrole. This range of aromatics were chosen due to the varying degree of solubility with water, π character, and electronic characteristics. The initial screening of these aromatics for liquid clathrate
formation showed that only the aromatics with an extremely low solubility with water exhibit the ability to form liquid clathrates, but, upon further examination it was observed that this was not the only factor that need be considered for liquid clathrate formation due to nitrobenzene not forming a liquid clathrate. Electron donating and withdrawing ability as well as the nature of the aromatics’ π systems also do not seem to have an apparent bearing on liquid clathrate formation.

3.3.2 Aromatic Content and Characterization of the Liquid Clathrates

In order to understand the effect of liquid clathrate formation on the physical properties of the mixtures, viscosity and density were measured of not only the liquid clathrate mixtures, but of a solutions that liquid clathrate formation was not observed (Table 1). In all liquid clathrates there was a large decrease in viscosity (up to ~ 75%) but only a slight decrease in density (~ 8%). This large decrease in the liquid clathrate viscosity suggests that the aromatic liquids can disrupt the intramolecular interactions of the EIL. In contrast, in the case of benzylamine which is completely miscible with [BMIM][DCA], the decrease in viscosity is less (~ 50%) than that of a liquid clathrate at a similar concentration of molecular liquid in IL. The completely miscible molecular liquid does not possess the same associative interactions as the liquid clathrates, thus unable to disrupt the intra-IL interactions to the same degree. The roughly 50% decrease in viscosity at a 1:1 molar ratio of molecular liquid to IL would also be characteristic of a simple dilution effect of the IL.

An in-depth spectroscopic (IR and NMR) study was conducted seeking to gain an understanding of the chemical nature of the mixtures. NMR spectra (1H and 13C) were obtained of the benzene, o-xylene, m-xylene, p-xylene, toluene clathrates and for solutions of aniline, benzylamine, and tetrahydrofuran. An increase in shielding, and therefore an
increase in electron density, around the imidazolium portion of the cation of all of the liquid clathrates as well as the simple mixtures with miscible aromatic molecular liquids was observed. There is also an observed decrease in shielding, and therefore electron density, around the carbons of the dicyanamide anion (Figure 3.3). This shift of the anion peak downfield is an indication that the anion is becoming less basic overall, which would correspond with a decrease in electron density around the anion. This trend is seen in all of the liquid clathrate mixtures, whereas there is no observed shift when looking at the completely miscible mixture of [BMIM][DCA]*0.45 tetrahydrofuran (Figure 3.4). This lack of shift indicated, in this completely miscible mixture, there is no electron donation occurring between the anion and the cation as seen in all of the liquid clathrates. These trends lead to the idea that the electronic interactions that are occurring between the aromatic and the IL are causing a general flow of electron density to be centered about the cation. This is most likely accomplished through the electron ring current of the benzene and the π system of the IL. These interactions lend support to the model of the aromatic on both sides of the cation and the anion on top of the cation when locally ordered in the liquid clathrate form.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Viscosity at 40 °C (cP)</th>
<th>Density at 40 °C (g/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BMIM][DCA]</td>
<td>17.6</td>
<td>1.06</td>
</tr>
<tr>
<td>[BMIM][DCA]•0.30 m-xylene</td>
<td>10.52</td>
<td>1.02</td>
</tr>
<tr>
<td>[BMIM][DCA]•0.40 p-xylene</td>
<td>8.29</td>
<td>1.02</td>
</tr>
<tr>
<td>[BMIM][DCA]•0.50 o-xylene</td>
<td>7.28</td>
<td>1.01</td>
</tr>
<tr>
<td>[BMIM][DCA]•0.90 toluene</td>
<td>6.58</td>
<td>1.00</td>
</tr>
<tr>
<td>[BMIM][DCA]•2.10 benzene</td>
<td>4.43</td>
<td>0.98</td>
</tr>
<tr>
<td>1:1 [BMIM][DCA]:BnzNH₂</td>
<td>9.36</td>
<td>1.03</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.60</td>
<td>0.86</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.56</td>
<td>0.85</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>0.70</td>
<td>0.85</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>0.50</td>
<td>-</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>0.51</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 3.3  Downfield portion of $^{13}$C-NMR spectra of neat [BMIM][DCA] (bottom), IL/benzene liquid clathrate (middle), and neat aromatic (top).
Figure 3.4  Downfield portion of $^{13}$C-NMR spectra of neat [BMIM][DCA] (bottom), IL/THF simple mixture (middle), and neat molecular liquid (top).
Infrared spectroscopy was performed on the benzene, \textit{o}-xylene, \textit{m}-xylene, \textit{p}-xylene, and toluene clathrates and for 1:1 molar solutions of aniline and benzylamine. In all cases, there was a general trend of the nitrile stretch shifting to a higher wave number indicating the anion to be slightly more positive in the presence of benzene; this would coincide with the donation of electron density seen in the NMR of the anion (Figure 3.5). The most telling data that can be seen from the IR is the large shifts seen in the aromatic out of plane bending mode (Figure 3.6). While this shift is present in the non-LC forming mixtures as well, the shift is much larger in the liquid clathrates. As the figure shows, the out of plane bending of benzene is shifted to a higher wavenumber relative to the neat aromatic indicating much higher energy is required for this out of plane bend to occur while only a slight shift is noted for the same concentration of benzylamine. This indicates that the clathrates are more ordered that the non-LC forming mixtures in that the orientation of the aromatic in the liquid clathrate is ordered enough for the electronic interactions to have an effect on the bending energy. This is most likely caused from the interaction of the ring current and the IL causing a bond energy change in the aromatic –C-H bonds. As stated previously, this is a good indication of higher ordering in the liquid clathrate form compared to a simple solvation with a non-liquid clathrate former.
Figure 3.5  Nitrile stretch of [DCA]$^-$ anion exhibiting a blue shift to a higher energy indicating the anion is slightly more positive in liquid clathrate form.
Figure 3.6  Infrared spectroscopy showing comparison of the aromatic out of plane bending mode of a liquid clathrate (left) and completely miscible molecular liquid mixture (right).
Routine physical property characterization through differential scanning calorimetry revealed some extremely interesting trends when liquid clathrate formers were compared to non-liquid clathrate mixtures. In all cases for the liquid clathrate formers, a melting was observed very close to the melting point for the neat aromatic at liquid clathrate concentration, which covered a wide range of aromatic concentration in the IL (Figure 3.7). In contrast, non-liquid clathrate formers only showed a $T_m$ when the molar amount of aromatic was greater than that of the IL (Figure 3.8). This indicates the nature of the IL-aromatic interaction in the liquid clathrates is an ordered associative interaction that is constantly in flux giving the aromatics the ability to nucleate and crystallize at any concentration of aromatic (below liquid clathrate concentration as that is the limit of aromatic in the IL), whereas the non-liquid clathrate IL-aromatic interaction is to a solvation degree where once the amount of IL is enough to interact with each aromatic molecule, the aromatic is unable to nucleate.
Figure 3.7  DSC of mixtures of the liquid clathrate-aromatic benzene with [BMIM][DCA]. Nucleation of the aromatic is still present even at $\chi_m$ of aromatic as low as 0.5 (e). (e) $\chi_m = 0.5$ (d) $\chi_m = 0.58$ (c) $\chi_m = 0.64$ (b) $\chi_m = 0.68$ (a) $\chi_m = 1.00$. 
Figure 3.8  DSC of non-liquid clathrate mixtures of [BMIM][DCA] and 1,2,4-triazole (left), 4-NH₂-1,2,4-triazole (middle), and Nitrobenzene (right). Each graph shows three mixtures with $\chi_m$ of aromatic of 1.0 (red), 0.9 (green), and 0.5 (blue).
3.4 Conclusions

Not only has the range of salts supporting liquid clathrate media been expanded in this work, but the nature of the ion-aromatic electronic interactions, through spectroscopy, has been studied much more in-depth than previously seen and the physical property deficiencies that we targeted have been improved through the liquid clathrate model. The nature of these liquid clathrates has shown that with the addition of an aromatic to an EIL that the physical properties can be positively altered. In this case, aromatics were added to [BMIM][DCA] and a sharp decrease in viscosity was observed with only a slight decrease in density. This is a crucial feature moving forward for this material to be considered as a future replacement for current state of the art energetic materials.

An in depth spectroscopic analysis indicated a shift in electron density from the dicyanamide anion and the benzene to the aromatic portion of the imidazolium ring. This electron density shift is indicative of the anion becoming slightly more positive when complexed in liquid clathrate form. This trend is seen in all of the liquid clathrates studied. An interesting contrast is the case of [BMIM][DCA] and tetrahydrofuran mixture. THF is completely miscible in the EIL and the spectroscopy displays no apparent shifts indicating that the level of interaction among the miscible liquids is to a much lesser degree than that of the ion-aromatic interactions observed in the liquid clathrates.

Infrared spectroscopy showed a blue shift in the nitrile stretching frequency to a higher energy in the liquid clathrates. This would indicate that the nitrile is slightly less basic which strongly agrees with the idea of electron donation observed from the NMR. The major takeaway from the IR spectroscopy can be brought forth through the
observation of the out of plane bending mode of the aromatics in the liquid clathrates compared to the out of plane bending mode of the aromatics in non-liquid clathrate formers. In the studied case, the out of plane bending mode of benzene when complexed in the liquid clathrate exhibited a shift to a much higher energy in relation to neat benzene. In contrast, the completely miscible molecular liquid benzylamine only showed an extremely small shift in relation to the neat aromatic. This indicates a higher energy is required for this stretch to occur leading one to believe that the liquid clathrates are more ordered. They are more ordered in the since that the associative interactions of the liquid clathrates are strong enough to limit the movement and freedom of the aromatic and cause this increase in the energy of the out of plane bend, whereas the interaction of the completely miscible liquid is in a solvation sense and it has freedom of movement and there is no restriction of the out of plane bending.

Differential scanning calorimetry revealed interesting thermal behavior comparisons between the liquid clathrate forming aromatics and the completely miscible molecular liquids. In all liquid clathrate cases, a melting was observed close to the melting point of the neat aromatic. As the amount of aromatic increases in the IL approaching liquid clathrate concentration, the observed thermal transitions increase in relative order which would agree with the conclusion from the IR that the liquid clathrates are exhibiting a higher order than the completely miscible mixtures at the same concentration. The thermal behavior of the completely miscible molecular liquids trended pretty normally with only a melting point depression observed which is most likely due to the dilution effect from the IL. The level or ordering of the thermal
transitions was not observed to be changing with the completely miscible molecular liquids.

A range of characterization techniques show that, not only are liquid clathrates a consistent and reproducible way to controllably alter and improve deficient physical properties of the IL, but liquid clathrates exhibit strong electronic interactions that should be considered when designing future liquid clathrates in not only the area of energetic materials, but in other areas such as separations and solvent systems.
CHAPTER 4

DESIGN OF THE ELECTRONIC PROPERTIES OF ENERGETIC LIQUID CLATHRATES TO ENHANCE HYPERGOLIC PROPERTIES

4.1 Introduction

Ionic liquids are now being utilized as energetic materials based on their ability to be hypergolic with a variety of oxidizers. The first foray into the use of ILs as hypergolic fuels was initiated by Schneider and coworkers at the Air Force Research Laboratory utilizing the dicyanamide anion as a trigger ion for the hypergolic reaction with WFNA. This initial push into the field of hypergolic ILs heavily focused on the use of the anion as a ‘hypergolic trigger’ for the decomposition process. As previously mentioned, the dicyanamide anion was the initial focus with work then moving to the nitrocyanamide anion, a nitro-variation of the dicyanamide anion. From here the work moved to discover new anions that would be hypergolic with greener oxidizers compared to HNO₃ or N₂O₄. This was achieved through the synthesis of a boroaluminum-hydride anion which was hypergolic with hydrogen peroxide. Around this same time, researchers were pushing the boundaries of structural moieties that could be used as platforms for hypergolic molecules. One of the major benefits of an IL being that both the cation and anion can be independently designed led the way for researchers to begin to
look at the possibility of designing hypergolicity into the cation portion of the IL. This was achieved in 2009 with the 2,2-dialkyltriazanium cation. This cation, with a variety of anions including dicyanamide, nitrate, and nitrocyanamide, was shown to be hypergolic.\textsuperscript{30}

It is at this point that our group took an interest in designing EILs with hypergolicity in mind and how we could improve upon the current platform of hypergolic EILs. Our first attempt at improving the hypergolic EIL platform was with the first reported solubilization of boron nanoparticles in the EILs [BMIM][DCA] and [MAT][DCA].\textsuperscript{3} Not only were the loaded EILs more dense, but in the case of the loaded [MAT][DCA] samples the hypergolic reaction exhibited much more vigorous reactions leading researchers to believe that the nanoparticles positively enhanced the ignition. Our next strategy was to target the EILs’ physical properties for improvement in the hypergolic ignition delay. With this came the solubilization of graphene in [MAT][DCA].\textsuperscript{31} This solubilization of graphene in the EIL acted to ‘lubricate’ the ionic liquid by reducing the intramolecular interactions in the IL, and consequently, reduce the viscosity of the material allowing for the material to be hypergolic at temperatures not previously reported.

It is in this same vein that we sought to use the liquid clathrate platform to improve targeted physical properties of current EILs. This was achieved, as stated above, by the addition of aromatics to current EILs to form energetic liquid clathrates. These energetic liquid clathrates exhibited reduced viscosity compared to the parent EIL while only showing a slight reduction in density which is crucial for future consideration as an energetic material. With the in-depth spectroscopy study that was conducted, we had a
strong foundation for what interactions were occurring in the system and we wanted to delve into how these electronic interactions affected the resulting energetic performance in the hypergolic reaction. Herein we report how the donation of electron density from the anion to the cation negatively affects the hypergolic reaction through increased acidity of the anion while in liquid clathrate form and discouraging the hypergolic decomposition pathway. These experimental finding are augmented by theoretical modeling calculations performed by Dr. Chambreau of AFRL at Edwards Air Force Base.

4.2 Experimental

4.2.1 Chemicals

Benzene, toluene, o-xylene, m-xylene, p-xylene, 1,2,5-trimethyl-pyrrole, 2,5-dimethyl-furan, tetrahydrofuran, 1-methyl-pyrrole, 2,5-dimethyl-pyrrole, aniline, benzylamine, nitrobenzene, and WFNA were purchased from Sigma Aldrich (St. Louis, MO) and used as received. [BMIM][DCA] was purchased from IoLiTec. High vacuum drying for 48 hours was performed on the ILs, otherwise they were used as received.

4.2.2 Experimental Hypergolic Ignition Testing

Hypergolic ignition testing was performed on all of the liquid clathrates as well as select completely miscible molecular liquid mixtures. The ignition test was performed by placing 500 μL of 99% WFNA in a cuvette using a Redlake MotionPro HS-4 at 1000 fps. 10 μL of liquid clathrate fuel was dropped into the oxidizer from a syringe. The time the fuel hit the oxidizer was designated time zero with the time of first observation of flame
ignition designated as time final. The difference in these times, in milliseconds, yields ignition delay for the fuel.

4.2.3 Theoretical Model Calculations of Liquid Clathrates

Theoretical calculations were performed by Dr. Steven Chambreau at the Air Force Research Laboratory at Edwards Air Force Base, California. These density functional theory calculation were performed at the M06/6-31+G(d,p) level. The M06 suite of functionals is a set of meta-hybrid functionals that are constructed with empirical fitting of parameters, but are constrained to the uniform electron gas. The 6-31+G(d,p) basis set is a split-valence double-zeta basis set.

4.3 Results and Discussion

4.3.1 Experimental Hypergolic Ignition Testing

The liquid clathrates formed with the IL and the aromatics were tested for hypergolicity along with select completely miscible mixtures. The trend (Table 1) that was revealed by the ignition testing was extremely interesting and showed nice correlations with the previous spectroscopic data. A major increase in ignition delay was observed as the amount of aromatic content increased. This can be seen in that the highest aromatic content liquid clathrate, [BMIM][DCA]•2.10 benzene, rarely reacted vigorously enough to spontaneously ignite. As the maximum aromatic content went down in the liquid clathrates, the ignitions got more consistent and closer to the baseline time and power of the neat IL [BMIM][DCA].

There are two possible hypotheses that could explain this increase in ignition delay with increasing concentration of aromatic. One would be the idea that it is simply a
dilution factor in the fuel, that with the addition of aromatic, there are less of the dicyanamide anions to decompose and start the ignition pathway. While this is a valid thought, we report here how spectroscopy in conjunction with the experimental hypergolicity can explain the increase in ignition delay through the electronics of the system. Dr. Chambreau and coworkers published an article in 2008 that details the generally accepted decomposition mechanism for the hypergolic reaction of the dicyanamide anion and WFNA (Figure 4.1). On analysis of this mechanism, it can be seen that the initial step involves electronic resonance in the dicyanamide anion, and then protonation of the terminal nitrogen of the anion by the nitric acid. This resonance indicated a high amount of electron density concentrated on the anion. This high amount of electron density is required for the initial protonation step by the nitric acid to occur, and it has to happen fast enough to generate enough heat in the reaction to spontaneously ignite. We reported above that when the EIL is complexed in liquid clathrate form, there is a significant electron density donation from the anion to the cation that was observed in the spectroscopy. The large donation of electron density causes the anion to be become slightly more positive and slightly less basic, which is supported by data in the IR spectra. This less basic anion has less electron density than the parent EIL and does not have enough electron density to promote the protonation of the terminal nitrogen by the WFNA. With the protonation of the anion being slightly less favorable, it is causing the protonation to slow to the point where the reaction is not happening fast enough for spontaneous ignition to occur. This is in strong agreement with the experimental hypergolicity in that the spectroscopy shows that the higher the aromatic content of the liquid clathrate, the higher the electron density donation from the anion to the cation, and,
consequently, the higher the ignition delay. Another result pointing to electronics being the cause behind the increase in ignition delay is the [BMIM][DCA]/aniline simple mixture ignition delay times. Aniline has been shown to be hypergolic with WFNA\textsuperscript{35} in different solutions in the past and this can provide some insight into the ignition delay times. This simple mixture still showed an increase in ignition delay, which again, point in the direction of the electronics causing this longer ignition delay compared to a simple dilution. If it was just a simple dilution, the ignition delay of [BMIM][DCA]/aniline mixture would not show an increased ignition delay due to aniline being hypergolic as well. There would be the same number of hypergolic trigger groups is solution as compared to the neat parent IL. This evidence strongly point to the electronics of the system causing this large increase in ignition delay.
Table 4.1  Ignition delays of liquid clathrate fuels.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Ignition Delay (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BMIM][DCA]</td>
<td>50</td>
</tr>
<tr>
<td>[BMIM][DCA]•0.30 m-xylene</td>
<td>64</td>
</tr>
<tr>
<td>[BMIM][DCA]•0.40 p-xylene</td>
<td>75</td>
</tr>
<tr>
<td>[BMIM][DCA]•0.50 o-xylene</td>
<td>76</td>
</tr>
<tr>
<td>[BMIM][DCA]•0.90 toluene</td>
<td>177</td>
</tr>
<tr>
<td>[BMIM][DCA]•2.10 benzene</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Figure 4.1  Comparison of the hypergolic reaction of WFNA and the DCA anion compared to the same reaction with WFNA and a liquid clathrate.
4.3.2 Theoretical Model Calculations of Liquid Clathrates

Dr. Steven Chambreau performed theoretical modeling calculations of the highest occupied molecular orbital in a neat IL and a theoretical liquid clathrate at the M06/6-31+G(d,p) level. The HOMO of the neat IL [EMIM][DCA], as we would expect, exhibits a large concentration of the HOMO electron density around the anion with only a small portion in the π system of the imidazolium cation (Figure 4.2). In large contrast, the HOMO of the theoretical liquid clathrates [EMIM][DCA]•1.00 benzene (Figure 4.3) and [EMIM][DCA]•2.00 benzene (Figure 4.4) show large shifts of the electron density that was concentrated on the anion, now residing on the cation. The geometry seen in the model with two units of benzene shows an orientation of the aromatic and the EIL that would agree with what is observed in the spectroscopy in that the aromatic surrounds the cation with the anion above. The electron density donation noted above also agrees strongly with the experimental NMR spectroscopy reported above where a downfield shift of the dicyanamide carbon indicates an electron density donation and the anion becoming slightly more positive and less basic. This slightly more positive and less basic anion is not favorable for protonation by the WFNA and slows the reaction of the anion and nitric acid to the point where the reaction does not happen fast enough for it to spontaneously ignite as we see in the experimental hypergolicity with the [BMIM][DCA]/benzene liquid clathrate.
Figure 4.2  HOMO of [EMIM][DCA] showing a large concentration of electron density around the dicyanamide anion. Model provided by Dr. Steven Chambreau.
Figure 4.3  HOMO of [EMIM][DCA]•1.00 benzene showing the significant electron density donation from the anion to the aromatic portion of the imidazolium cation. Model provided by Dr. Steven Chambreau.
Figure 4.4  HOMO of [EMIM][DCA]•1.00 benzene showing the significant electron density donation from the anion to the aromatic portion of the imidazolium cation. Model provided by Dr. Steven Chambreau.
4.3.3 Conclusions

Experimental hypergolic ignition delays in tandem with theoretical modeling calculations agree strongly with spectroscopic observation reported earlier. These spectroscopic observations showed that, when in liquid clathrate form, there was a significant electron density donation from the anion to the cation making the anion slightly more positive and less basic. This slightly more positive and less basic anion is not favorable to be protonated fast enough to spontaneously ignite. This is reflected in the hypergolic ignition delays with the higher aromatic content liquid clathrates exhibiting high ignition times with the highest aromatic content liquid clathrate showing no ignition. Theoretical modeling agrees with the experimental results in that with the addition of an aromatic to the IL, there is an electron density donation from the anion to the cation. The majority of electron density concentration in the theoretical models was centered on the anion in the parent IL, but when an aromatic was introduced into the system forming a theoretical liquid clathrate the electron density in the HOMO shifts drastically to the cation. These results provide significant proof for the hypothesis that the increase in ignition delay is purely electronic compared to a simple dilution effect from the aromatic.

With this in-depth knowledge of the molecular level electron interactions of the liquid clathrates, future work in this area can be centered on designing the electronics of the aromatic additive to discourage donation of electron density from the anion to the cation, and, possibly, encourage electron density acceptance to the anion. Another route forward would be to design an energetic aromatic additive, such as trinitrotoluene, that would pack a significant energetic increase in the EIL and not decrease the ignition delay
to a point where the material is unusable. This knowledge of the liquid clathrate electronics can be utilized to move forward in several different paths. This work reported here shows not only the correlation of the electronics of system to the energetic potential of the system, but also that a two pronged attack of experimental and theoretical strategies will be a useful tool in the area moving forward.
CHAPTER 5

CONCLUSIONS

Ionic liquids have improved and morphed into materials of vast applicability. From their beginning as electrolytes, to being utilized as designer solvents, to being the answer to pharmaceutical problems such as polymorphism and low solubility, and to being considered as advanced energetic materials; ILs will continue to expand the boundary of the portfolio of uses. This ability to adapt and continue to improve IL applicability stems from the tunability and compartmental design made available to IL researchers. These developing improvements through tunability and compartmental design are only the beginning. With each new generation of problems presented will give rise to new generations of answers brought about by the innovative physical and chemical properties of this class of salts. The electronics of these systems are clearly what drives the unique properties and an ever changing and ever evolving knowledge base is required to properly utilize the power of these ionic liquids.

Using ionic liquids as energetic materials is not a novel application, but utilizing the ILs’ ability to form liquid clathrates to target and improve physical properties is a step in the right direction of effectively and efficiently utilizing the strengths of ILs while addressing some of the few inherent deficiencies to improve upon the current EIL platform. This model provides an in-depth knowledge into the electronics of the system which can be utilized to design new ILs and new additives for specific uses. The liquid clathrates provide a low viscosity platform from which many avenues could be pursued
forward in designing new age energetic materials. Not only does this work provide a platform to move forward with liquid clathrates, but the approach can also be utilized in other areas apart from energetic materials. The unique electronic interactions can be exploited in the materials’ possible ability to solvate and extract other materials. There are many possibilities in which the unique electron configuration of the liquid clathrates could benefit in separations and in the synthesis of designer solvents.

Finally, this work reported here provides insight into the ability to control and exploit the unique electronic properties of ILs and liquid clathrates. With the knowledge of the electron interactions of these systems, there are limitless design opportunities to efficiently invent new ILs and aromatic additives to synthesize novel liquid clathrate systems that could not only improve upon the physical properties of the parent IL as seen in this work, but also improve upon the energetic characteristics as well. If the electronics of the system could be designed in such a way as to promote electron acceptance by the anion while at the same time decreasing viscosity, researchers would be well on their way to finding an excellent candidate as a next generation energetic material. This work has shown only a small part of the promise that ILs hold in their ability to be modified by small scale additives. Molecular aromatics and nanoparticles are only the beginning of research into modifying bulk ILs, and, soon to follow, will be additives that truly take advantage of the uniqueness of the ion pair. The research presented here exemplifies the promise of ionic liquids moving forward in the energetics community in that they offer a unique platform from which to add, modify, and tune the ILs to whatever specific application is needed. The flexibility and functionality is unique and provides many successful avenues moving forward.
REFERENCES


