EXPERIMENTAL INVESTIGATION OF IONIC LIQUID MIXTURES FOR ELECTROSPRAY PROPULSION

by

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ABSTRACT

In recent years, there has been a dramatic increase in the number of small satellites (namely MicroSats, NanoSats, and CubeSats) in earth orbit; many of these are launched without propulsion systems. Multi-mode propulsion systems, capable of operating in either chemical or electric mode, have been proposed as attractive candidates for use in small satellites. Such systems are mass and volume optimal and flexible in terms of thrust requirements. Most previous work on multi-mode systems has focused on chemical mode performance. The work in this dissertation focuses on the electric mode performance of these propulsion systems.

The work in this research is comprised of three separate but related technical papers, each adding insight into the characterization and design of the electrospray (electric) mode of multi-mode propellant systems. The first paper focuses on determining species in the electrospray plume of a specific propellant, composed of 1-ethyl-3-methylimidazolium ethylsulfate ([Emim][$EtSO_4$]) and hydroxylammonium nitrate (HAN), previously optimized for chemical mode performance. This paper shows HAN, a common energetic component, is present in the plume. The second paper identifies how changes in ionic liquid (IL) mixture ratio affects the species present in the plume and shows clear variations in plume species with mixture ratio for [Emim][$EtSO_4$] and ethylammonium nitrate mixtures. The last paper quantifies how non-linearity in physical properties within IL mixtures impacts propellant performance. Predictions assuming linear mixing of properties over-predict emission current and thrust by up to 45% and 20%, respectively, when compared to calculations based on experimental mixture data.

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NOMENCLATURE

Symbol	Description
amu	Atomic mass
$[BF_4]$	Tetrafluoroborate
EAN	Ethylammonium Nitrate
[Emim]	1-ethyl-3-methylimidazolium
$[EtSO_4]$	Ethyl sulfate
$f(\varepsilon)$	Function of the dielectric constant.
ΔG_{rxn}	Gibbs Free Energy of Reaction
[HAN]	Hydroxylammonium nitrate
I	Current
Κ	Conductivity
$\dot{m}$	Mass flow rate of propellant
m/q	Mass to Charge Ratio
Q	Flow rate
V_{acc}	Accerlerating voltage
γ	Surface tension
ε	Dielectric constant
ρ	Density

1. INTRODUCTION

This dissertation provides a compilation of work focused on the characteristics, physics, and performance of multi-mode propulsion systems using ionic liquids (ILs). Multi-mode propulsion systems can provide both chemical and electrical propulsion modes while utilizing the same propellant and, in principle, shared feed systems and tankage. Previous efforts in this area have primarily focused on optimizing mixtures of ionic liquids for chemical mode performance; this has mainly been done through modeling efforts that used the NASA CEA program [1]. The purpose of the work presented in this dissertation is to study the electrospray characteristics of ILs and mixtures of ILs proposed for propulsive applications. Many multi-mode propellants and chemical propellants currently in development contain hydroxylammonium nitrate (HAN). HAN is of interest in chemical propulsion modes as a potential replacement for traditional hydrazine or as an energetic component that is added to other liquid propellants to form energetic mixtures. HAN, however, has not been specifically identified as electrosprayable in mixtures or solid form prior to this work. In addition to the focus on electrospray characteristics and performance of ILs in mixtures, including the investigation of HAN as a constituent in such mixtures, the non-linearity of the physical properties of ILs in mixtures is also examined in the present work. Physical properties of mixtures of ILs are not well predicted by simple mole or mass averaged mixing laws. Because of this, designing and optimizing multi-mode propellants for use in the electric mode is challenging without adequate understanding of the non-linearity of mixture properties and current lack of validation data for modeling and simulation codes in development.

As will be detailed in subsequent work, experimental mass spectra have been measured for neat (pure) samples of 1-ethyl-3-methylimidazolium ethyl sulfate ([Emim][$EtSO_4$]), ethylammonium nitrate (EAN), a mixture of 41% [Emim][$EtSO_4$] with 59% HAN by mass, and mixtures of [Emim][$EtSO_4$] with EAN. There are many unique peaks observed in the HAN-[Emim][$EtSO_4$] mass spectra that are not present in the [Emim][$EtSO_4$] spectra. This allows for the identification of the nitrate anion and both proton-transferred neutral forms of HAN (i.e., hydroxylamine and nitric acid) in the anion plume; no unique peaks are observed in cation mode. Both sets of mixed liquids show emissions containing ions from both liquids, i.e., cation and anion swapping. The addition of EAN changes the amount of such mixed emissions in the plume such that no mixed species are definitively present at 25% EAN while mixed species are observed at 50% EAN. This observation matches previously noted phenomenon in hydrogen bond restructuring within [Emim][$EtSO_4$] water mixtures. Addition of EAN is also shown to produce additional peaks in the emissions from [Emim][$EtSO_4$] in both modes (unlike that observed with HAN); EAN also has both nitrate and ethylammonium ions present in the liquid and in their proton transferred constituents.

Analytical predictions of thruster performance are produced based on experimentally acquired physical properties of surface tension, density, and conductivity (hence are based upon the actual non-linearity of these characteristics). In comparison, thruster performance calculations that utilize mixture properties based on simple linear mixing laws are shown to be larger. This is true for all three IL mixture sets examined in the present work. The maximum observed difference for the performance estimates utilizing linear mixing laws is 45% (over-prediction) of emission current in mixtures of [Emim][EtSO$_4$] and EAN. HAN is also observed to increase predicted electric mode performance by increasing mixture conductivity; however, there are saturation limit concerns when HAN is used to form an IL mixture.

The organization of the following sections is as follows. Section 1 (This section) provides an overview of and broad background for this research. Paper I, Paper II, and Paper III are the three journal papers that account for the bulk of this work, and Section 2 provides a recap of major conclusions and summary of the work subsequently presented in this dissertation (contained within the three articles subsequent to this overview). More specifically, in Section 1, a brief review of the general development and applications of ionic liquids and their mixtures is provided. A review is also provided of previous development efforts involving the specific applications of ionic liquids as space craft propellants and includes discussion regarding propulsion systems utilizing such propellants as well as the broader context of the use of ionic liquids in multi-mode space propulsion. Paper I is a published paper where hydroxylammonium nitrate is found within an electrospray plume. This finding is novel as previously no studies have identified this common propellant component within an electrospray plume; thus, this is the first time where this component is found to function in electrospray mode. Paper II follows up the work done in Paper I by presenting a paper focused on identifying how changes in mixture ratio (of IL components) affect changes in electrospray plume composition. Paper II uses EAN in place of HAN to provide a wider range of potential mixtures and definitively identifies changes in plume composition due to changes in mixture ratio of component ILs. Paper III details how variations in mixture ratio for four different pairs of ionic liquids affects predicted performance. In doing this, Paper III highlights major concerns with assuming linear mixing of physical properties during preliminary design and provides validation data for modeling and simulation efforts. Lastly, Section 2 then provides a summary of conclusions and recommendations of the overall work as provided in the three papers within the dissertation. These papers are as follows:

1. Hydroxylammonium Nitrate Species in a Monopropellant Electrospray Plume (Paper I),
2. Mass spectrometric investigation of mixtures containing ionic liquids 1-ethyl-3-methyl-imidazolium ethylsulfate and ethylammonium nitrate (Paper II), and
3. Effect of Nonlinear Mixing on Electrospray Propulsion Predictions (Paper III).

1.1. IONIC LIQUIDS (OVERVIEW)

In this section, a brief history of ionic liquids will be presented along with information on their use as contemporary propellants. ILs have many favorable physical properties for use as electrospray propellants such as a low melting temperature and a high density, surface tension, and conductivity [2]. The usefulness and complexity of IL mixtures will also be discussed; essentially, the large number of potential ions for use in mixtures holds promise for designing liquid properties [3].

1.1.1. A Brief History of Ionic Liquids. Ionic liquids are molten salts that exist with anions and cations in the liquid form. A subset of ILs is designated as room temperature ionic liquids (RTIL), since these ILs exists in the liquid phase at room temperature. The first RTIL was reported in 1914 by Hurley and Wier when they observed EAN to melt at 12 °C [4]. RTILs are good candidates for propellants as their low melting temperature aids in storability; some RTILs are even more easily stored (i.e. require less energy to keep above their melting temperature) than state-of-the-art hydrazine [1]. Recently, interest in ILs has grown substantially as IL's have the potential to become designer solvents [3].

Ionic liquids are commonly divided into subcategories in order to aid classification. One way to classify ILs is based on their proton donor/acceptor ability. Protic ionic liquids (PILs) generally have a high affinity for proton donor/acceptor exchange. Conversely, aprotic ionic liquids (AILs) generally do not have a high affinity for proton donor/acceptor exchange. The PILs are synthesized by reacting a Brønsted base with a Brønsted acid. In this reaction a hydrogen ion from the acid transfers to the base creating an anion and cation. Protic ILs are also characterized by their tendency to form large multi-dimensional hydrogen bond networks [5, 6]. Aprotic ionic liquids, specifically imidazole based AILs, have been the subject of significant contemporary research and have been noted to be less likely to form large hydrogen bond networks [7].

1.1.2. Contemporary Propellants. Ionic liquids are being investigated as candidate propellants. Specifically, hydroxylammonium nitrate (HAN) and HAN based mixtures are currently under consideration/development to replace hydrazine. Hydrazine is still considered to be the state-of-the-art chemical monopropellant. However, it has many disadvantages despite its significant heritage. Hydrazine was first used as a fuel component for the German ME 163 rocket powered fighter interceptor during World War 2 and has remained a staple propellant due to its stability and relative ease of storage [8] and remains the propellant of choice for many space based systems. However, the toxic nature of hydrazine is an important disadvantage for use as a propellant; considerable work is therefore now being done to identify a 'green' and preferably non-carcinogenic-vapor-toxin replacement for hydrazine. One such candidate in the category of ionic liquids is HAN [8]. Recent studies have shown that ILs may have equivalent performance to hydrazine without the toxicity concerns and, in some instances, are easier to store [1].

Ionic liquids are currently the standard propellants of choice for electrospray systems. The LISA Pathfinder mission flight tested an electrospray thruster created by Busek with an ionic liquid propellant [9]. During the LISA Pathfinder mission, the ionic liquid propellant feed electrospray system met 100% of the stated mission goals [10]. The Busek thruster had a thrust range of 5-30 μN, thruster response time of less than 100s (between minimum and maximum thrust), and an operation time of 60 days; additionally, the thrust precision was better than 0.1 μN, and the noise was less than 0.1 $\mu N/\sqrt{Hz}$ [11]. The in-development electrospray-microtube propulsion system proposed by Berg also seeks to use ionic liquid propellants along with several other systems under development. Berg's propellant is a mixture of two different sets of cations and anions forming an ionic liquid mixture. Additional development efforts are discussed in Section 1.2.1 Stand-Alone Electrospray Propulsion Systems. [1]. Such ionic liquid mixtures can also be referred to as double salts due to their nonlinear mixing nature [3].

1.1.3. Double Salt Ionic Liquids. Double salts have been known since at least 1907 when Ida Freund coined the term. Freund observed that when salts are mixed in solution the resulting mixture may have different properties than would be predicted assuming additive properties [12]. This characteristic extends to ILs (molten salts) in that their mixture properties may not even be bounded by those of their parent ILs [3]. There are almost an infinite number of ion pairings that can be used to form ionic liquids, especially when examining pairings of two or more ionic liquids (i.e., three or more distinct ions) [13]. The difficulty in characterizing mixtures of ILs is the complicated nature of the ionic interactions that occur in such mixtures. For instance, if two liquids with cation-anion pairs of A-B and C-D are mixed, ions can swap or, at the minimum, electrostatically interact with the ions from the other liquid. The ionic liquid mixture can then have additional ion pairings of A-D or B-C; these new ionic interactions may be what gives rise to the so called "double salt" nature of ionic liquids where the change in distribution of ions on the microscopic level manifests itself in changes in macroscopic properties (i.e., density, conductivity, etc.) [3, 13].

The large number of potential cations and anions available for combination when synthesizing ionic liquids and IL mixtures, coupled with the ability to design combinations of these ions with specific properties, make Ionic liquids and IL mixtures attractive for specialized applications. There are a broad number of applications for ionic liquids; however, research on their mixtures has been limited so far [3]. Some mixtures of ionic liquids appear to behave ideally in that resulting physical properties of the solution obey mole or mass-averaged mixing laws; in other mixtures, the resulting physical properties of the solution vary in a non-linear fashion with relative component quantities [3]. Significant work has been done attempting to explain the non-linear trends in physical properties, produce physical property predictions, and analyze under what circumstances non-linear behavior may occur [3]. Classical molecular dynamics (MD) simulations have recently shown promise in predicting physical properties of mixtures by accounting for the inter-ion effects; however, these simulations studies are limited in number and often have limited validation data [7]. Challenges with mixture property predictions have not halted designing mixtures for specific applications but they have slowed the development process of mixtures. The potential of being able to ‘tune’ physio-chemical properties makes mixtures of ILs attractive for specialized applications [3]. The application of interest in this work is the design of spacecraft propellants; all three papers presented here address this challenge in some capacity.

1.2. ELECTROSPRAY PROPULSION SYSTEMS

Electrospray propulsion has been a major focus of interest in the propulsion community; most relevant to this work is the fact that electrospray is being considered as the electric mode for the multi-mode system currently in development by Dr. Berg [1]. This section provides background on the history of electrospray and electrospray propulsion; work in this area has culminated in a successful mission. Subsequently, the specifics on how electrospray relates to the development of an integrated “multi-mode” system will be discussed.

1.2.1. Stand-Alone Electrospray Propulsion Systems. The study of electrospray systems began with Geoffrey Taylor’s work on electro-hydrodynamics of water droplets in electric fields. In this work, Taylor was able to identify that a sufficiently strong electric field acting on a charged liquid causes a jet of the charged liquid to emanate from the tip of a cone [14]. Taylor elegantly described the formation of what would later become known as the “Taylor Cone” as the point when electrostatic forces reach perfect equilibrium with the maximum surface tension. With a slight increase in electric field gradient, the result is a jet emission [14]. Colloidal electrospray thrusters are based on this process; electrospray thrusters operating in pure ion emission mode (i.e. emitting only ions not jets of liquid/droplets from the meniscus) also rely on strong electric fields to pull ions off the meniscus. By applying a sufficiently strong electric field (on the order of 1 V/nm) ions are pulled off the liquid surface, the linear momentum imparted to the generated ions provides the impulse (i.e. thrust) to the spacecraft.

First attempts to design thrusters based on ion extraction from liquids with electric fields were called FEEP thrusters (Field Emission Electric Propulsion). FEEP thrusters use liquid metals as their ion propellants; these are thrust limited since they operate in field emission mode and thus are only imparting momentum on single metal atoms [15]. FEEP thrusters are only operated in cation mode and require the use of a beam neutralizer to maintain a neutrally charged spacecraft and ion beam [16]. These systems have been commercialized for small satellites by Enpulsion with specific impulse up to 6,000 seconds and thrust of up to .4 mN (at 3,300 seconds) [17].

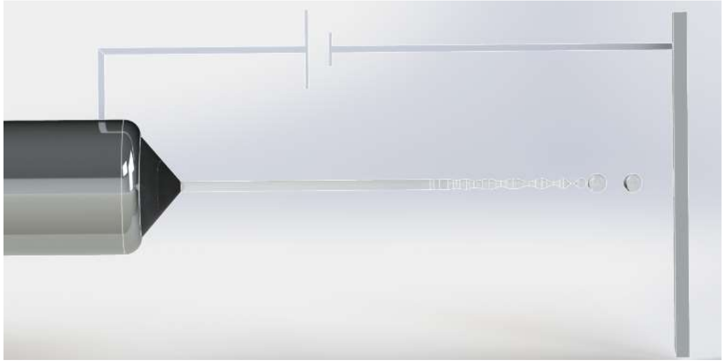

Figure 1.1: Illustration of capillary electrospray emission

Modern ionic-liquid based electrospray thrusters have surmounted several of these challenges. Figure 1.1 illustrates capillary electrospray emission. In Figure 1.1, the capillary is on the left with the extractor grid on the right; a large electric potential is applied between the two. The electric field deforms the meniscus and electrostatically extracts ions and droplets, the composition of ions and droplets depends on flow rate [18]. Ionic liquid propellant is fluid dynamically pumped into the capillary and serves as the ion source. In their liquid form, Ionic liquids exist as a set of cations and anions making them attractive ion sources. By operating the electrospray thruster in an AC mode, the craft can be kept charge neutral by emitting X cations with a negative applied electric potential (between emitter and extractor), followed by X anions by reversing the polarity. Such an architecture has been described by Berg who also reported performance of electrospray of ILs in both cation and anion emission modes [1]. A controller would likely be necessary to control charge build up by switching emission modes. This is similar to what is used with Enpulsion's FEEP thruster to control the usage of the beam neutralizer [17]. Electrospray thrusters may avoid the use of beam neutralizers by operating in an alternating polarity mode, and thus avoid the corresponding mass penalty. Sometimes it is advantageous to operate only in cation mode; for instance, Busek Co operated in only cation emission mode during the LISA Pathfinder mission for simplicity and used a beam neutralizer to maintain charge neutrality. By selecting ILs with large cations and anions, more thrust can be realized from each ion emitted. More thrust is realized by increasing the mass-to-charge ratio; however, this additional thrust comes at the detriment of specific impulse. specifically, for a given applied voltage, having higher ion mass yields more imparted linear momentum to the ion by the electric field (i.e.

higher thrust to the spacecraft). Lighter ions have higher velocities for a given electric field strength when compared to heavier ions and are thus transfering momentum more mass efficiently to the spacecraft (i.e. lighter ions have a higher specific impulse). The thrust/specific impulse tradeoff is discussed by Chiu et al. along with voltage constraints pertinent to satellite systems [16]. Modern electrospray thruster designs have proposed the idea of "multi-plexing," which involves arrays of electrospray emitters operating simultaneously to increase thrust while maintaining specific impulse [19]. The Space Propulsion Lab at MIT, under direction from Lozano, has been developing a passively fed electrospray thruster system using externally wetted needles for small satellites with success [20] and King has developed and demonstrated electrosprays from ferrofluids [21]. Ionic liquid electrospray thrusters are attractive for spacecraft due to less demanding storage constraints for IL propellants than hydrazine or liquid metal thrusters (due to lower melting temperature) and their flight demonstration as high precission thrust devices [1].

1.2.2. Integrated Multi-Mode Systems. In the literature, the terms "dual-mode" and "multi-mode" both refer to the use of two (or more) distinct propulsion systems, with "multi-mode" being the more general term. The use of the term "multi-mode" or "dual-mode" can refer to two complementary chemical mode propulsions systems, two electric mode systems, or a chemical and electric system. One example of an operational "dual-mode" propulsion system in which both modes were chemical was the Mars Global Surveyor mission that utilized hydrazine as a monopropellant (for attitude control) and as a component for a bipropellant (for flight maneuvers) [22]. Another example of such a system is a chemical-electric dual mode system where the modes complement each other by providing both high thrust and high specific impulse (fuel efficiency) performance options. By combining two different propulsion modes, there can be a broader mission envelope of accomplishable delta-Vs [1]. Mass savings from shared components within a multi-mode system, by integrating propulsion systems together, can lead to an overall system that is more mass optimal than two separate state-of-the-art systems that do not benefit from shared hardware or propellant [23]. Another salient point of such integrated systems is that the optimal specific impulse for each mode is different, stemming from different performance in one mode dictating a different fraction of work needing to be accomplished by the other mode. For instance, a 250 second chemical-mode system would require a 1,000-1,200 second electric mode system as an optimal complementary system; this is currently a performance benchmark that electrospray systems can achieve [24].

Small satellite propulsion systems are currently of significant interest. Ideally, a propulsion system for small satellites would be robust, i.e., optimal for most mission requirements and inexpensive to integrate as these satellites are much less expensive than conventional satellites. The tight constraints on mass and volume make such a design challenging; however, “multi-mode” or “dual-mode” systems hold much promise in providing a robust system that can be easily integrated into satellites [24]. To have the most useful propulsion system for a given mass/volume with a large range of potential maneuvers, each mode of the propulsion system (i.e., chemical and electric) would share as much common hardware as possible along with the propellant [24]. A shared propellant would maintain maximum mission flexibility by allowing in-mission allocation of propellant so that all is available for use in either the chemical mode, electric mode, or any combination thereof [24].

For both thrust systems to share a common propellant, the propellant needs to be capable both of effective combustion for use in the chemical mode, as well as efficient in terms of the electric mode. Additionally, the propellant would need to function in both anion and cation emission modes during electrospray to avoid the requirement of a beam neutralizer and thus save the associated mass [16]. The design of a propellant compatible with the constraints of both chemical and electric modes is of paramount importance to the development of a robust multi-mode system.

Much work has been done on designing a “multi-mode” system and designing a propellant to function within this architecture. Berg et al. identified several different ionic liquids as good candidates for multi-mode propulsion applications [25, 26] under a proposed architecture of a capillary-electrospray (electric) catalyzing microtube (chemical) dual mode system [1]. Mundahl continued this work by characterizing the linear burn rate and decomposition characteristics of several candidate propellants [27-30]. Berg optimized the composition of these liquids, using NASA’s Chemical Equilibrium with Applications (CEA) program for chemical mode performance by determining what composition led to the best thrust. Berg then went on to investigate the catalytic microtube portion of this system [31]. The Chemical mode is a well characterized problem with existing methodology and known tools for optimizing the design.

The electrospray (electric) mode has not been studied as extensively as the chemical mode. One common energetic propellant component (HAN) has not been observed in an electrospray plume prior to this work (the focus of Paper I). The effects of mixture ratio variation on plume composition has also not been examined (the focus of Paper II); however, changes in plume composition would affect the average mass-to-charge ratio of emitted species and thus performance. Changes in plume composition may also provide insight into the fundamental, microscopic changes that give rise to non-linear mixing and identify changes in the type of species in the plume [13]. Additionally, little work has been done to quantify the degree of impact nonlinear mixing has on electrospray performance, or how one would go about designing an electric mode propellant using mixtures of ILs; there are many unanswered questions on this topic (Paper III). The potential for designing physio-chemical properties for optimality within the constraints of a "multi-mode" propulsion system is significant. Specifically, Paper III addresses this important issue.

1.3. CONCLUSION

Ionic liquids and their mixtures are of broad interest as potential designer solvents. Mixtures of ionic liquids have the potential for development of designer solvents or even as designer liquids for specific applications. The potential to fine-tune physio-chemical properties of such mixtures makes them particularly attractive as designer spacecraft propellants. Unfortunately, the "double salt" nature of ILs makes them difficult to design. Mixtures of ILs generally do not obey conventional mole averaging or mass averaging mixture laws and the physical properties of mixtures may even be outside the range of the parent ILs combined to form the mixture.

Ionic liquids have opened new avenues in the development of electrospray propulsion systems. Increased molecular weight of these ions, the ready availability of both cations and anions for emission, and their low melting temperatures make ILs attractive as electrospray propellants. Additionally, the potential to have a multi-mode thruster with both capillary electrospray and chemical microtube capabilities with shared hardware (to reduce system mass and increase performance density) make capillary electrospray thrusters very attractive for study.

The shift in satellite architectures from large satellites towards 'constellations' of smaller satellites has created a need for smaller satellite propulsion systems. Ideally, these systems would be as robust, easy to integrate, and have close to optimal performance regardless of what mission the propulsion system is called on to perform as possible. To maximize the utility of such a system the system should have a propellant that can be completely expended in chemical mode, electric mode, or any ratio of the two modes. The system should have the ability to alternate between these two modes as desired.

Multi-mode systems have been studied and are currently under development; previous research has focused on chemical mode performance aspects of multi-mode propellant design and system design. Primarily, previous work has sought to find a liquid that can be electrosprayed but which is then optimized, in terms of composition, for chemical mode performance. Both the "double salt" nature of such a propellant design and the electric mode performance of such mixtures of liquids is thus the focus of this work, especially electrospray of HAN since HAN is a component of fundamental interest to energetic mixture research. HAN is a common ionic liquid additive to form energetic mixtures and has been featured in previous multi-mode propellant research. A better understanding of the electric mode is needed to perform system level optimization that correctly incorporates considerations from both modes. The “double salt” nature of IL mixtures makes it particularly challenging to optimize the electric mode performance of these liquids, since prediction toolboxes are still in development. The objective of this work is to answer some of the questions limiting electrospray propellant design. The specific milestones for this work are reported in Section 1.4 OBJECTIVES.

1.4. OBJECTIVES

There are several areas related to IL mixture propellant design that this work focuses on. These are all relevant to electrospray propulsion systems, either specifically or generally. The objectives for the work, including major cases and issues investigated and assessed in this work, are described as follows:

- Identify species in a plume of IL mixtures containing HAN and determine if HAN can be identified in the plume (Paper I).
- Observe how composition electrospray plumes change with systematic variations of liquid composition and identify if there are “species swapping” species, i.e., species with ions from both ILs, in the plume as would be expected for double salts (Paper I and Paper II).
- Identify how strongly non-linear mixing can affect predicted electrospray performance for IL mixtures (Paper III).
- Provide validation data for MD simulations as these are needed so that MD can continue developing into a tool for numerical predictions of electrospray performance in IL mixtures [7] (Paper II and Paper III).

PAPER

I. HYDROXYLAMMONIUM NITRATE SPECIES IN A MONOPROPELLANT ELECTROSPRAY PLUME

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ABSTRACT

A mixture of 1-ethyl-3-methylimidazolium ethyl sulfate ([Emim][EtSO$_4$]) and hydroxylammonium nitrate (HAN) is an energetic monopropellant potentially suitable in a multi-mode chemical-electric microtube-electrospray micropropulsion system. In this work, electrospray plume mass spectra are compared between the monopropellant mixture and neat [Emim][EtSO$_4$]. This comparison clearly indicates new and additional species present in the plume due to the addition of HAN. Mass spectra from 20-600 amu/q were obtained over a variety of angles and flow rates from 2 pL/sec to 3 nL/sec in both cation and anion extraction modes. Mass spectrum dependence on flow rate and angular orientation agree qualitatively well with literature. Results indicate the presence of HAN-based species in anion mode, but no HAN-based species in cation mode. Three of the four monomer species from the monopropellant are apparent in the plume; $[\mathrm{Emim}]^+$, $[\mathrm{EtSO_4}]^-$, and $[\mathrm{NO_3}]^-$ are observed, while $[\mathrm{HA}]^+$ is noticeably absent. Results also show emission of both proton-transferred covalent forms of HAN: [HA-H] and $[\mathrm{HNO_3}]$. Swapping of anion and cation species between the constituents of the monopropellant mixture is also observed.

1. INTRODUCTION

Hydroxylammonium nitrate (HAN)-based monopropellants are being explored for multi-mode spacecraft propulsion [1-12]. Multi-mode propulsion refers to the use of two or more integrated but fundamentally distinct propulsive modes used on a single spacecraft. Recently proposed systems make use of a combination of a high-specific-impulse (usually electric) mode and a high-thrust (usually chemical) mode. This combination can be beneficial in two primary ways: 1) it allows an increase in mission flexibility [12, 13], and 2) it enhances the potential to design a more efficient orbital maneuver [14-17]. In certain mission scenarios, the utilization of essentially separate (non-integrated) high-specific-impulse and high-thrust (hybrid) propulsion systems has been shown to be beneficial in terms of spacecraft mass savings, and/or for increasing deliverable payload [14, 16, 18]. An even greater mass benefit can be realized by using a shared propellant and/or hardware between thrusters. The mass savings realized from using shared propellant and hardware can allow thrusters to have relatively lower performance when operating in either or both modes while still achieving the desired total system performance with reduced total system mass (when compared to state-of-the-art no-commonality configurations) [3, 12]. Therefore, in order to achieve the full potential of a multi-mode propulsion system, it is desirable to utilize a single propellant for both modes, such that all propellant may be used regardless of the specific choice or order of maneuvers [12].

Recent research has identified a promising monopropellant for a chemical microtube-electrospray propulsion system.[3]. This monopropellant is a mixture of 1-ethyl-3-methylimidazolium ethyl sulfate ([Emim][$EtSO_4$]) and hydroxylammonium nitrate (HAN) at a 59:41 HAN-[Emim][$EtSO_4$] ratio by mass. This mixture ratio has been optimized to provide chemical performance similar to other state-of-the-art monopropellants such as hydrazine, LMP-103, and AF-M315E (~250 sec theoretical with a nozzle). Theoretically it has a highly competitive density specific impulse of 354,750 kg-s/m3 (compared with 365,000 kg-s/m3 for AF-M315E) and maintains a lower combustion temperature (1850 K vs. 2100 K) easing thermal constraints on catalyst materials [3]. This monopropellant has been theoretically investigated [2, 3], synthesized, and shown to demonstrate favorable thermal and catalytic decomposition within a micro-reactor [4, 5, 8]. The monopropellant has also been shown to have stable high performance in an electrospray emitter [6] and has demonstrated burn rate similar to other HAN-based monopropellants [9, 10].

This HAN-[Emim][$EtSO_4$] monopropellant is different from traditional electrospray propellants. It is a double-salt ionic liquid (DSIL) containing two anions and two cations [19], whereas traditional electrospray propellants contain only one cation and one anion (e.g., [Emim][Im], [Emim][BF_4]), a.k.a. neat ionic liquids (ILs). Pure HAN is ionic and exists as a solid monoclinic salt at room temperature [20], but readily dissolves into [Emim][$EtSO_4$] creating a mixture of two salts or a double salt. The mass spectra of emitted ions and droplets are well-known for electrospray of neat ILs [21-23] but have not been studied for DSILs. Further, there is no data in the literature for electrospray of a mixture containing HAN, as a DSIL or otherwise. Lozano has studied the species and energies emitted by a single externally wetted needle with [Emim][BF_4] [24]. Miller et. al. have investigated the ion and droplet contribution in capillary electrospray of [Bmim][DCA] [21], as well as an extensive investigation of [Emim] and [Bmim] cations paired with [Im], [DCA], and [BF_4] anions [22]. A few studies that electrosprayed mixtures were done by Garoz and de la Mora [25], Guerrero et al. [26], and Garoz et al. [27], but no study has reported electrospray of a mixture containing HAN. Garoz and de la Mora used time-of-flight for formamide and methylammonium formate mixtures and have predicted propulsion performance [25]. Guerrero et al. explored propylene carbonate mixtures with [Emim][Im] or [Emim][BF_4] and have used time-of-flight measurements to predict propulsion performance [26]. Garoz et al. studied the properties of electrospray liquids that result in pure ion emission and focused on neat [Emim][$GaCl_4$], [Emim][$C(CN)_3$], and [Emim][$N(CN)_2$] [27].

The focus of this work is mass spectrometry of the DSIL monopropellant HAN-[Emim][$EtSO_4$]. Quadrupole mass spectrometry is used to identify the mass of ions emitted by a capillary emitter within the mass range 20 – 600 amu/q in both cation and anion emission modes. A representative mass spectrum of the HAN-[Emim][$EtSO_4$] monopropellant is compared with that of neat [Emim][$EtSO_4$]. This allows for the first time the identification of HAN species present within an electrospray plume.

2. EXPERIMENTAL SETUP

In this section, characteristics of the investigated propellants are discussed. Descriptions of the electrospray source and the spectrometer are also presented.

2.1. HAN-[Emim]-[$EtSO_4$] MONOPROPELLANT

The process for synthesizing the HAN-[Emim][$EtSO_4$] monopropellant is described extensively in previous studies [4, 7, 8]. The same synthesis path is used here, starting with raw 24% aqueous HAN (Sigma Aldrich) and >95% pure [Emim][$EtSO_4$] (Sigma Aldrich). The final mixture ratio is 59:41 HAN-[Emim][$EtSO_4$] by mass, which results in a density of 1.53 g/cc and very low water content. This is in good agreement with linear mixing of HAN (1.84 g/cc) and [Emim][$EtSO_4$] (1.24 g/cc), which would suggest a density of 1.59 g/cc, based on theoretical mixing laws described in Ref. [19]. A major challenge for multi-mode chemical-electrospray monopropellants is water content. Most HAN-based monopropellants have significant (~>10%) water content [10, 28-33]. While the presence of water is beneficial for the chemical mode, it may be detrimental for the electric electrospray mode. Water is volatile, so when electrospraying in space or ground-based vacuum facilities, its inclusion may lead to bubble formation in the electrospray feed system. Any bubble formation prohibits or causes intermittent Taylor cone formation, adversely affecting ion and droplet extraction, thus negatively affecting propulsion performance. The HAN-[Emim][$EtSO_4$] monopropellant investigated in the present work has very little to no water content. Specifically, recent nuclear magnetic resonance spectroscopy (HNMR) studies have shown that the synthesis path used in this work has <1% water content [7].

The chemical structure of the HAN-[Emim][$EtSO_4$] propellant constituents are shown Figure 1. The chemical formula for $[Emim]^+$ $[EtSO_4]^-$ is $[C_6H_{11}N_2]^+$ $[C_2H_5SO_4]^-$. HAN has an ionic and a proton transferred (sometimes referred to as covalent) form [34]; both forms are shown in Figure 1. In the gas phase, there are three electrically neutral forms of HAN as a single molecule (monomer). The first is the ionic form, pairing hydroxylammonium with nitrate, while the other two involve proton transfer from hydroxylammonium to nitrate creating hydroxylamine and nitric acid. The ionic HAN molecule chemical formula is $[HONH_3]^+$ $[NO_3]^-$ with an ionic bond between the molecules. $[HONH_3]^+$ will be subsequently referred to as $[HA]^+$ in the following discussion. In the proton transferred form, the HAN molecule chemical formula is $[HONH_2][HNO_3]$. For convenience, $[HONH_2]$ will be henceforth referred to as [HA-H]. This molecule has multiple hydrogen bonds between the hydroxylamine and nitric acid molecules. The proton transfer reaction has a relatively low energy of 13.6 kcal/mol in the gas phase [34]. It is unclear how the presence of solvent ([Emim][$EtSO_4$]) affects the energy of this reaction. It may be possible for both ionic and proton transferred forms to exist together in solution. In the liquid phase of the monopropellant under investigation here, the prevalence of this proton transfer reaction and the resulting concentrations of hydroxylamine/hydroxylammonium and nitric acid/nitrate are unknown. However, both ionic and proton-transferred species are observed in the mass spectra that are presented subsequently.

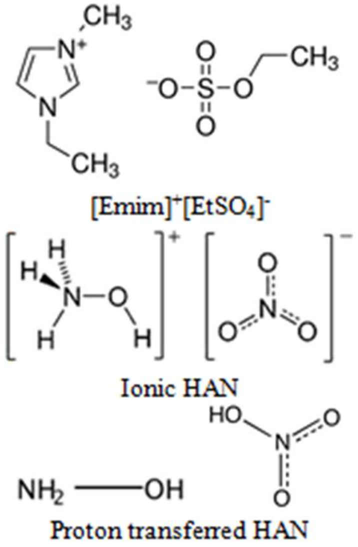

Figure 1: Chemical structure of the constituents of the HAN-based monopropellant. $[Emim]^+$ $[EtSO_4]^-$ and both the ionic $[HA]^+$ $[NO_3]^-$ and proton-transferred (covalent) $[HA\text{-}H][HNO_3]$ forms of HAN

2.2. NEAT [Emim][EtSO4]

The constituents of the energetic HAN monopropellant are HAN and $[Emim][EtSO_4]$. Ideally, spectra of neat $[Emim][EtSO_4]$ and neat HAN would be compared with spectra of the monopropellant mixture. However, neat HAN exists as a solid at room temperature and therefore cannot be electrosprayed with this setup. Aqueous HAN solutions are also impractical to electrospray in vacuum due to the volatility of water. Instead we focus on comparing neat $[Emim][EtSO_4]$ spectra with spectra from the HAN-$[Emim][EtSO_4]$ monopropellant, and attribute differences to the presence of HAN. [Emim][$EtSO_4$] was obtained (purity > 95% from Sigma Aldrich) and volatile impurities were allowed to outgas in a vacuum environment for 8 hours at a nominal pressure of $1x10^{-6}$ Torr. The spectra of this liquid in isolation shows clear indications of both monomer $[Emim]^+$ and $[EtSO_4]^-$ ions, as well as other species that have been identified previously in the literature.

2.3. ELECTROSPRAY SOURCE

The electrospray source has been described in previous work [6, 21, 22]. A schematic of the setup is shown in Figure 2. The source has an extractor plate with a 1.5-mm-diameter aperture and a conductive 50-µm-inner-diameter stainless steel capillary needle (PicoTip MT320-50-5-5) emitter. The emitter tip and extractor are set approximately 1.5 mm apart. This blocks off-axis emissions greater than approximately 30° off centerline. The emitter-extractor assembly is mounted on a rotatable stage. The emitter-extractor assembly and rotation stage are mounted at the end of an arm attached to a vacuum flange with propellant/liquid feed-through and high-voltage feed-through connections. This entire assembly is secured to a vacuum chamber and is operated in vacuum at a nominal pressure of $1x10^{-6}$ Torr. A 100-µm ID silica capillary connects the emitter capillary to the propellant reservoir. When spraying neat [Emim][$EtSO_4$], the reservoir is a pressure feed system that is typical for characterizing ionic liquids using this experimental setup [21]. When operating with the monopropellant, the reservoir is situated on a syringe pump (Harvard Elite Module Picopump) external to vacuum. The syringe pump provides more precise volumetric flow rate control (± 2%) and increases the range under investigation. It also allows experiments to be conducted at the low flow rates desired for multi-mode micropropulsion operation. This apparatus is essentially the same in principle and effect as a pressure fed mode in electrospray emission [35]. Both setups require the silica capillary to pass through a custom feed-through on the vacuum flange.

For the experiments discussed in the present work, a 3.0 kV potential difference is applied between the emitter and extractor. When referenced to facility ground, the emitter is biased at +0.5 kV and the extractor at -2.5 kV for cation emission. Anion emissions are obtained by switching the polarity, that is setting the emitter bias at -0.5 kV and the extractor at +2.5 kV. This potential difference has been shown to provide stable emission of this liquid for the capillary size used in this work [6] and agrees well with theoretical predictions of the starting voltage for electrosprayed liquids and liquid metal ion sources [36]. Flow rates investigated in this study range from 2.0 pL/s to 3.0 nL/s with corresponding emitter currents of 600 to 1100 nA. For most flow rates, spectra were acquired at emitter angular orientations of -30º to 10º in 5º increments, as well as at an angular orientation of -45°.

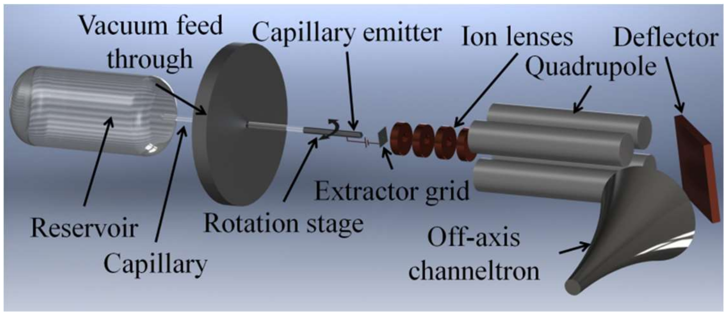

Figure 2: Diagram of mass spectrometer experimental setup showing the reservoir, capillary, vacuum feed-through, capillary emitter, rotation stage, extraction grid, ion lenses, quadrapole mass filter, and off-axis channeltron detector

2.4. QUADRUPOLE MASS SPECTROMETER

The diagnostic used in this study is a quadrupole mass spectrometer. This instrument has been described previously [22, 37]. The emitted electrospray species initially pass through a series of ion lenses to focus the ion beam before it enters the quadrupole. The charged particles then pass through the quadrupole where the mass-to-charge ratio (amu/q) of the particles is selected. After selection based on amu/q, the particles are detected using an off-axis channeltron single-channel electron multiplier with an accompanying deflector. The channeltron is connected to an event counter such that the arrival of a particle at the channeltron registers an event or "count." At a particular amu/q, the counts are integrated for three 25 ms durations for the cation mode and three 100 ms durations for the anion mode. A longer integration time is used in the anion mode in order to average out the larger noise that is inherent to the anion mode. This increased noise is due to the higher applied voltages that are required to attract anions due to the channeltron. The mass step size of the quadrupole instrument was set at 2 amu/q. A calibration experiment conducted directly before this work showed agreement with expected species to within 2 amu/q. Hence it is expected that the amu/q of peaks in the spectra presented below should be accurate to within 2-3 amu/q.

3. RESULTS

This section provides mass spectra results for the monopropellant and neat [Emim][EtSO$_4$]. Qualitative analysis of flow rate and angular orientation effects show trends typical of what is found in previous work for other propellants, and therefore will only be briefly discussed here. As the emitted ions pass through the quadrupole with significant kinetic energy, the resolution of the spectra peaks tends to be degraded, the “zero mass” tends to extend to larger amu/q values, and a general overall baseline is present in the spectrum. These results are similar to previously published phase space data taken over ranges of amu/q, angle, and intensity [22, 37]. A larger droplet concentration, identified as a larger overall baseline in the spectrum, is observed on and near the centerline. The droplet contribution increases with flow rate and the presence of droplets extends to approximately 15° off-axis, results that both agree with literature [21, 22, 38]. No emitted species are found at an angle of -45°. This is expected since emission greater than ~30° off axis is geometrically blocked by the extractor. Spectra are observed to be symmetric about the centerline and in some cases include dual peaks at 5° to 10° off-axis due to emission from the neck region of the Taylor cone. This is a phenomenon previously identified by Lozano [39]. As flow rate increases, the intensity of peaks in the spectra decreases, signifying a decrease in ion emission and an increase in droplet emission, similar to what is documented in the literature [21, 22, 37, 40, 41]. The main focus of the present work is a comparison of spectra taken from the HAN-[Emim][$EtSO_4$] monopropellant mixture with spectra from neat [Emim][$EtSO_4$], and thereby obtaining identification and characterization of HAN-based species within the spectra.

3.1. NEAT [Emim][$EtSO_4$]

Neat [Emim][$EtSO_4$] spectra were acquired using the pressure feed system and the bubble method for prescribing and determining flow rate, as described by Miller [21]. In this method, bubble velocity within the fluid filled capillary is used to calibrate the liquid flow rate dependence on pressure. Representative spectra, at one angle and flow rate combination, are presented for both anion and cation modes in Figure 3 and Figure 4, respectively. These spectra have the number of counts scaled by the intensity of the ion inherent to that mode ($[EtSO_4]^-$ at 126 amu/q for anion mode and $[Emim]^+$ at 111 amu/q for cation mode). The droplet baseline signal has been removed for the neat spectra shifting the spectrum baseline to zero.

The anion spectra of neat $[Emim][EtSO_4]$ at 1.25 nL/s and -15° off axis is shown in Figure 3. Peaks are clearly present at 45, 65, 79, 97, 126, 147, 214, and 280 amu/q. The $[EtSO_4]^-$ anion (mass 126 amu) is clearly evident at 126 amu/q. The peaks at mass values smaller than 126 may be due to fragments (detached molecular chain from the ion). Some of these peaks and corresponding mass values have been reported previously for the $[EtSO_4]^-$ anion. Politi et al. [42] observed peaks at 63, 80, 96, and 125 amu/q in their investigation. They did not identify a species at 45 amu/q because their investigation started at 50 amu/q. The largest amu/q anion observed here, but not shown in Figure 3, is the dimer $[Emim][EtSO_4]\ [EtSO_4]^-$, occurring at 363 amu/q. There are no additional peaks observed above 363 amu/q.

The cation spectra of neat $[Emim][EtSO_4]$ at 1.25 nL/s and -15° off axis is shown is shown in Figure 4. Peaks are clearly present at 28, 41, 55, 68, 83, 96, 111, 140, and 348 amu/q. The $[Emim]^+$ cation (mass 111 amu) is clearly evident at 111 amu/q. Again, the peaks at mass values smaller than 111 amu/q are due to fragmentation which is in line with fragmentation previously observed for [Emim] in this setup [40]. When compared to the electrospray mass spectra obtained for [Emim][Im] by Chiu [40], the cation species presented here have the same [Emim] peak at 111 amu/q and also species identified around 95 and 150 amu/q. Quantum chemistry calculations show fragments of neutral [Emim] are likely to form at these amu values [40]. In contrast to the data presented by Chiu, the data set of Figure 4 shows additional species, potentially due to fragmentation or an impurity (due to the <5% impurities in the raw [Emim][$EtSO_4$] liquid). The mass spectra presented here are focused on the mass range under 350 amu/q, for direct comparison with the propellant spectra, vs. Chiu's focus on spectra out to 1,000 amu/q to investigate dimer species populations. This range allowed the quadrapole to be optimized for maximum beam throughput and thus maximum peak intensity for the $[Emim]^+$ and $[EtSO_4]^-$ ions. The quadrapole was also set for a wider resolution compared to Chiu's work and was set to a minimum resolving power to minimize the system bias against any mass peaks. Operating with these settings increases the sensitivity of the instrument to species in this lower amu/q range. The largest amu/q cation observed here is the dimer $[Emim]^+$ [Emim][$EtSO_4$], occurring at 345 amu/q and shown in Figure 4. There are no additional cation peaks observed above 345 amu/q.

The identified peaks and corresponding species are summarized in Table 1 and Table 2 for anion and cation modes, respectively. Tandem mass spectrometry (MS-MS) could be employed to more precisely characterize the species responsible for the unidentified peaks. MS-MS is a diagnostic technique in which one MS system is used for coarse isolation of a particular amu/q spectrum peak, and then a second MS system is used to finely resolve that peak and separate species with similar amu/q. This can be done at a high enough level of precision for the composition of unidentified peaks to be determined, such as fragments and impurities [43]. The focus of this work is determining the additional species due to the addition of HAN. The unidentified [Emim][EtSO$_4$] species present in the neat spectra are also present in the propellant plume.

3.2. HAN-[Emim][EtSO$_4$] MONOPROPELLANT

Experimental mass spectrum results were obtained for anion and cation emission modes of the electrospray source operating with the HAN-[Emim][EtSO$_4$] mixture monopropellant, and are presented in Figure 3 and Figure 4, respectively. Like the neat [Emim][EtSO$_4$], these spectra have the number of counts scaled by the intensity of the ion inherent to that mode ([EtSO$_4$]$^-$ at 126 amu/q for anion mode and [Emim]$^+$ at 111 amu/q for cation mode). Differences between the neat spectra and monopropellant spectra are the main focus of this work and are discussed in the following sections.

A representative mass spectrum for anion mode emission is shown in Figure 3 for a flow rate of 50 pL/s and an angular orientation of -15º. The monopropellant baseline signal remains in the figure to better differentiate it from the neat spectra in the same figure. Data are not reported at amu/q less than 20 due to the low quadrupole mass offset (zero mass). Additionally, data are not reported at amu/q greater than 300 as there were no peaks observed past 300 amu/q. This is an interesting result. While neat [Emim][EtSO$_4$] exhibits ion clusters, such as an anion dimer we observed at 363 amu/q, the presence of HAN appears to reduce or even eliminate this species. The presence of HAN may increase the inter-molecular distance between [Emim] and [EtSO$_4$] species within the mixture. This would weaken the intermolecular force between the [Emim] and [EtSO$_4$] ions in the mixture, which may then be evidenced by reduced emission of bonded ion clusters in the plume. Additionally, this would suggest that as the level of

HAN in the mixture is decreased, the presence and intensity of larger ion clusters, e.g., dimers and trimers, would increase.

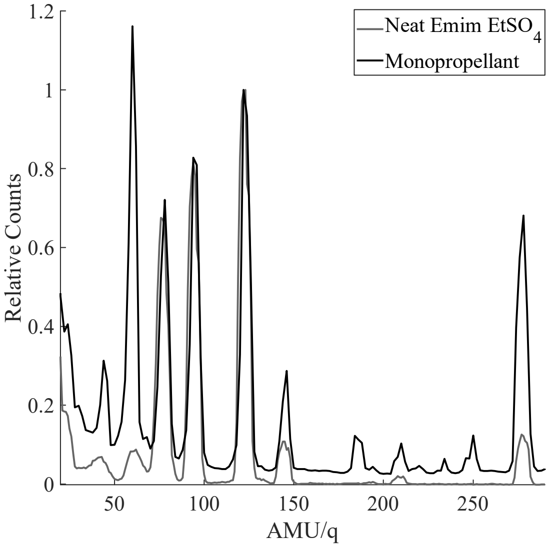

Figure 3: Anion mass spectra for neat [Emim][EtSO4] and the HAN based monopropellant at 15° off axis

Figure 3 shows clear peaks in the mass spectrum for anion emission of the monopropellant. Peaks are evident at 46, 62, 65, 80, 98, 126, 148, 190, 196, 212, 222, 237, 252, and 280 amu/q. Over all flow rates and angular orientations investigated, these are the dominant peaks found in all spectra. Compared with the neat spectra, the monopropellant shows evidence of additional species. Specifically, within the neat spectra, eight unique peaks below 300 amu/q in the mass spectrum are identifiable, whereas the monopropellant spectrum has fourteen. These are tabulated side-by-side in Table 1. All of the spectra peaks present in the neat [Emim][EtSO4] below 300 amu/q are also present in the monopropellant spectra, suggesting that the fragmentation of [EtSO4] is not explicitly dependent on HAN. There are six additional peaks and corresponding species below 300 amu/q in the monopropellant spectra.

Table 1: Mass-to-charge ratio of anion species identified in neat [Emim][EtSO$_4$] and monopropellant plume mass spectra

Neat [Emim][EtSO$_4$] [amu/q]	**Monopropellant [amu/q]**	**Species**	**Reference**	**Reference liquid**
45	46	Speci from [Emim][EtSO$_4$]	--	--
	62	[NO$_3$]	--	--
65	65	Speci from [Emim][EtSO$_4$]	[42]	[EtSO$_4$] in urine
79	80	Speci from [Emim][EtSO$_4$]	[42]	[EtSO$_4$] in urine
97	98	[HSO$_4$]	[42, 44]	[EtSO$_4$] in urine, [Emim][EtSO$_4$]
126	126	[EtSO$_4$]	[42]	[EtSO$_4$] in urine
147	148	Speci from [Emim][EtSO$_4$]	--	--
	190	2[HNO$_3$][NO$_3$] And/or [HNO$_3$][EtSO$_4$]	[45]	HEHN
	196	[HA-H][HAN][NO$_3$] And/or 2[HA-H] [EtSO$_4$]	--	--
214	212	Speci from [Emim][EtSO$_4$]	--	--
	222	[HNO$_3$][HAN][NO$_3$] And/or [HAN][EtSO$_4$]	--	--
	237	[Emim]+2[NO$_3$]	--	--
	252	2 [HNO$_3$] [EtSO$_4$]	--	--
280	280	Speci from [Emim][EtSO$_4$]	--	--
363		[Emim]+2[EtSO$_4$]	--	--

One of the additional anion species is the nitrate [NO$_3$]$^-$ anion (mass 62 amu) at 62 amu/q. The other anion species of the mixture, [EtSO$_4$]$^-$, is at 126 amu/q. The peaks at 190, 196, 222, 237, and 252 amu/q in Figure 3 appear to correspond with some of the mass values based on combinations of species expected in the liquid. Possible mass values are obtained by looking at different permutations of [Emim]$^+$, [EtSO$_4$]$^-$, [HA]$^+$, [NO$_3$]$^-$, [HA-H] and [HNO$_3$] that result in a -1 net charge. The mass of these possible clusters was compared to the amu/q values of spectra peaks. Based on this method, the peak at 98 amu/q may be due to [HSO$_4$]$^-$ off of the [EtSO$_4$]$^-$ ion (mass of 97 amu), as it appears in both the neat and monopropellant spectra, and has been observed as an element in [Emim][$EtSO_4$] mixtures before [44]. A combination of 2[HNO_3] with [NO_3]$^-$ has a mass of 188 amu and corresponds with the 190 amu/q peak. This 190 amu/q peak may also be due to [HNO_3][$EtSO_4$]$^-$ (mass 189 amu) or a combination of both of these species. The current quadrupole MS technique cannot differentiate between these species. The 196 amu/q peak may show the presence of [HA-H][HAN][NO_3]$^-$ and would indicate a pairing of a complete HAN molecule with hydroxylamine and nitrate species within the same emitted ion. The combination of 2[HA-H][$EtSO_4$]$^-$ (mass 192 amu) may also be present within the 196 amu/q peak. The peak at 222 amu/q may be due to the combination of [HNO_3][HAN][NO_3]$^-$ (mass 221 amu), and would also indicate there is pairing of HAN molecule with nitric acid and nitrate. This peak could also be due to [HAN][$EtSO_4$]$^-$ (mass 222 amu), which would indicate pairing of anions from both HAN and [Emim][$EtSO_4$] within the same emitted species. The peak at 237 amu/q appears to correspond with [Emim]$^+$ + 2[NO_3]$^-$ (mass 235 amu), where [Emim] is now bonded with the nitrate from the ionic form of HAN. The peak at 252 amu/q appears to correspond with 2[HNO_3][$EtSO_4$]$^-$ (mass 252 amu).

Table 1 summarizes these observed peaks in the anion mass spectra and their correlated species. Figure 3 also shows peaks in the spectra that do not directly correlate with theoretical mass calculations, yet also appear in the neat spectra. These are the peaks at 46, 80, 148, 212, and 280 amu/q. Some of these peaks are due to [Emim][$EtSO_4$] species, potentially ion fragmentation. Their composition is not a focus of this work; however, fragmentation is a known phenomenon for ionic liquids on this instrument [21]. Many of these potential fragments have also been seen in the neat spectra and in Politi's investigation of [$EtSO_4$] [42]. The anion mode has distinct peaks at 190, 196, 222, 237, and 252 amu/q. Placing the species emitted from the monopropellant and neat [Emim][$EtSO_4$] side by side in Table 1 aids in definitively stating which peaks are unique to the monopropellant. The peaks common to both liquids, yet unexpected from neat [Emim][$EtSO_4$] are identified as species due to [Emim][$EtSO_4$].

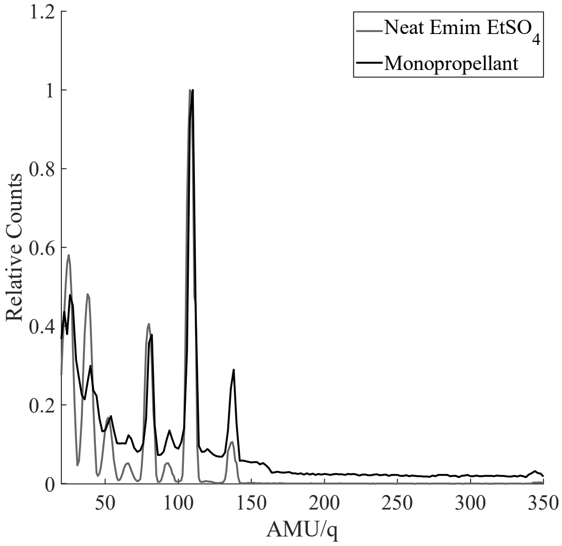

Figure 4: Cation mass spectra for neat [Emim][$EtSO_4$] and the HAN based monopropellant at 15° off axis

Figure 4 shows clear peaks in the mass spectrum for cation emission of the monopropellant for a flow rate of 50 pl/s and an angular orientation of -15º. Peaks are evident at 29, 41, 55, 69, 83, 95, 111, 139, and 345 amu/q. Over all flow rates and angular orientations investigated, these are the dominant peaks found in all spectra. Compared with the neat spectra, the monopropellant shows the same species. While the [Emim]$^+$ (mass 111 amu) cation is clearly present at 111 amu/q, the other cation in the mixture, $[HA]^+$ (mass 35 amu), is not present. All of the species within the cation spectra appear to be attributable purely to the [Emim][$EtSO_4$]. New species due to the addition of HAN are not apparent.

Table 2: Mass-to-charge ratio of cation species identified in neat [Emim][$EtSO_4$] and monopropellant plume mass spectra

Neat [Emim][$EtSO_4$] [amu/q]	**Monopropellant [amu/q]**	**Species**	**Reference**	**Reference liquid**
28	29	Speci from [Emim][$EtSO_4$]	--	--
41	41	Speci from [Emim][$EtSO_4$]	--	--
55	55	Speci from [Emim][$EtSO_4$]	--	--
68	69	Speci from [Emim][$EtSO_4$]	--	--
83	83	Speci from [Emim][$EtSO_4$]	--	--
96	95	Speci from [Emim][$EtSO_4$]	--	--
111	111	[Emim]	[40]	[Emim][Im]
140	139	Speci from [Emim][$EtSO_4$]	--	--
348	345	2[Emim]+[$EtSO_4$]	--	--

4. DISCUSSION

This section provides further discussion on important aspects of the experimental results. Perhaps most importantly, for the first time, HAN species are identified as being emitted via electrospray.

4.1. MONOMER SPECIES PRESENT IN THE SPECTRA

There are four possible monomer species for the HAN-[Emim][$EtSO_4$] DSIL monopropellant: cations: $[Emim]^+$ (111 amu), $[HA]^+$ (34 amu), and anions: $[NO_3]^-$ (62 amu), $[EtSO_4]^-$ (126 amu). The $[Emim]^+$ and [NO_3]- are present in the spectra. Figure 4 shows a peak at 111 amu/q corresponding with $[Emim]^+$. Figure 3 clearly shows a peak at 62 amu/q corresponding with $[NO_3]^-$. There are no other species expected to give rise to those masses. The $[EtSO_4]^-$ anion peak is clearly evident at 126 amu/q in Figure 3 for both the neat $[Emim][EtSO_4]$ and the monopropellant mixture and aligns with what has been seen previously [42]. However, the monopropellant spectra may also contain some $[HNO_3][NO_3]^-$ (mass 125 amu). Both $[EtSO_4]^-$ and $[HNO_3][NO_3]^-$ have been reported in the literature [42, 45]. If $[HNO_3][NO_3]^-$ is present within the monopropellant spectra, the relative intensity at 126 amu/q should be greater in the monopropellant than in the neat $[Emim][EtSO_4]$, when the 126 amu/q peak is compared relative to other peaks within the same spectra. The intensity of the 97/98 amu/q peak was used as a benchmark, since it has also been seen in other spectra [42]. The 126 amu/q intensity was compared to the 97/98 amu/q intensity by averaging the ratio of these two peaks across all testing conditions (angles, flow rates) for the same liquid. Then the average 126 to 97/98 intensity ratio of neat $[Emim][EtSO_4]$ was compared to the average ratio of the monopropellant. Results show the ratio is between 1 and 2.5 for both liquids, with no discernable difference between the liquids. In other words, our results cannot conclusively say $[HNO_3][NO_3]^-$ is, or is not, present in the spectra. The only definitive conclusion is that the 126 amu/q monopropellant peak contains $[EtSO_4]^-$ and may also contain $[HNO_3][NO_3]^-$. Finally, the $[HA]^+$ cation does not appear in the cation spectra. There is no identified peak at its expected singly charged mass of 34 amu/q in any of the spectra. The closest peak is at 29 amu/q as shown in Figure 4, and this is beyond the 2-3 amu/q resolution of the instrument. Further, the 29 amu/q species also exists in the neat $[Emim][EtSO_4]$ spectra, and therefore is not expected to be HAN related. Thus, we conclude that the $[HA]^+$ cation is not observed as a monomer in the spectra.

4.2. PRESENCE OF PROTON-TRANSFER SPECIES

Proton-transfer species are present in the monopropellant anion spectra, but not the cation spectra. The proton-transfer species of HAN are [HA-H][HNO_3], and these are also referred to as the covalent form of HAN. Numerous peaks in the anion spectra may contain these species, for instance, 190, 196, 222 and 252 amu/q in Figure 3 all align with expected masses for clusters containing proton transferred species. Proton transfer has been seen in other ionic liquids with nitrate functional groups. Patrick et al. showed that proton transfer in 2-hydroxylethylhydrazinium nitrate ([HEH]+[NO_3]$^-$, a.k.a. HEHN) is energetically favorable via the loss of nitric acid. They also found resulting proton transferred species experimentally in electrospray tandem mass spectrometry [46]. Additionally, Prince et al. observed both [HE] and [HNO_3] proton-transferred species in their investigation of HEHN from externally wetted titanium emitters [45]. Despite seeing the [HE][HEH]$^+$ and [HNO_3][NO_3]$^-$ dimers, and the 2[HNO_3][NO_3]$^-$ trimer, they did not identify [HNO_3][HEH]$^+$ or [HE][NO_3]$^-$, suggesting the proton-transferred species only pair with their counterpart. In contrast, our present results show both covalent species paired with the monomer anion. The tabulated anion spectra peaks shown in Table 1 indicate 2[HNO_3][NO_3]$^-$ at 190 amu/q and [HA-H][HAN][NO_3]$^-$ may be present at 196 amu/q. Similar to results shown by Prince et al. [45], 2[HNO_3][NO_3]$^-$ at 190 amu/q is identified in the spectra results provided in Table 1. Prince et al. [45] also identified [HNO_3][NO_3]$^-$ at 125 amu/q. Their neat HEHN does not have another ion to mask the presence of [HNO_3][NO_3]$^-$ so it was easily identified in their work. As discussed in the previous section, the monopropellant here has another ion ([$EtSO_4$]$^-$) at 126 amu/q and the composition of the monopropellant peak at that amu/q is unclear. Prince also identified additional solvated states of $[HE][HEHN]_n[HEH]^+$, but no solvated states of $[HNO_3][HEHN]_n[HEH]^+$. The present results do not show any cation solvated states with a full [HAN] molecule or proton transferred species, where Prince saw the species $[HEH]^+[HE]$ at 153 amu/q in cation emission mode [45]. However, anion solvated states with both [HA-H] and $[HNO_3]$ are observed, but only for n = 1. Specifically $[HA\text{-}H][HAN][NO_3]^-$ and $[HNO_3][HAN][NO_3]^-$ are identified at 196 and 222 amu/q, respectively, as seen in Table 1. Finally, proton-transfer species pairing with the anion of the solvent are also observed. In particular $[HNO_3][EtSO_4]^-$, $2[HA\text{-}H][EtSO_4]^-$, and $2[HNO_3][EtSO_4]^-$ anion peaks are shown in Figure 3 and tabulated in Table 1. More details on swapping of anion and cation species within the mixture are presented in the next section. Proton transferred species were not observed in cation mode. In fact, HAN-related species are not found within the cation spectra of Figure 4.

The results presented here indicate proton-transferred species can be emitted from a different molecule with nitrate functional group, HAN, as opposed to HEHN. Further, the results presented here indicate that these species can be emitted from a mixture. This is a new result, not previously reported in the literature. Present results indicate that both proton-transferred covalent species can be paired with both ionic species for HAN and with $[EtSO_4]$, unlike the neat ionic liquid results for HEHN. Also, results presented here show these species are present over a wider range of flow rates than previously shown. This range has now been shown to extend from the low flow rate externally wetted studies of Prince et al. (~2 ng/s) [45] to the higher flow rate capillary emitter range investigated here (7 – 4600 ng/s).

4.3. SWAPPING OF ANIONS AND CATIONS IN THE MONOPROPELLANT MIXTURE

Numerous species identified in the monopropellant spectra show pairing of ionic and covalent forms of HAN, as well as swapping of cations and anions between the constituents of the mixture. Swapping of anions and cations is possible because the monopropellant investigated here is a mixture of ionic liquids. Here, we find in the electrospray plume that [HAN] anions and cations can be bound to the [$EtSO_4$] anion. This type of behavior is also indicative that the mixture is a DSIL as opposed to a simple mixture [19].

Monopropellant anion results of Figure 3 and Table 1 may indicate pairing of each [HNO_3], 2[HNO_3], 2[HA-H], and [HAN] with [$EtSO_4$]$^-$. Interestingly, while we see 2[HA-H], we do not see [HA-H] paired with [$EtSO_4$]$^-$, which would appear at 160 amu/q. Also, while we see [HAN][$EtSO_4$]$^-$ we do not see [HAN] paired solely with [NO_3]$^-$. We identify [Emim]$^+$ paired with 2[NO_3]$^-$, but the anion spectra do not show [Emim]$^+$ paired with [$EtSO_4$]$^-$. That is, the anion spectra do not show an [Emim][$EtSO_4$] combination. We do not see any species at 160 amu/q ([HAN][NO_3]$^-$ or [HA-H][$EtSO_4$]$^-$), nor do we see any species greater than 280 amu/q ([HA]$^+$ +2[$EtSO_4$]$^-$ or [Emim]$^+$[$EtSO_4$]$^-$[NO_3]$^-$ or [Emim]$^+$ +2[$EtSO_4$]$^-$). We do see a peak at 280 amu/q but cannot link it directly to any of the expected species.

The absence of [Emim][$EtSO_4$] in the monopropellant anion spectra may not be surprising considering the mole fraction of the mixture. While the mass fraction is 59% HAN to 41% [Emim][$EtSO_4$], the mole fraction is 78% HAN to 22% [Emim][$EtSO_4$], indicating there are 3.55 times as many HAN molecules as [Emim][$EtSO_4$] molecules. Based on this, one might expect more HAN-related species to be emitted into the plume.

The spectra also show that numerous other species besides monomers are present in the plume (including droplets that are not analyzed here), and in some cases those species contain both HAN and [Emim][EtSO$_4$] related species. Unfortunately, it is impossible using the current data to quantify the plume ratio of HAN-related vs. [Emim][EtSO$_4$]$^-$ related species or interrogate droplet compositions quantitatively.

The absence of [Emim][EtSO$_4$] in the monopropellant anion spectra may also not be surprising considering the presence of HAN species on the mixture. The presence of HAN may increase the inter-molecular distance between [Emim] and [EtSO$_4$] species within the mixture. This would weaken the intermolecular forces between the [Emim] and [EtSO$_4$] ions in the mixture, which may then be evidenced by reduced emission of bonded ion clusters in the plume (i.e., reduction or elimination of dimer, trimer, or larger ion clusters). Additionally, this would suggest that as the level of HAN in the mixture is decreased, the presence and intensity of larger ion clusters, e.g., dimers and trimers, would increase. While we do not see [Emim][EtSO$_4$] in the monopropellant anion spectra, we do see [Emim][EtSO$_4$] at 345 amu/q in the monopropellant cation spectra.

Numerous species were identified in the anion spectra showing swapping of anions and cations, and no such species have been identified within the cation spectra of Figure 4 and Table 2. The peak at 345 amu/q is attributed to 2[Emim]$^+$[EtSO$_4$]$^-$, which would indicate that [Emim][EtSO$_4$] is present within the cation spectra. While we see 2[Emim]$^+$[EtSO$_4$]$^-$ in the cation spectra, we do not see 2[Emim]$^+$[NO$_3$]$^-$ though [NO$_3$]$^-$ is present in the anion mode. Unlike the anion monopropellant mode, the cation mode shows no unique peaks present and thus no species swapping. The monopropellant cation spectra appear to be indistinguishable from the neat [Emim][EtSO4] cation spectra, whereas the monopropellant anion spectra is different than the neat spectra and appears to contain all the HAN-related species.

5. CONCLUSION

A HAN-based monopropellant mixture was electrosprayed over the wide flow rate range of 2 pL/s to 3 nL/s in a 50 μm capillary emitter. Electrospray mass spectra were taken over this wide flow rate range and at various angles out to 45° off axis. Cation and anion mass spectra were investigated in detail over a mass range of 20 – 600 amu/q. No peaks were evident above 350 amu/q in the monopropellant mass spectra, so the focus was then limited to 20-350 amu/q. The mass spectrum examined over this flow rate range contains small n = 0 and 1 states of neat ions, and n = 1 and 2 clusters/solvated states, from proton transferred species and species swapping between the two ionic liquids. There was also evidence of droplets being present on and near centerline, but these were not the focus of this work. Larger ion clusters were not observed and may be absent due to weakened intermolecular forces within the mixture due to the presence of HAN. Specifically, introduction of physically smaller anions and cations (i.e., HAN) into the [Emim][$EtSO_4$] may cause the radial distribution function of those ions to shift to larger radii, reducing the intermolecular forces between those ions, and thereby reducing or eliminating them from being extracted together into the plume. Despite the apparent complexity of the monopropellant ionic liquid mixture, with its 4 ions and 2 neutral species from the proton transfer of HAN, both the angular distribution of the plume mass spectra and the effects of flow rate agree qualitatively with the existing literature on other investigated electrospray propellants.

Plume mass spectra of the HAN-[Emim][EtSO$_4$] mixture demonstrate results that are new and novel for electrospray propellants. The [Emim][EtSO$_4$] neutral pair is found in cation spectra for both the neat liquid and monopropellant mixture, but it is noticeably absent from the anion spectra of the monopropellant, despite being present in the neat anion spectra. Numerous spectrum peaks remain unidentified, for both cation and anion modes. The unidentified peaks are presumably due to impurities or fragments from [Emim][EtSO$_4$] because they are seen in both monopropellant and neat [Emim][EtSO$_4$] spectra. Both ionic and proton transferred forms of HAN were observed. While proton-transfer species of ionic liquids have been observed previously in electrospray plumes, the results obtained here show for the first time that both proton-transferred species may be paired with both ionic species of HAN in the plume. These proton transferred forms of HAN are observed to be emitted with the [EtSO$_4$] anion. Proton transferred species do not appear to be as readily emitted in cation mode. Overall, the monopropellant cation spectra appears to be indistinguishable from the neat [Emim][EtSO$_4$] cation spectra, whereas the monopropellant anion spectra is different than the neat spectra and appears to contain all the HAN-related species. Additionally, evidence of proton-transfer species in an electrospray plume has now been demonstrated over a much wider flow rate range (7-4600 ng/s), showcasing the importance of including these species in modeling efforts.

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II. MASS SPECTROMETRIC INVESTIGATION OF MIXTURES CONTAINING IONIC LIQUIDS 1-ETHYL-3-METHYL-IMIDAZOLIUM ETHYLSULFATE AND ETHYLAMMONIUM NITRATE

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ABSTRACT

The ionic liquids 1-ethyl-3-methylimidazolium ethyl-sulfate ([Emim][EtSO$_4$]) and ethylammonium nitrate (EAN) are electrosprayed in both anion and cation modes as neat (pure) liquids and at three different mixture ratios of 75%, 50%, and 25% by mass [Emim][EtSO$_4$]. The electrospray plume is interrogated via mass spectrometry. Quantum mechanics calculations are used to aid assignment of species to observed spectral peaks thereby illustrating how the plume composition changes with mixture ratio; variations in plume composition are noteworthy for use as validation cases in molecular dynamic tool development. Novel to this work is the presence of all four parent ions and proton-transferred EAN species, including nitrate and nitric acid, along with evidence of water-

[$EtSO_4$] species in the plume. In addition, there are several “mixed species” in the plume that require ions/neutrals from both ionic liquids. The number of such mixed species is maximum at a 25% by mass [Emim][$EtSO_4$] mixture ratio due to hydrogen bond restructuring within these liquids.

1. INTRODUCTION

Liquids composed of molten salts are known as ionic liquids (ILs). ILs and their mixtures are of interest in many different disciplines [1], such as physical chemistry, molecular dynamics, energetic liquids, and as designer solvents. One possible dichotomy for ionic liquids generalizes the various liquids based on their composition: protic ionic liquids (PILs) and aprotic ionic liquids (AILs) [2]. PILs are formed by a proton-transfer reaction between a Brønsted acid and a Brønsted base where a hydrogen atom transfers from the acid to the base. PILs form strong hydrogen bond networks [2, 3]. AILs generally do not form strong hydrogen bonds. AILs are discussed in [4].

There is increasing interest in mixtures of two or more ionic liquids as the ability to mix multiple cations and anions holds promise for fine-tuning physical properties and even creating designer solvents. Mixtures containing one PIL and one AIL have, however, not been studied extensively to date [4]. These mixtures are important to the energetic propellant community as replacements for conventional chemical thruster propellants. PILs have been shown to chemically decompose in pure form and in some mixtures [5-8]. Therefore, the investigation of the characteristics and behavior of mixtures of a PIL with an AIL can provide important practical and fundamental information relevant to the energetics community and provide a validation study for development of modeling tools. Such modeling tools for IL could investigating more of the near infinite potential combinations of PILs and AILs than are practical to investigate experimentally; however, such tools are still in development.

Of interest in this study are two specific liquids, the AIL 1-ethyl-3-methylimidazolium ethyl-sulfate ([Emim][EtSO$_4$]) and the PIL ethyl ammonium nitrate (EAN). These liquids have been the subject of numerous fundamental and applied experimental and numerical investigations. [Emim][EtSO$_4$] has been studied extensively as an energetic liquid component in chemical propellants [5, 9-12] and also as an AIL of fundamental interest [13-17]. EAN is believed to be the first identified room-temperature ionic liquid [2] and contains the nitrate anion used in previous mass spectra studies [12, 18]. EAN has been the subject of significant investigation in the literature both in mixtures and pure form [3, 4, 6, 19-24]. For instance, Docampo-Ãlvarez et al. sought to model mixtures of EAN and [Emim][BF$_4$] to determine physical properties and specifically noted a lack of experimental data to aid validation of their modeling work [4], a gap this work seeks to bridge. Systematic experimental electrospray mass spectrometry investigations of mixtures of ILs are notably absent in literature [12, 25]. Thus, the pairing of these two liquids is of interest for a) fundamental science because it identifies how species emissions change with varying mixture ratio and b) applications requiring energetic liquid mixtures (e.g. propellants community).

The primary objective of this work is identification and comparison of the electrospray species of [Emim][EtSO$_4$], EAN, and mixtures of the two liquids. The variation of species based on mixture ratio is assessed and quantum mechanical calculations are used to aid in the determination of species. Comparison of neat mass spectra versus mixture mass spectra is of particular interest. Previous work on one specific mixture ratio of hydroxylammonium nitrate (HAN) with [Emim][$EtSO_4$] was unable to identify species unique to pure HAN, since HAN is solid at room temperature [12]. This previous work did not study the effect of changing the mixture ratio [12]. Changing the mixture ratio may modify the intermolecular interactions occurring within the liquid phase, giving rise to changes in electrospray species. Previous research has shown that, for liquid mixtures similar to those investigated here, changes in intermolecular interactions within the liquid are manifest within spectroscopic results [6, 14, 16]. Specifically, Alonso-Matilla found electrospray emission current, droplet size, and propulsion efficiency varies with mixture ratio for a given flow rate, i.e. different mixture ratios directly affected the size of emitted droplets [6]. Sarkar found that changes in mixture ratio of [Emim][$EtSO_4$] when mixed with polar ionic liquids yielded altered hydrogen bond structures within the mixture; these changes were observed through variations of average solvation time and rotational relaxation time [26]. Zhang found that changes in mixture ratio of [Emim][$EtSO_4$] with water resulted in selective restructuring of the hydrogen bond network, as measured by HNMR and infrared spectroscopy, leading to direct hydrogen bonding between water and the aromatic ring in [Emim] at water mole fractions above 0.6 [27]. Thus, we anticipate that mixtures may give rise to electrospray species containing ions/neutrals from both liquids (i.e. mixed species) and unique to specific mixture ratios. The work in the present investigation provides experimental information critical to the development, validation and verification of modeling and simulation (M&S) approaches aimed at accurately approximating the electrospray plume in addition to the bulk liquid environment of mixtures of ionic liquids. The lack of available experimental data on these mixtures has hindered the validation of previously published M&S efforts [4].

2. EXPERIMENTAL PROCEDURES

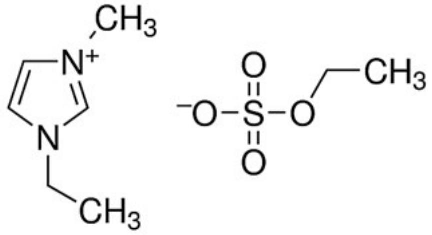
In this section, the experimental methods and procedures are described. The methodology used to provide the ionic liquid samples is described first. This is followed by a description of the electrospray mass spectra source and quadrupole instrument.

2.1. SAMPLE SYNTHESIS

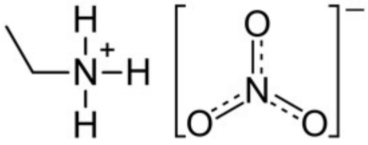
The ionic liquids used in this work were procured commercially and processed as described below. [Emim][$EtSO_4$] was obtained from Sigma Aldrich at a ≥ 95% purity level, while EAN was obtained from Iolitec at > 97% purity. These liquids were prepared before electrospray as the presence of volatile impurities, especially water, may cause bubble formation in the fluid feed system during electrospray operation. The volatile impurities in these samples were removed according to methods previously developed and validated [11], and briefly described here. Each neat ionic liquid was dried in vacuum (10^{-3} Torr) for 24 hours to remove impurities. Mass loss was observed during this step, most notably in EAN. Mixed samples were created by combining the two ionic liquids together at desired mass ratios. The mixed samples were dried for an additional 12 hours in vacuum (at 10^{-7} Torr) before electrospraying. The samples had an overall mass between 2.0 and 4.0 g at a precision of 0.01 g, resulting in an uncertainty in mass ratio of

<1%. For this work, the stated mixture ratio refers to the mass fraction of [Emim][$EtSO_4$] present in the sample.

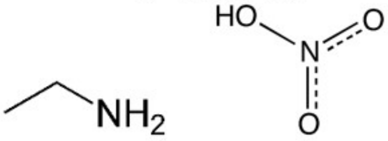
Chemical structures of the investigated ionic liquids are depicted in Figure 1. The chemical formula for $[Emim]^+ [EtSO_4]^-$ is $[C_6H_{11}N_2]^+ [C_2H_5SO_4]^-$ and can be seen in Figure 1a. EAN can exist in two forms: an ionic form (Figure 1b) and a neutral proton-transferred form (Figure 1c). Therefore the EAN super molecule can give rise to three different neutral forms: a charge neutral pairing of ethylammonium cation and nitrate anion $[EA]^+ [NO_3]^-$ (Figure 1b), a neutral proton donor ethylamine [EA-H] (Figure 1c left), and a neutral proton acceptor nitric acid [HNO_3] (Figure 1c right).



a) $[Emim]^+[EtSO_4]^-$



b) Ionic EAN



c) Proton transferred EAN

Figure 1: Chemical structure of the constituents of the mixtures investigated here: $[Emim]^+ [EtSO_4]^-$ (a) and both the ionic $[EA]^+ [NO_3]^-$ (b) and proton-transferred (covalent) [EA-H][HNO_3] (c) forms of EAN

2.2. ELECTROSRAY MASS SPECTRA SOURCE AND QUADRUPOLE INSTRUMENT

A schematic showing the in-vacuum electrospray source and quadrupole mass analyzer used in this work is shown in Figure 2. This instrument has been used and described extensively in literature [5, 12, 28, 29], and is only briefly described here. The distal coated capillary emitter has a 50 µm inner diameter (PicoTip MT320-50-5-5). The extractor plate has an aperture approximately 1.5 mm in diameter and is placed approximately 1.5 mm downstream of the emitter. Due to the geometry of the extractor plate (finite thickness, separation distance, and orifice size) emission is blocked beyond approximately 30° off-axis. The extractor and emitter are placed on a rotational stage in vacuum to provide angular measurements. The stage is mounted to a six-inch vacuum flange with multiple available feedthrough ports. Fluid is fed from the reservoir to the capillary emitter via a 100 µm inner diameter fused silica capillary that transitions through a custom vacuum feedthrough. A second feedthrough provides high voltage connections to the emitter and extractor. The fluid is pumped into the 100 µm capillary via a Harvard Elite Module PicoPump syringe pump with a volumetric control of ± 2% over the range of flow rates investigated (external to vacuum). In this case, the syringe is the reservoir. The emitter, capillary and syringe are all replaced when switching between samples to avoid contamination. The usage of a syringe feed system is equivalent in function to the pressure-fed system [30], which has seen extensive use in relevant literature.

The spectra were obtained with a nominal applied voltage of 2.3 kV between the extractor and emitter. The potential difference is applied as +/- 0.5 kV on the emitter and -/+ 1.8 kV on the extractor. Specifically, a 2.3 kV potential was used for the anion mode and a -2.3 kV potential was used for cation mode. This applied potential is similar to the value used previously [12] and is in agreement with theoretical calculations for determining the starting voltage in liquid metal electrosprays [31]. Mass spectra were obtained over angular orientations in 5° increments from -45° to 45°.

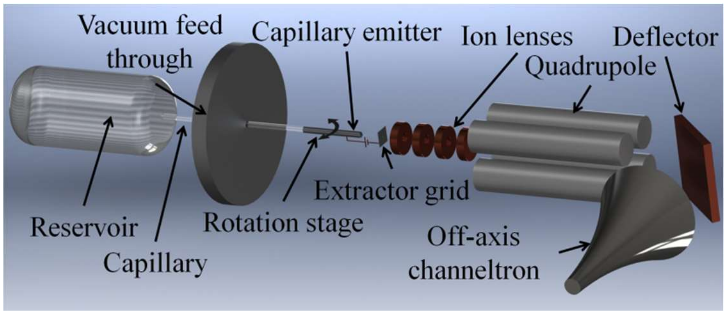


Figure 2: Diagram of mass spectrometer experimental setup showing the reservoir, capillary, vacuum feedthrough, capillary emitter, rotation stage, extraction grid, ion lenses, quadrupole mass filter, and off-axis channeltron detector

A quadrupole mass spectrometer was used to obtain spectra of the electrospray. This quadrupole mass spectrometer (Extrel, 19 mm rods, 1.2 MHz) has been used extensively in literature by Miller and Chiu [29, 32]. The electrospray emitted from the capillary source is focused by the ion lenses to maximize signal at the channeltron through the quadrupole. The quadrupole sorts the species by their respective charge-to-mass ratio. The sorted ions that pass through the quad are then deflected into an off-axis, single-channel channeltron operating in event counting mode. Calibration experiments at these kinetic energies yielded m/q values within 2-3 m/q over the 40-500 amu range. As a result of the significant ion kinetic energy, artifacts occur at low m/q values resulting in an extended "zero mass" contribution. There is often an additional artifact present at large m/q values while operating in anion mode. The combination of larger detector voltages for anion operation and the larger RF amplitudes leads to arcing events detected by the channeltron at high m/q values while the electrospray is operational.

3. EXPERIMENTAL RESULTS

This section presents the mass spectra for neat [Emim][$EtSO_4$], neat EAN, and three different mixtures of these liquids. Specifically presented here are the anion and cation mass spectra of both neat liquids and a 50:50 by mass mixture. In addition, the tabulated peaks of both neat liquids, 25, 50, and 75% [Emim][$EtSO_4$] by mass mixtures are shown, along with assigned species. The main objective of this work is the comparison of spectra and species at various mixture ratio. Discussion on how and why the electrospray composition changes with mixture ratio is reserved for the subsequent discussion section (Section 4).

3.1. ANION AND CATION MASS SPECTRA RESULTS

Mass spectra are presented in Figure 3 for a) anion mode and b) cation mode. These spectra are representative of all results obtained in this study. In Figure 3, both the 100% [Emim][$EtSO_4$] and 50:50 mixture spectra are reported at 50 pL/s flow rate, while the 100% EAN spectra is reported for 3 nL/s. All spectra in Figure 3 were acquired at 15° off-axis to avoid the large baseline due to droplets on/near centerline. The higher flow rate of 3 nL/s for neat EAN was required for stable electrospray. EAN spectra were not obtainable in cation and anion modes at 50 pL/s due to known and observed volatility, i.e.

by increased base pressure when exposed to vacuum [25]. Weingartner had difficulty with EAN volatility due to water content [23]. Borrajo-Pelaez reports on challenges with EAN anion electrospray due to volatility [33], and volatility has been cited as inhibiting electrospray of EAN in vacuum at low flow rates [6, 19]. Our work also visually observed EAN boiling off the meniscus. In Figure 3, anion spectra are normalized such that the peak at approximately 126 m/q is equal to one, while the cation spectra are normalized based on the 111 m/q peak for neat [Emim][EtSO$_4$] and the 50:50 mixture spectra, and the 140 m/q peak for neat EAN. Two normalization conditions are used for cation mode so that EAN has similar magnitude with the other two spectra.

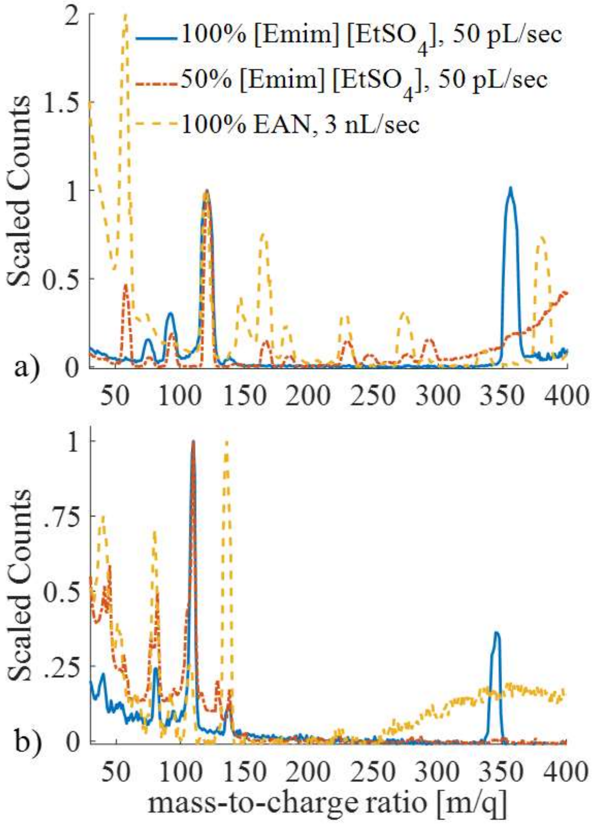


Figure 3: Mass spectra for a) anion and b) cation emission modes

In the spectra of Figure 3, and all the results and discussion that follow, we identify "peaks" at mass-to-charge ratios where the signal-to-noise ratio is greater than 2. The noise was taken as the baseline level at a larger m/q value (specifically a slightly larger m/q after the increased counts from a detected peak returned to baseline). This criterion was used as opposed to selecting a specific offset of m/q due to concerns of using a peak with an automated selection. For neat [Emim][EtSO$_4$], peaks, in order of decreasing intensity, occur at 361,126, 98, 80, and 143 m/q for anion mode and 111, 348, 81, and 138 m/q for cation mode. The neat EAN spectrum shows peaks, in order of decreasing intensity, at 140, 46, 84, 55, 111, and 95 m/q for cation mode. The anion EAN spectra shows a peak at 62 m/q, which appears to be about twice as intense as 125 m/q, followed by 164, 384, and 151 m/q at progressively smaller intensities. Figure 3 also presents the anion and cation spectrum for the 50:50 mixture. Anion peaks at 62, 79, 99, 126, 148, 171, 189, 233, 251, 280 and 297 m/q, and cation peaks at 55, 83, 111, 130, 139, 152, 173, 190, 211, 225, 281, and 345 m/q are observed. The most intense peaks are the 126 m/q and 111 m/q for anion and cation mode, respectively, and these peaks are also the most intense in neat [Emim][EtSO$_4$]. The peaks of these anion and cation spectra are tabulated in Table 1 and Table 2, respectively.

3.2. ASSIGNMENT OF SPECIES

Chemical species are assigned to peaks by comparing the spectra m/q value with the calculated mass of all possible combinations of ions and neutrals in the liquid, assuming singly charged species over the investigated range of m/q. In some cases, there are multiple combinations that give rise to the same or similar mass. We report in Tables

1 and 2 all possible species within a 3 m/q tolerance for anion and cation species, respectively. Theoretical m/q values are also provided. Some species within the mass tolerance are energetically unlikely based on quantum mechanics calculations described in the discussion section, and we strikethrough these species. References to literature sources that support the identified species are also provided in Tables 1 and 2. Finally, some measured m/q values do not match the calculated mass of any combination of ions and neutrals expected in the liquid. In this case, we simply report the species as “species from parent liquid”. These species could be molecular fragments due to the strong electric field or an impurity in the sample. In many cases, these unknown species have also been identified in previous research.

4. DISCUSSION

4.1. OBSERVED SPECIES IN PLUME

All 4 monomer species are observed in the electrospray. Specifically, $[EA]^+$, $[Emim]^+$, $[EtSO_4]^-$, and $[NO_3]^-$ are observed at all mixture ratios where they are present in the liquid. The observation of the EA molecule in the plume is particularly notable when compared to previous investigation of an $[Emim][EtSO_4]$ - hydroxylammonium nitrate (HAN) mixture wherein the hydroxylammonium (HA) ion was absent in the cation spectra [12]. The absence of the HA+ cation was attributed to the HA+ ion mass, 32 amu, falling below the minimum detection limit of the instrument; HA+ could not be confirmed as neutral contribution since HAN was not electrosprayed. In that work, the mass fraction of HAN was 59% or, equivalently, 78% by mole.

Table 1: Mass-to-charge ratio of anion spectra peaks and corresponding species

Spectra Peaks [m/q]							**Previously Reported**	
% $[Emim][EtSO_4]$								
100	**75**	**50**	**25**	**0**	**Species**	**Theoretical [m/q]**	**Ref.**	**Liquid**
	62	63	62	62	$[NO_3]$	62	--	--
				78	Species from EAN	--	--	--
80	79	79	80		Species from $[Emim][EtSO_4]$	--	[34]	$[EtSO_4]$ in urine
98	100	99	98		$[HSO_4]$	97	[17, 34]	$[Emim]$ $[EtSO_4]$, $[EtSO_4]$ in urine
	125*	125*	125*	125	$[NO_3]+[HNO_3]$	125	[18]	HEHN
126	126	126	126		$[EtSO_4]$	126	[34]	$[EtSO_4]$ in urine
143					$[HSO_4]+[C_2H_5OH]$	143	[12]	$[Emim]$ $[EtSO_4]$
	147	148			Species from $[Emim][EtSO_4]$	147	[12]	$[Emim]$ $[EtSO_4]$
			151	151	$[NO_3]+[EA\text{-}H]+[EA\text{-}H]$	152	--	--
			161		$[HSO_4]+[HNO_3]$	161	--	--
		171	169	169	$[NO_3]+[EA+NO_3]$	170	--	--
		189	189	187	$[NO_3]+2[HNO_3]$	188	[12, 18, 35]	HAN, HEHN, EAN
		233		231	$[NO_3]+[HNO_3]+[EA+NO_3]$	233	[35]	EAN
			237		$[EtSO_4]+[EA+NO_3]$ or $[NO_3]+[Emim+NO_3]$ or $[EtSO_4]+[HNO_3]+[C_2H_5OH]$ or $[HSO_4]+3[C_2H_5OH]$ or $[HSO_4]+[HSO_4+EA]$	234, 235, 235, 235, 240	--	--
		251			$[HSO_4]+[EA\text{-}H]+[EA+NO_3]$ or $[HSO_4]+[EA+NO_3]+[C_2H_5OH]$ or $[EtSO_4]+[HNO_3]+[HNO_3]$	250, 251, 252	--	--
			255		$[EtSO_4]+[HNO_3]+[HNO_3]$	252	--	--
	280	280	281	279	$[NO_3]+[EA+NO_3]+[EA+NO_3]$	278	[35]	EAN
				296	Species from EAN	--	--	--
		297	298		$[EtSO_4]+[HNO_3]+[EA+NO_3]$ or $[NO_3]+[HNO_3]+[Emim+NO_3]$ or $[EtSO_4]+[EA+EtSO_4]$ or $[EtSO_4]+[Emim+NO_3]$	297, 298, 298, 299	--	--
			323		$[NO_3]+[EA\text{-}H]+[EAN]+[EAN]$	323	--	--
				340	$[NO_3]+[HNO_3]+[EAN]+[EAN]$	340	--	--
361	360				$[EtSO_4]+[Emim+EtSO_4]$	363	[12]	$[Emim][EtSO_4]$
			362		$[EtSO_4]+[HNO_3]+[EA+EtSO_4]$ or $[NO_3]+[HNO_3]+[Emim+EtSO_4]$ or $[EtSO_4]+[Emim+EtSO_4]$	361, 362, 363	--	--
				384	$[NO_3]+[EAN]+[EAN]+[EAN]$	384	[35]	EAN

*Denotes a peak potentially masked by a more pronounced peak.

Proton-transferred species are observed in the electrospray. In this work, proton-transfer refers to transfer of a hydrogen atom from ethylammonium to nitrate forming ethylamine and nitric acid neutrals as shown in chemical reaction (1) and illustrated in Figure 1.

Table 2: Mass-to-charge ratio of cation peaks and corresponding species

Spectra Peaks [m/q] % [Emim][EtSO$_4$]							**Previously Reported**	
100	**75**	**50**	**25**	**0**	**Species**	**Theoretical [m/q]**	**Ref.**	**Liquid**
	43	46	46	46	[EA]	46	[36]	Dopamine
	54			55	Species from [EAN]	--	--	--
	68				Species from [Emim][EtSO$_4$]	--	[12]	[Emim][EtSO$_4$]
81	82	83	83		Species from [Emim][EtSO$_4$]	--	[12]	[Emim][EtSO$_4$]
	84*	84*	84*	84	Species from EAN	--	--	--
				95	[EA]+[EA-H]	91	--	--
111	111	111	111		[Emim]	111	[12, 37]	[Emim][Im]
	111*	111*	111*	111	[EA]+[HNO$_3$]	109	--	--
		130			--	--	--	--
138					Species from [Emim][EtSO$_4$]	--	[12]	[Emim][EtSO$_4$]
	139	139			[EA]+[EA-H]+[EA-H] or [EA]+[EA-H]+[C$_2$H$_5$OH] or [EA]+[C$_2$H$_5$OH]+[C$_2$H$_5$OH]	136, 137, 138	--	--
			140		[EA]+[C$_2$H$_5$OH]+[C$_2$H$_5$OH]	138	--	--
				140	Species from EAN	--	--	--
		152	155		[EA]+[EA+NO$_3$] or ~~[EA]+[HNO$_3$]+[C$_2$H$_5$OH]~~ or ~~[Emim]+[EA-H]~~ or [Emim]+[C$_2$H$_5$OH]	154, 155, 156, 157	--	--
		173	175		[EA]+[HNO$_3$]+[HNO$_3$] or ~~[Emim]+[HNO$_3$]~~	172, 174	--	--
		190			[EA]+[HSO$_4$+EA]	189	--	--
		211			--	--	--	--
			216		[EA]+[HNO$_3$]+[EA+NO$_3$] or [EA]+[EA+EtSO$_4$] or [Emim]+[EA+NO$_3$] or [Emim]+[HNO$_3$]+[C$_2$H$_5$OH]	217, 218, 219, 220	--	--
		225			--	--	--	--
		281	283		[EA]+[HNO$_3$]+[EA+EtSO$_4$] or [Emim]+[HNO$_3$]+[EA+NO$_3$] or [EA]+[Emim+EtSO$_4$] or [Emim]+[Emim+NO$_3$]	281, 282, 283, 284	--	--
348	348	345	347		[Emim]+[Emim+EtSO$_4$]	347	[12]	[Emim][EtSO$_4$]

*Denotes a peak potentially masked by a more pronounced peak.

Similar nitrate-based proton transfer has also been observed in previous work with [Emim][EtSO$_4$] and HAN [12], EAN [22, 35], and HEHN [18, 38]. Specifically, the [NO$_3$] +[HNO$_3$], [NO$_3$] +2[HNO$_3$], [EtSO$_4$] +2[HNO$_3$] species previously observed by Wainwright et al. [12] in [Emim][EtSO$_4$]-HAN mixture are also observed in this [Emim][EtSO$_4$]-EAN work. Proton-transferred HAN is known to be energetically favorable [21]. However, the energetic calculations and experimental work are less clear regarding proton transfer in EAN. Gas phase calculations by Alavi and Thompson show the zero-point energy (i.e. absolute minimum energy) of ionic EAN vs proton-transferred EAN is within 1%, while the Coulombic energy slightly favors ionic EAN [39]. However, those gas phase calculations may not fully capture what is happening in the liquid mixture. The synthesis process for ionic EAN involves reacting [EA-H] and [HNO$_3$], and some [HNO$_3$] may remain after this process. Neat EAN is observed to evaporate proton-transferred species in the presence of high vacuum and this is the energetically favorable means of vaporization [19]. Another potential catalyst of proton transfer is fluid dynamic heating of the liquid during constriction in the electrospray Taylor cone, which is known to cause substantial heating [40], or from decomposition of the EAN dimer as has been observed by Patrick and Annesley [22]. Additionally, Kennedy et al. identified 188 and 233 m/q anion emissions for EAN, and they attribute these peaks to proton-transferred species [35].

$$[EA] + [NO_3] \xrightarrow{yields} [EA - H] + [HNO_3] \tag{1}$$

The spectrum for neat [Emim][EtSO$_4$] presented in Figure 3 is similar to that presented by Wainwright et al. [12]. However, Figure 3 is missing anion peaks at 65 and 280 m/q, and cation peaks at 55, 69, and 95 m/q compared to Ref. [12]. Wainwright et al. were unable to assign species to these peaks and therefore attributed them to fragments or impurities from the [Emim][EtSO$_4$] sample [12]. These differences may be due to aging of the sample. The data of Ref. [12] were acquired over a year after sample acquisition, while the data of Figure 3 were acquired within three months. [Emim][EtSO$_4$], specifically [EtSO$_4$], is known to degrade in the presence of water. Water reacts with ethyl sulfate to form ethanol and hydrogen sulfate as described in chemical reaction (2). Ficke also identifies and describes this reaction [17]. The products are observed unambiguously at 98 and 143 m/q in neat anion [Emim][EtSO$_4$] emissions as [HSO$_4$] and [HSO$_4$] +[C$_2$H$_5$OH], respectively.

$$H_2O + [EtSO_4] \xrightarrow{yields} [C_2H_5OH] + [HSO_4] \quad (2)$$

4.2. QUANTUM MECHANICAL SPECIES CONSIDERATIONS

To complement the species assignments made on mass spectra, quantum mechanics (QM) calculations were performed. Gibbs Free Energy of Reaction (ΔG_{rxn}) values are computed using GAMESS, at the MP2/6-311++g(d,p) level for 298 K, with anticipated precision of ±0.1 eV [41, 42] for several anticipated or potentially observed ion clusters. Under the assumption that dissociation of clusters proceeds though a loose transition state, the Gibbs Free Energy computed values provide a rough estimate to the gas-phase stability of a subject cluster at 298 K. Values for specific reactions are obtained by calculation of the various product and reactant species and determined in the usual way. Specifically, a potential parent cluster is identified as being unstable if the Gibbs energy of reaction is below +0.1 eV for any dissociative pathway. The computed reaction energy values serve a three-fold use: they assist in identifying species that might constitute a spectral feature found in the experimental results, they assist in eliminating from consideration species that are likely unstable, and they aid justification of the absence of species from the spectra. As the focus of this work is on experimental results, and due to the large number of possible anions, cations, and neutral species, ion clusters at and above 190 m/q are not calculated. Optimized geometries and energies of relevant species are provided in the supplemental information.

At first glance, there appear to be several potential low solvated ion clusters that are not observed in the experimental mass spectra, namely anion clusters [NO_3] +[EA-H] and [HSO_4] +[EA-H], at 107 and 142 m/q, respectively. The [NO_3] +[EA-H] cluster has a calculated ΔG_{rxn} of +0.07 eV for dissociation into [NO_3] and [EA-H] which indicates the cluster is only slightly stable at 298 K. Definitively observed clusters in the experiment typically have ΔG_{rxn} values between +0.4 and +0.7 eV at room temperature. If the expected uncertainties are incorporated into the reported [NO_3] +[EA-H] cluster ΔG_{rxn} value (-0.03 to +0.17 eV), this cluster could spontaneously decay at this temperature. Similarly, dissociation of [HSO_4] +[EA-H] has a ΔG_{rxn} of -0.003 eV. Both potential compositions have ΔG values for dissociation within the expected uncertainties of the methodology used in this study and are thus not definitively stable.

Several observed peaks have multiple species assignments that satisfy the observed m/q ratio, namely the 139, 155, and 173 m/q cation peaks have 3, 4, and 2 assignments, respectively. The 139 m/q peak is assigned as either [EA] +2[EA-H], [EA] +[EA-H] +[C_2H_5OH], or [EA] +2[C_2H_5OH]. [EA] +2[EA-H] and [EA] +[EA-H] +[C_2H_5OH] are stable and unlikely to undergo spontaneous decay because they have ΔG_{rxn} = 0.4 and 0.3 eV, respectively. The 155 m/q peak could be [EA] +[EA+NO_3], [EA] +[HNO_3] +[C_2H_5OH], [Emim] +[EA-H], or [Emim] +[C_2H_5OH]. [EA] +[EA+NO_3] is known to be stable [22]. [Emim] +[C_2H_5OH] is also stable with ΔG_{rxn} = 0.17 eV. [EA] +[HNO_3] +[C_2H_5OH] and [Emim] +[EA-H] are most likely to dissociate because their ΔG_{rxn} values are 0.05 and 0.01 eV, respectively. The 173 m/q peak could be [EA] +2[HNO_3] or [Emim] +[HNO_3]; [EA] +2[HNO_3] is stable with ΔG_{rxn} = 0.14 eV, while [Emim] +[HNO_3] may spontaneously decay with ΔG_{rxn} = -0.01 eV. The calculations do not capture nor imply any decay rates for these reactions.

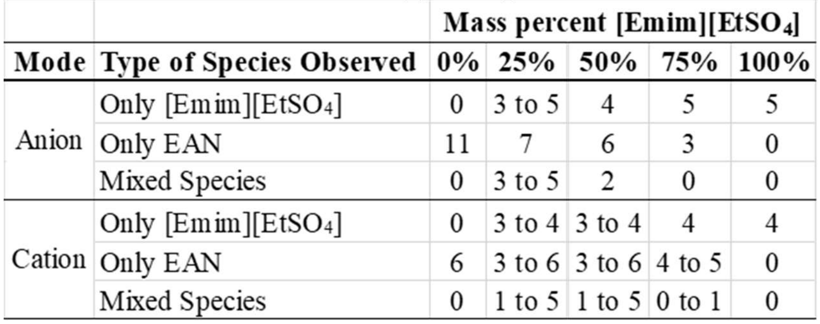
QM calculations can help clarify peaks where the methodology identified above may incorrectly provide identification. For instance, the 151 m/q anion peak has been identified as [NO_3] +2[EA-H]; however, the ΔG_{rxn} value is -0.02 eV. Additionally, a stable composition is calculated for a 92 m/q cation (not observed) of [EA] +[C_2H_5OH] with ΔG_{rxn} of 0.53 eV. The absence of a 92 m/q cation peak may be due to low signal-to-noise ratio or actual absence. We can identify a peak at 91 m/q, but it has signal-to-noise ratio of 1.15.

4.3. MIXED SPECIES VARIATION WITH MIXTURE RATIO

Bonded ions and neutrals from different parent species (i.e. mixed species) are observed in the electrospray. Further, multiple, different, mixed species are observed; the presence of these mixed species varies with mixture ratio. The presence and number of mixed species is indicative of changes in the intermolecular bonding between the parent species, specifically, changes in the hydrogen bond network of the liquid. A hydrogen bond network is a network formed by ions being bound via electrostatic attraction between an electronegative atom on one ion and a proton on another molecule. EAN and [Emim][$EtSO_4$] are both known to form extensive hydrogen bond networks [16, 43]. EAN's hydrogen bond network is similar to water, i.e., they are both extensive and three-dimensional [3]. The hydrogen bond network in [Emim][$EtSO_4$] is known to change as a function of mixture ratio with water and other polar liquids [14, 16] (note that we use EAN, which is also polar). Specifically, previous studies found that there is a critical ratio of six water molecules to four [Emim][$EtSO_4$] molecules, i.e. a mole ratio of 6 to 4, where the water molecules relax the hydrogen bonds between [Emim] and [$EtSO_4$], and hydrogen bonding between water and both ions is maximized. This is partially due to the large number of hydrogen bond sites available on the [Emim] and [$EtSO_4$] ions [16]. We believe we see similar phenomenon in our [Emim][$EtSO_4$]-EAN mixtures. We assume the number of different mixed species in the electrospray is indicative of the extent or level of hydrogen bonding in the liquid phase. Our analyses then suggest that hydrogen bonding is maximized at a mole ratio of EAN to [Emim][$EtSO_4$] near 7 to 3, or about 2.3 to 1.

Data in Tables 1 and 2 are used to identify the number of different species that are only [Emim][$EtSO_4$], only EAN, or have ions/neutrals from both (mixed species). The number of different species is reported in Table 3. The number of different species has uncertainty because some peaks in the spectra could be multiple species. To illustrate this uncertainty, we report the number of species in the form X to Y, where X refers to the number of species unambiguously meeting the criteria, while Y denotes all possible species that might meet the criteria. Table 3 shows that the number of only [Emim][$EtSO_4$] species increases with increasing mass percent of [Emim][$EtSO_4$], while the number of only EAN species decreases. This trend is more pronounced in anion mode. The number of mixed species appears to have a maximum around 25% [Emim][$EtSO_4$]. In anion mode, there are 3 to 5 mixed species at 25% [Emim][$EtSO_4$], while in cation mode there are 1 to 5. The molar ratio of EAN to [Emim][$EtSO_4$] at 25% mass percent [Emim][$EtSO_4$] is 2.3 to 1.

Table 3: Number and type of species observed



		Mass percent [Emim][$EtSO_4$]				
Mode	**Type of Species Observed**	**0%**	**25%**	**50%**	**75%**	**100%**
Anion	Only [Emim][$EtSO_4$]	0	3 to 5	4	5	5
	Only EAN	11	7	6	3	0
	Mixed Species	0	3 to 5	2	0	0
Cation	Only [Emim][$EtSO_4$]	0	3 to 4	3 to 4	4	4
	Only EAN	6	3 to 6	3 to 6	4 to 5	0
	Mixed Species	0	1 to 5	1 to 5	0 to 1	0

5. CONCLUSIONS

Electrospray mass spectra for two ionic liquids ([Emim][$EtSO_4$] and EAN) are obtained and analyzed in this study. Spectral characterizations are obtained for the pure (neat) liquids as well as for three different mixtures of the liquids. The analysis of these liquids are relevant to fundamental investigations as well as to applications within the electric propulsion community. Results of this investigation show the presence of all four ions ($[Emim]^+$, $[EtSO_4]^-$, $[EA]^+$, and $[NO_3]^-$) in the mixture electrospray plume. This result is in contrast to a previous mass spectrometric study of a HAN-$[Emim][EtSO_4]$ mixture which did not identify the $[HA]^+$ ion within the electrospray plume. However, the $[EA]^+$ ion is clearly identified in the current study and demonstrates conclusively that all four ions in this double salt liquid are electrosprayable. All monomers are identified in the plume spectra for all mixture ratios as well as in the plumes for the pure liquids. By comparing both sets of neat spectra with spectra for intermediate mixture ratios, it is conclusively demonstrated that the peaks, and thus the species, present in the plume vary with mixture mass ratio. In this investigation, quantum mechanical calculations are used to provide clarification into which compositions are most likely when multiple species are potentially present for a given peak.

The mass spectra information obtained and presented in this investigation are useful for modeling and simulation (i.e. molecular dynamics) validation studies. Both of the ionic liquids studied here have known potential functions. Mixtures of these two specific liquids are also of interest to the community (note that one is a PIL and the other an AIL). Information on the mass spectrometry associated with the electrospray of mixtures of these liquids allow direct identification of species variation with mixture ratio in both cation and anion modes. Specifically, it is observed that at a mixture ration corresponding to 75% $[Emim][EtSO_4]$ the mass spectra is simply characterized by a superposition of peaks from both neat spectra; however, for lower $[Emim][EtSO_4]$ fractions, unique "mixed species" appear in the plume. This indicates at these lower fractions that ions/neutrals from both liquids are being forming into "mixed species." This change in species present is attributed to hydrogen bond restructuring and occurs between 0.4 and 0.7 mole fraction of EAN within the mixture. This is similar hydrogen bond restructuring in mixtures of water and [Emim][$EtSO_4$] known to occur at a 0.6 water mole fraction. The spectra information presented in this work provides useful data for the validation of numerical models developed to study IL mixtures; spectral results here are fundamentally relevant to both cation and anion modes. Additionally, a transition due to inter ionic interactions is demonstrated, multiple species are identified within the plume, including both ionic and proton transferred forms of the PIL.

This work is related to previous work that studied a mixture of 41% [Emim][$EtSO_4$] and 59% HAN, by mass. This work definitively confirms the presence of [NO_3] within the plume. It has been suggested that ionic liquids with nitrate components are likely to have nitrates within the plume, which would be particularly useful in terms of energetics from a propulsion standpoint. The presence of several fragments from [Emim][$EtSO_4$], previously observed and reported in the literature, are also confirmed in this work. This result indicates that fragments may exist that may not be included in, but which may be important for accurate simulations. The emission of several emitted species, hypothesized to exist in previous work with HAN [12], are confirmed in the present work. These species are anion emissions [NO_3] +[HNO_3], [NO_3] +2[HNO_3], [Emim] +2[NO_3], and [$EtSO_4$] +2[HNO_3]. This result demonstrates that characterization and incorporation of proton transferred and ionic species into modeling simulations of IL mixtures containing nitrate is necessary to fully capture species present in the plume. Proton transferred species have been observed at a wider range of mixture ratios and emission modes in this work than previously reported, their presence is also rationalized from fundamental (i.e. quantum mechanical) energy calculations; previously observed proton transferred species in the HAN-[Emim][$EtSO_4$] mixture were only observed in anion mode at a single mixture ratio. Proton transferred species are definitively observed in this work at mixture ratios of 25% and 50% [Emim][$EtSO_4$] and potentially observed at 75% [Emim][$EtSO_4$], for both cation and anion modes. In addition, the existence of [Emim] +2[NO_3] and [$EtSO_4$] +2[HNO_3] in the plume represents a molecular level pairing between fuel and oxidizer. This suggests that this combination may be of interest as an energetic mixture.

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III. EFFECT OF NONLINEAR MIXING ON ELECTROSPRAY PROPULSION PREDICTIONS

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1. INTRODUCTION

Ionic liquids (ILs) and ionic liquids mixtures are of broad interest and have a wide range of actual and potential applications, including as spacecraft propellants [1, 2]. ILs are promising as electrospray propellants due to favorable physical properties such as high surface tension and conductivity and often negligible vapor pressure [2, 3]. Neat (pure) 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF_4]) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Emim][Tf2N]) are well-studied state-of-the-art electrospray propellants. More recently, IL mixtures have been investigated for use as multimode propulsion propellants, wherein one propulsion mode is an electrospray thruster and the other a chemical thruster [2, 4-7]. Previous work on chemical mode performance for several IL mixtures has been reported by Berg [2]. However, analysis and prediction of electrospray propulsion performance for IL mixtures has not been previously studied in detail and is the focus of this work.

An empirically-derived model relating electrospray propulsion performance with propellant physical properties was developed by Fernandez de la Mora [8]. This model predicts emission current, thrust, and specific impulse for a given flow rate and extraction voltage from conductivity, density, surface tension, and dielectric constant values. While physical properties of many neat ILs have been measured and reported in literature [1, 9-12], properties for mixtures are only beginning to be explored and documented. It is tempting to assume that physical properties of a mixture will vary linearly with the constituents' mixture ratio; however, physical properties of IL mixtures do not necessarily obey linear mixing laws and are perhaps more aptly labeled "double-salts" instead of "simple mixtures" [1]. Ãlvarez et al. show density and conductivity vary nonlinearly for mixtures of [Emim][BF_4] and EAN and identify a local minimum in conductivity for their mixtures [13]. In their review of IL mixture physical properties, Chatel et al. show that a mixture's departure from linear mixing is related to the disparity in physical size of ions in the mixture. In general, ILs with anions and cations of disparate size tend to exhibit nonlinear mixing, some of which can be approximated with an electrical circuit analog or molar volume approach [1]. No one method of mixture property prediction is universal in application or acceptance [1]. In the following sections we investigate how real nonlinear behavior for some propulsion-relevant IL mixtures results in lower predicted performance compared to an ideal linear mixing model and quantify the importance of nonlinear mixing on propulsion performance predictions.

Four IL mixtures are selected for this study. The first set of hydroxylammonium nitrate (HAN) and 1-ethyl-3-methylimidazolium ethyl sulfate ([Emim][$EtSO_4$]) are selected due to previous investigation into their use as a multimode propellant [2, 5-7].

Ethylammonium nitrate (EAN) contains sufficient oxygen for combustion and when mixed with sulfolane [$C_4H_8O_2S$] can function as an electrospray propellant [14]. Mixtures of EAN and [Emim][$EtSO_4$] are selected because EAN has attractive properties for multimode propulsion and all mixtures of these liquids exist in liquid state at room temperature (unlike [Emim][$EtSO_4$]/[HAN] mixtures). Additionally, because experimental and MD conductivity and density literature data exists for mixtures of 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF_4]) and EAN [13], this mixture is selected for comparative purposes. The final mixture investigated contains [Emim][BF_4] and [Emim][$EtSO_4$], providing data for a mixture with a shared cation.

2. EXPERIMENTAL PROCEDURES

The ILs used in this study were obtained from commercial sources. EAN was obtained from Iolitec at 97% purity. Samples of [Emim][$EtSO_4$], [Emim][BF_4], and HAN (24% aqueous solution) were obtained from Sigma Aldrich at 95% purity, 99% purity, and 99.999% purity, respectively. Solid HAN was prepared from the aqueous solution according to procedures described by Rasmont that yield about 1-2% water content [15]. The ILs were exposed to high vacuum (10^{-6} Torr) for 24 hours before mixing to remove volatile impurities. Mixed samples were prepared in quantities larger than 4 g to the desired mixture ratio with a precision within 0.01 g (i.e. less than 0.5% error in mass percentage). In this work, mixture ratio refers to the mass-based ratio of components in the mixture for a given sample. Samples containing HAN were stored in vacuum to avoid water absorption. Samples not containing HAN were stored in atmosphere and were reexposed to vacuum for greater than 1 hour before physical properties were obtained to remove any accumulated water contamination.

Physical properties of density, conductivity, and surface tension were measured using commercially-available measurement apparatus. Density was obtained using a 2 mL Pyrex pycnometer (specific-gravity bottle) from Fisher Scientific and a Torbal AGC500 Bench scale with an accuracy of 0.001 grams; the total overall uncertainty is 0.14%. Conductivity was measured using an OAKTON Cond 6+ conductivity meter accurate to within 1% over the full range of 0.00 to 200 mS/cm. This meter was calibrated using two RICCA conductivity standards of 7,000 μS/cm and 50,000 μS/cm from Cole Parmer. A Ramé-Hart 500 Series Tensiometer, precision of 0.01 dynes/cm, was used for measuring surface tension.

3. RESULTS AND DISCUSSION

In this section, experimental physical property data for the IL mixtures are presented and compared with literature data. Electrospray propulsion performance predictions are then made using the experimentally obtained physical properties and compared with predictions that assume linear mixing.

3.1. PHYSICAL PROPERTY RESULTS

The conductivity (K), surface tension (γ), and density (ρ) experimental data are shown for mixtures of the selected ILs at room temperature (22° C) in Figure 1. Specifically, the properties of ILs are measured both for pure liquids and mixtures of

[Emim][EtSO$_4$] with EAN, [Emim][EtSO$_4$] with [Emim][BF$_4$], and [Emim][BF$_4$] with EAN, at mixture ratios of 25, 50, and 75%, as shown. Additionally, [Emim][EtSO$_4$] is mixed with HAN to form 41%, 50%, and 75% [Emim][EtSO$_4$] by mass liquid mixtures. This set is limited by the saturation limit of HAN in [Emim][EtSO$_4$] (since HAN is solid at room temperature). Error bars for these data are plotted in Figure 1, but in many cases are smaller than the marker.

The pure sample physical properties agree with literature data for both surface tension and density measurements. Conductivity values for the pure ILs also agrees with literature data, with expected differences due to temperature variations. The experimental density results for pure [Emim][EtSO$_4$] of 1.212 ± 0.057 g/cc, [Emim][BF$_4$] of 1.286 ± 0.002 g/cc, and EAN of 1.214 ± 0.005 g/cc are within 2.5% of reported literature values of 1.240 ± 0.004 [9], 1.2798 ± 0.0002 [12], and 1.212 g/cc [16], respectively. The measured surface tension values of 47.16 ± 2.36, 51.19 ± 0.09, and 50.76 ± 0.24 dynes/cm match values reported in literature to within 3.5% for pure [Emim][EtSO$_4$] (47.25 ± 0.05 [9]), [Emim][BF$_4$] (50.1 ± 0.1 [12]), and EAN (46.6 to 49.1 dynes/cm [17]), respectively. The conductivity value for pure [Emim][BF$_4$] of 14.32 ± 0.14 mS/cm agrees with linear interpolation of data obtained for two temperatures (15 and 25 °C) by Stoppa yielding 14.05 ± 0.07 mS/cm at 22 °C [10]. The conductivity value of 21.6 ± 0.22 mS/cm for EAN is similar to that given in literature of 24.8 ± 1.24 mS/cm at 25 °C [13] (representing a 13% difference); this difference is likely due to temperature differences since increasing temperature increases conductivity (see also [10]). The conductivity value obtained here for pure [Emim][EtSO$_4$] of 3.41 ± 0.034 mS/cm is over 40 times larger than the 80 μS/cm literature reports [9]. We measured conductivity for

[Emim][EtSO$_4$] three times using the same methods and procedure as the other liquids studied; these result varied by only 1%. Fernandez [9] cited Sigma Aldrich, the chemical supplier, as the source of the 80 μS/cm value; when contacted Sigma Aldrich, was unable to provide information concerning this data or its acquisition. Compared with Fernandez [9], our measured conductivity for [Emim][EtSO$_4$] is much closer to the conductivity of the other imidazolium-based IL in this study. Specifically, [Emim][BF$_4$] conductivity is 4 times larger than [Emim][EtSO$_4$] in our results versus 180 times larger compared with Fernandez [9]. Finally, the mixture ratio dependence of density and conductivity for [Emim][BF$_4$]/EAN samples agree with previously published mixture data by Docampo-Ãlvarez [13]. The maximum difference between our conductivity data and theirs is 25% at a mixture ratio of 75/25 ([Emim][BF$_4$]/EAN), and may be attributable to temperature differences because their study was conducted at 25 °C.

The experimental data presented in Figure 2 show nonlinear mixing characteristics. This is most apparent in the conductivity values. Conductivity values at intermediate mixture ratios for all mixtures fall below what would be expected for linear mixing in terms of either mole or mass-averaged values. Specifically, linear mass-averaging over-predicts the measured conductivity values by a maximum of 109% for [Emim][EtSO$_4$]/EAN, 27.4% for [Emim][EtSO$_4$]/[Emim][BF$_4$], and 37.6% for [Emim][BF$_4$]/EAN when compared to experimentally measured values. The [Emim][BF$_4$]/EAN mixture shows a local minimum in conductivity at the 75:25 mixture ratio. Docampo-Ãlvarez [13] also observed the conductivity at this 75:25 mixture ratio to be below that of the neat liquids.

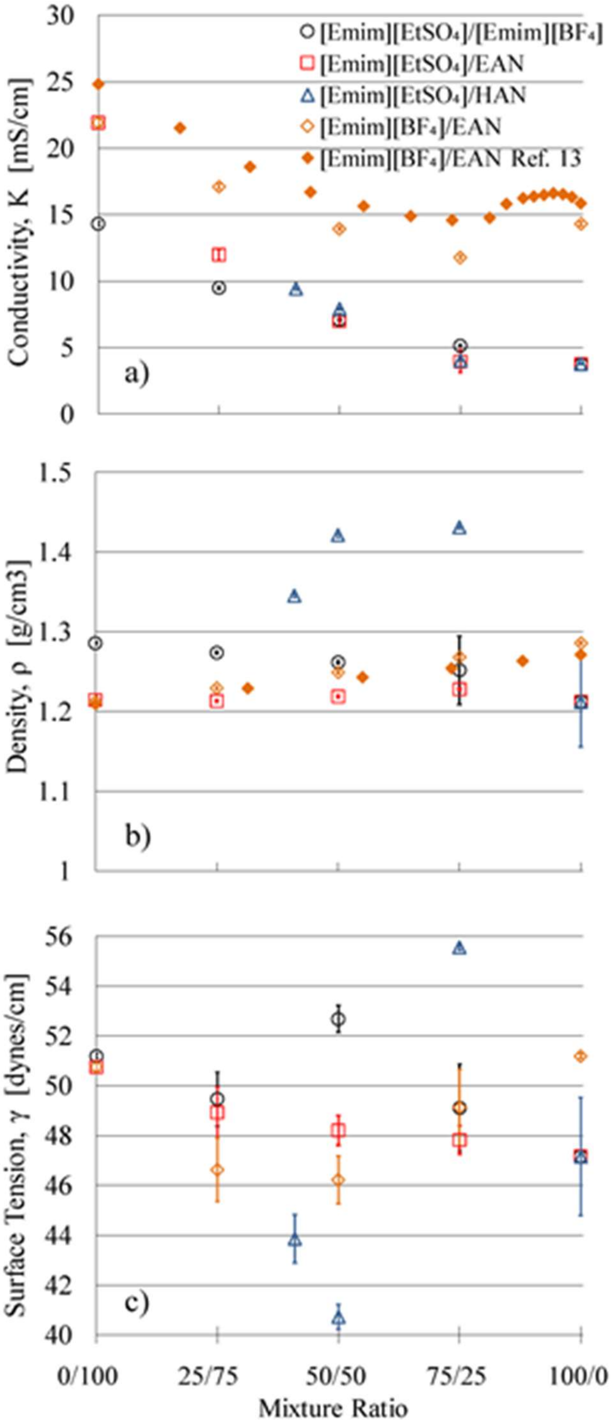

Figure 1: Experimental physical properties with varying mixture ratio of a) conductivity, b) density, and c) surface tension

3.2. PERFORMANCE PREDICTIONS

Fernandez de la Mora empirically derived performance predictions for electrosprays based on the liquid physical properties and liquid flow rate (Equation (1)) [8]. Equation (1) relates the current emitted by the cone jet (I(Q)) to the surface tension (γ), conductivity (K), liquid flow rate (Q), dielectric constant (ε), and a function of dielectric constant $f(\varepsilon)$. We use this model to compare performance predictions based on assumed linear mixing of physical properties vs. the real measured nonlinear mixing of physical properties, i.e. Figure 1. While we have measured surface tension, conductivity, and density (Figure 1), we have not measured dielectric constant. Huang and Singh measured dielectric constant of the neat liquids [Emim][EtSO$_4$], [Emim][BF$_4$], and EAN to be 35, 15, and 26.3, respectively [18, 19]. For mixtures, we assume the mixture dielectric constant is based on a linear mass average. Linear mixing of dielectric constant based on mixture mass percentage is supported by Mou et al. and Thomas et al. who found the complex dielectric permittivity and dielectric properties to obey linear mass mixing [11, 20]. The value for the function of the dielectric constant ($f(\varepsilon)$) is taken directly from Ref. [8] (Figure 11 in [8]). Specifically, the dielectric constants of our study ($15 \leq \varepsilon \leq 35$) are within the linear portion of the $f(\varepsilon)$ relationship that extends from $10 \leq \varepsilon \leq 40$ in Ref. [8].

Performance is predicted using both experimentally measured values for physical properties and calculated physical properties based on assumed linear mixing. For all predictions we assume a volumetric flow rate of 50 pL/s, which is near the lower bound investigated by Fernandez de la Mora and similar to currently proposed capillary electrospray thrusters (e.g., LISA Pathfinder flow rate of 185 pL/s per emitter [21]). The anticipated emission current is calculated directly via Equation (1):

From this expected current, the thrust (F) is computed with Equation (2). We assume an accelerating voltage V_{acc} of 2.3 kV because this voltage has been used in experimental electrospray for some of these mixtures [3]. Mass flow rate is based on the prescribed volumetric flow rate and experimentally determined density, Figure 1.

$$I(Q) = f(\varepsilon)\left[\frac{\gamma\, K\, Q}{\varepsilon}\right]^{0.5} \tag{1}$$

$$F = \sqrt{2V_{acc}\,\dot{m}\,I} \tag{2}$$

Predicted emission current is shown in Figure 2. Results for [Emim][$EtSO_4$]/HAN and [Emim][$EtSO_4$]/EAN are presented in Figure 2A, and results for [Emim][$EtSO_4$]/[Emim][BF_4] and [Emim][BF_4]/EAN are presented in Figure 2B. Figure 2 shows the predicted emission current for real measured physical properties of the mixtures (data points) and physical properties that assume linear mixing (dashed curves). For HAN/[Emim][$EtSO_4$], HAN increase the predicted emission current; this is predominantly due to HAN increases the conductivity from 3.72 mS/cm (pure [Emim][$EtSO_4$]) to 9.42 mS/cm at 59:41 HAN/[Emim][$EtSO_4$] by mass.

Figure 2 shows the linear mixing assumption over-predicts current, with a maximum over-prediction of 45% for [Emim][$EtSO_4$]/EAN at 75:25. Over prediction of current translates into over-prediction of thrust, with a maximum over-prediction of 20%. Table 1 shows the percent over prediction in current and thrust when assuming linear mixing vs. measured physical properties data. Specific impulse is also over-predicted and is similar to thrust because density only varies slightly with mixture ratio for these mixtures.

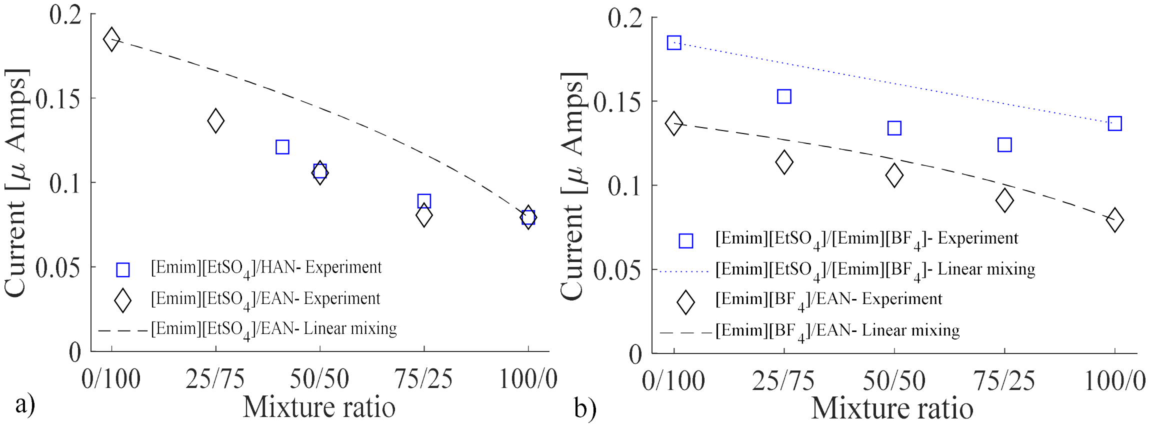

Figure 2: Emission current vs mixture ratio at 50 pL/s flowrate for a) [Emim][EtSO4]/HAN and [Emim][EtSO4]/EAN and b) [Emim][EtSO4]/[Emim][BF4] and [Emim][BF4]/EAN

Table 1: Percent over-prediction when assuming linear mixing as opposed to the empirically determined nonlinear mixing

	Current Prediction			Thrust Prediction		
IL Mixture	**75/25%**	**50/50%**	**25/75%**	**75/25%**	**50/50%**	**25/75%**
[Emim][EtSO4]/EAN	44.9	20.4	21.7	20.4	16.8	10.3
[Emim][EtSO4]/[Emim][BF4]	10.3	5.0	11.8	5.0	4.4	5.7
[Emim][BF4]/EAN	19.6	9.4	13.0	9.4	9.4	6.3

4. CONCLUSIONS

These results suggest nonlinear mixing of ionic liquids must be accounted for during propellant design and electrospray performance predictions, otherwise predictions can be off by up to about 50%. Physical property data (density, conductivity, surface tension) obtained experimentally for all pure ILs tested in this study ([Emim][EtSO$_4$], EAN, and [Emim][BF$_4$]) agree with literature data to within 13%. Physical properties for mixtures of these ILs vary nonlinearly with respect to mixture mass ratio; in all cases investigated here, measured conductivity values are below linear mixing predictions. Thus, assuming linear mixing leads to over prediction of electrospray propulsion performance; for mixtures of [Emim][EtSO$_4$] and EAN, a linear mixing assumption results in over-prediction of emission current by up to 45% and thrust by up to 20% compared with predictions using real measured physical properties. For mixtures of [Emim][BF$_4$] and EAN the over prediction is 20% and 9% for current and thrust, respectively, and for [Emim][EtSO$_4$] and [Emim][BF$_4$] it is 12% and 6%, respectively. Results also show IL mixtures can have properties outside the bounds of their parent's physical properties. For instance, a 75/25 [Emim][BF$_4$]/EAN mixture has conductivity of 11.8 mS/cm, which is below both neat [Emim][BF$_4$] (14.3 mS/cm) and neat EAN (21.6 mS/cm). This causes mixtures of [Emim][EtSO$_4$] with EAN and [Emim][BF$_4$] with EAN to have a performance minimum at a mixture ratio around 25% EAN by mass.

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SECTION

2. CONCLUSIONS AND RECOMMENDATIONS

2.1. CONCLUSIONS

Previous investigations into ionic liquid mixtures as propellants focused on optimizing chemical mode performance in a multi-mode (spacecraft) propulsion architecture. This work describes research relating to the electric propulsion mode, i.e., it is directed at electrospray mode operations of such ionic liquid mixtures. A logical starting point in this work was to determine whether HAN is present in an electrospray plume when an IL mixture containing HAN is undergoing electrospray. This is noteworthy as many current propellant development efforts involve HAN as a component of interest. Subsequent work then focuses on analyzing how variations in the mixture ratio of two ionic liquids in a mixture of one AIL and one PIL affected the observed species in the plume. Finally, an assessment of non-linear mixing effects on analytical performance predictions are provided for several IL mixtures. This is done by comparing performance predictions based on experimentally determined physical property data at intermediate mixtures with performance predictions based on linearly mass averaged physical property data.

To investigate electrospray plume composition, the AFRL Kirtland quadrupole mass analyzer was used in conjunction with a capillary emitter mounted on a rotation stage. This instrument provided angle and flowrate resolved plume mass spectra for both the cation and anion mode. Cation and anion mass spectra were taken from the electrospray plumes of neat (pure) [Emim][$EtSO_4$], EAN, mixtures of EAN with [Emim][$EtSO_4$], and a mixture of [Emim][$EtSO_4$] (41% by mass) with HAN (59%) and were characterized using this instrument. From these spectra, peaks were observed at several different mass to charge ratios. Each peak represents a different species emitted into the plume. By comparing these measured peak values with known ions and neutrals, anticipated species were assigned to the plume.

Cation and anion mass spectra for neat [Emim][$EtSO_4$] and a mixture of [Emim][$EtSO_4$] with HAN (41% and 59% by mass respectively) were acquired for comparison. Cation and anion mixture spectra were acquired over a flowrate range of 2pL/s to 3 nL/s for the mixture. The spectra follow previously identified literature trends on angle and flow rate. By comparing the neat IL spectra with the mixture spectra, several new species are identified as present in the mixture plume that are not present in the neat ionic liquid. Many [Emim][$EtSO_4$] related species appear in both sets of spectra, including both the [Emim] cation and the [$EtSO_4$] anion. Noteworthy HAN-based species identified are the Nitrate anion and both proton transferred HAN species (nitric acid and hydroxylamine); the proton transferred neutral species are emitted with an anion attached charging them and allowing their detection. The mixture cation spectra are notably absent of any unique HAN signatures; this may be due to the $[HA]^+$ cation being below the minimum detectable mass to charge ratio of the instrument configuration. Cation and anion swapping are also observed in the plume where species containing ions from both liquid are present; this extends to HAN neutral species being emitted with the [$EtSO_4$] anion. HAN elements are observed in the anion electrospray plume of a mixture containing HAN, supporting the use of HAN as a component of electrospray propellant mixtures.

Cation and anion mass spectra were obtained for neat [Emim][EtSO$_4$], neat EAN, and mixture ratios of 75-25, 50-50, and 25-75 ([Emim][EtSO$_4$]-EAN). Both cations and both anions were observed in their respective mass spectra and for all three mixed liquid samples; this is noteworthy since the [HA]$^+$ ion was not observed previously in the cation mass spectra during investigations of a HAN-[Emim][EtSO$_4$] mixture. Additionally, proton transferred EAN is observed in the spectra. Comparison with both sets of neat spectra aids in peak assignments at intermediate mixture ratios. The mixture spectra showed clear changes with mixture ratio in both cation and anion mode unlike previous work. The plume composition also shows a transition where, for above 25% EAN, species swapping (i.e., species containing ions from both liquids are observed in the plume) is clearly present, but at 25% EAN no species are definitively observed. This is likely due to hydrogen bond restructuring and has been seen previously in mixture of [Emim][EtSO$_4$] and either water or other polar liquids. EAN is thus a promising IL as both ions are present in mixture electrospray plumes.

Analytical performance predictions were made for several different mixtures of ILs according to an empirical model. Namely, mixtures of [Emim][EtSO$_4$] with HAN, [Emim][EtSO$_4$] with EAN, [Emim][EtSO$_4$] with [Emim][BF$_4$], and [Emim][BF$_4$] with EAN were investigated. The analytical performance predictions were made using an empirical model that relates conductivity, surface tension, density, and dielectric constant to electrospray current emissions. The physical properties of conductivity, surface tension, and density were measured experimentally for several sets of IL mixtures; literature results for dielectric constant were used.

Performance predictions using the experimentally obtained properties of conductivity, density, and surface tension at several different mixture ratios were compared with performance predictions assuming linear (mass averaged) mixture of properties. The physical properties for these mixtures all showed some degree of nonlinearity; conductivity showed the largest deviation from linear mixing. The [Emim][BF_4]-EAN mixture set has a conductivity minimum at the 25% EAN intermediate ratio; the 50% EAN case also has a conductivity value below the conductivity values of both neat liquids.

Non-linearities in mixture physical properties are not particularly surprising; however, this work provides for the first time the examination of the degree of effect this non-linearity has on thruster performance. When comparing the performance predictions based on linear mixing laws for mixture properties with those based on experimentally determined property measurements, there are several important findings. First, the nonlinearity actually (experimentally) observed in properties and resulting (predicted) performance leads to an over-prediction in performance when linear mixing is assumed. Most notably, predictions of performance based on linear mixing laws for the [Emim][$EtSO_4$]-EAN mixture set leads to a 45% over prediction in emission current and a 20% higher prediction in thrust then performance associated with intermediate mixture ratio experimentally determined physical property data. Additionally, both the [Emim][$EtSO_4$]-EAN and [Emim][BF_4]-EAN mixtures have minimums in anticipated performance at 25% EAN that are not captured by linear mixing models. Thus, where possible, when designing electrospray propellants, intermediate property data as obtained by experiment or as produced in high fidelity modeling efforts that have been validated by experimental data should be used instead of property characteristics based on linear mixing assumptions. In summary, predictions assuming linear mixing of physical properties show a tendency to over-predict performance for the samples investigated in this study.

2.2. RECOMMENDATIONS

There are a number of recommendations that represent logical continuation of the work reported here. Currently, methodology in propellant handling is focused on keeping moisture out; however, there have not been studies showing how much water content is 'too much' nor have there been studies specifically focusing on providing expected or anticipated degradations in performance due to water content. Thus, a study focusing on how performance predictions vary with water composition would be of interest. In addition, a study that focuses on characterizing water percentages at which evaporation and bubble formation becomes debilitating would also be valuable. Along similar lines, some propellants are known to degrade with time. For instance [Emim][$EtSO_4$] is known to degrade when water is present, and the [Emim][$EtSO_4$]-HAN mixtures are observed to precipitate crystals out of solution after several months of storage. Studies focused on these degrading effects would be beneficial.

More research should also be done conducted to investigate mixture variation effects on experimentally measured beam current values in order to compare with the analytic performance predictions that have been made in this study. Coupling such experimental results with the analytic models already available and with high fidelity numerical molecular dynamics simulations would be a powerful tool for the design optimization of future electrospray propellants.

Another potential extension of the current research involves the investigation of propellant composition optimization for use over an entire multi-mode mission. Chemical mode performance versus mixture ratio has been characterized in previous work; this study has analyzed electric mode performance. Thus, work that integrates these two modes of operation would be beneficial for the development of a truly optimized multi-mode propellant. The focus in such an investigation would be to determine the optimal mixture ratio in a multi-mode setting where the fraction of propellant used (Electric Propulsion or EP Fraction) in each mode is already known; this may yield a propellant that is sub-optimal in each mode, but is overall optimal for a specific EP Fraction. The HAN-[Emim][EtSO$_4$] composition is a poor choice for such a study since, for this propellant mixture, the chemically optimized composition is also the (analytically) optimized composition for the electric mode. In addition, a system level optimization study based on propulsion system mass with varied operation temperature would be of interest. Increasing temperature generally increases conductivity in ILs, hence suggesting that the associated electrical requirements of heating electrospray could lead to an increase in total system mass, or an increase in vapor pressure that could lead to propellant being lost through evaporation.

Studies that continue the mass spectra work presented in the current work are also potentially of interest. Mixtures containing a common anion or cation with a varying mixture ratio would be useful for better charecterising the hydrogen bond restructuring that has been observed in the [Emim][$EtSO_4$]-EAN study. Finally, investigation and characterization of ionic fragmentation in the plume would also be beneficial, especially in terms of the fragmentation of emissions from mixed ionic liquid sources. Most fragmentation studies to date have focused on neat (pure) ionic liquids.

APPENDIX A.

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APPENDIX B.

SUPPORTING INFORMATION: JOURNAL OF MASS SPECTROMETRY

This information is presented as supplemental material to the Journal of Mass Spectrometry paper (Paper II). Specifically, this information fleshes out the quantum mechanical calculations discussed and presented within Paper II.

B.1. ENERGY TABLES FOR ION CLUSTER DISSOCIATION

Table B.1: List of species short hands

Species	Abbreviation	Molecular mass [amu]
Nitrate	$[NO_3]^-$	62
Hydrogen sulfate	$[HSO_4]^-$	97
Ethylammonium	$[EA]^+$	46
1-ethyl-3-methylimidazolium	$[Emim]^+$	111
Nitric acid	$[HNO_3]$	63
Ethylamine	[EA-H]	45
Ethanol	$[C_2H_5OH]$	46

Table B.2: Optimized structure energies at MP2/6-311++g(d,p). Middle Column is E_0 + G_{corr}. Hartree converted to eV as 1 Hartree = 27.2114 eV and calculated at 298 K with no scaling of vibrational frequencies

Species	**ZPE-Corrected Gibbs Free Energies (eV), 298 K**	**Molecular mass [amu]**
$[NO_3]^-$	-7614.447645	62
$[HSO_4]^-$	-19010.48823	97
$[EA]^+$	-3675.574427	46
$[Emim]^+$	-9346.633291	111
$[HNO_3]$	-7628.498212	63
[EA-H]	-3666.151487	45
$[C_2H_5OH]$	-4206.768166	46
$[NO_3]^-$ +[EA-H]	-11280.66445	107
$[NO_3]^-$ +2[EA-H]	-14946.79522	152
$[HSO_4]^-$ +[EA-H]	-22676.63695	142
$[EA]^+$ +[EA-H]	-7342.427939	91
$[EA]^+$ +2[EA-H]	-11008.97958	136
$[EA]^+$ +[EA-H] +$[C_2H_5OH]$	-11549.51359	137
$[EA]^+$ +$[HNO_3]$	-11304.23358	109
$[EA]^+$ +2$[HNO_3]$	-18932.8689	172
$[EA]^+$ +$[C_2H_5OH]$	-7882.870208	92
$[EA]^+$ +$[HNO_3]$+$[C_2H_5OH]$	-15511.41723	155
$[Emim]^+$ +$[C_2H_5OH]$	-13553.57454	157
$[Emim]^+$ +[EA-H]	-13012.79608	156
$[Emim]^+$ +$[HNO_3]$	-16975.12019	174

Table B.3: Calculated Gibbs Reaction Free Energies (based on values in Table S2), calculated to three decimals for MP2/6-311++g(d,p) at 298 K

Potential Dissociation Reaction	**ΔG_{rxn} (eV)**
$[NO_3]^- + [EA\text{-}H] \xrightarrow{yields} [NO_3]^-$ & $[EA\text{-}H]$	0.065
$[NO_3]^- + 2[EA\text{-}H] \xrightarrow{yields} [NO_3]^- + [EA\text{-}H]$ & $[EA\text{-}H]$	-0.021
$[HSO_4]^- + [EA\text{-}H] \xrightarrow{yields} [HSO_4]^-$ & $[EA\text{-}H]$	-0.003
$[EA]^+ + [EA\text{-}H] \xrightarrow{yields} [EA]^+$ & $[EA\text{-}H]$	0.702
$[EA]^+ + 2[EA\text{-}H] \xrightarrow{yields} [EA]^+ + [EA\text{-}H]$ & $[EA\text{-}H]$	0.400
$[EA]^+ + [EA\text{-}H] + [C_2H_5OH] \xrightarrow{yields} [EA]^+ + [EA\text{-}H]$ & $[C_2H_5OH]$	0.317
$[EA]^+ + [HNO_3] \xrightarrow{yields} [EA]^+$ & $[HNO_3]$	0.161
$[EA]^+ + 2[HNO_3] \xrightarrow{yields} [EA]^+ + [HNO_3]$ & $[HNO_3]$	0.137
$[EA]^+ + [C_2H_5OH] \xrightarrow{yields} [EA]^+$ & $[C_2H_5OH]$	0.528
$[EA]^+ + [HNO_3] + [C_2H_5OH] \xrightarrow{yields} [EA]^+ + [C_2H_5OH]$ & $[HNO_3]$	0.049
$[Emim]^+ + [C_2H_5OH] \xrightarrow{yields} [Emim]^+$ & $[C_2H_5OH]$	0.173
$[Emim]^+ + [EA\text{-}H] \xrightarrow{yields} [Emim]^+$ & $[EA\text{-}H]$	0.011
$[Emim]^+ + [HNO_3] \xrightarrow{yields} [Emim]^+$ & $[HNO_3]$	-0.011

B.2. OPTIMIZED STRUCTURE COORDINATES USED FOR ENERGY CALCULATIONS

$[NO_3]^-$

N	0.0000000318	-0.0000000002	0.0000000000
O	1.2623517707	0.0000000001	-0.0000000000
O	-0.6311759013	-1.0932288284	-0.0000000000
O	-0.6311759012	1.0932288285	-0.0000000000

$[HSO_4]^-$

S	-0.1529336218	-0.0079887731	0.2412043059
O	-0.7818879322	-0.1390135312	-1.0843344578
O	0.1740836839	-1.2981832503	0.8723176489
O	-0.7372603631	1.0012022645	1.1245906511
O	1.3637743898	0.6776495155	-0.0935778738
H	1.7917438434	0.0414537746	-0.6785802744

$[EA]^+$

N	-1.1686382663	-0.3543668134	-0.0000004627
H	-1.1400786903	-0.9616743895	0.8253692668
H	-1.1400772230	-0.9616743263	-0.8253701640
C	-0.0004274109	0.6150795727	0.0000004561
H	-0.1238069590	1.2343459852	-0.8891796305
H	-0.1238073753	1.2343448130	0.8891812837
C	1.3080702169	-0.1507682686	0.0000002211
H	1.4073789994	-0.7745826290	-0.8922354555
H	2.1324229571	0.5647395886	-0.0000001855
H	1.4073795429	-0.7745824147	0.8922359374
H	-2.0721357916	0.1295788821	-0.0000012670

$[Emim]^+$

N	9.353387219	-0.36017209	-0.208404232
N	9.114047262	-0.711738426	1.929737116
C	8.637750486	-0.024526107	0.87751992
H	7.817455665	0.677260532	0.900568638
C	10.1548624	-1.503589055	1.50641709
H	10.69276416	-2.154826898	2.178739597
C	10.30811755	-1.278971862	0.158090392
H	11.00653469	-1.699005638	-0.549540254
C	8.579506886	-0.655584731	3.29855374

H	8.087351699	-1.599840706	3.531901488
H	7.862422247	0.162374858	3.355821462
H	9.402178911	-0.470731812	3.988760323
C	9.180149507	0.214181845	-1.560182946
H	9.055838927	-0.624420017	-2.248906259
H	8.24528277	0.777992041	-1.536962336
C	10.36210034	1.096232778	-1.935421115
H	10.48073132	1.910808471	-1.217283629
H	10.18701677	1.527725344	-2.923611329
H	11.28950119	0.520831472	-1.975797667

[HNO_3]

N	0.148116846	0.038699622	3.48035E-05
O	-1.128269319	-0.562256501	0.000212517
H	-1.724336792	0.204769711	0.000321249
O	0.160857746	1.253331621	6.17436E-05
O	1.05411152	-0.753604453	-0.000120313

[EA-H]

N	-1.3070319159	-0.0854191445	0.0000001876
H	-1.3915832117	-0.6877564076	0.8141532674
H	-1.3915850173	-0.6877519562	-0.8141557913
C	-0.0007509814	0.5773310141	0.0000005578
H	0.0369991300	1.2303356262	-0.8777023661
H	0.0369992743	1.2303347284	0.8777041506
C	1.2109742632	-0.3557846728	0.0000000725
H	1.2020690996	-0.9991091878	-0.8857525891
H	2.1474095173	0.2119490475	-0.0000003442
H	1.2020698418	-0.9991090473	0.8857528549

[C_2H_5OH]

C	-3.200165993	-1.82835917	0.294276895
C	-2.928057194	-0.412210002	-0.187415809
O	-3.630079337	0.563181298	0.580237776
H	-4.563784123	0.33840552	0.529745765
H	-4.258735451	-2.082060117	0.174785436
H	-1.871434067	-0.16382509	-0.070159384
H	-3.178902812	-0.317516947	-1.252083308
H	-2.614831807	-2.55203701	-0.281266644
H	-2.940629217	-1.924858481	1.351019273

$[NO_3]^-$ +[EA-H]

N	-1.61645	0.272865	0.845038
H	-1.80271	-0.72054	0.966967
H	-1.10529	0.348041	-0.03945
C	-0.72813	0.718188	1.919576
H	-0.42749	1.742624	1.685201
H	-1.29835	0.743969	2.858952
C	0.529138	-0.13446	2.105961
H	1.109836	-0.13765	1.181033
H	1.160674	0.257736	2.913182
H	0.258848	-1.16869	2.353918
N	1.18462	0.853608	-1.40983
O	2.301194	0.678687	-1.95837
O	0.230771	0.050394	-1.63748
O	1.001288	1.82239	-0.62133

$[NO_3]^-$ +2[EA-H]

N	-3.97904	-2.36682	3.913842
H	-3.43248	-2.9813	3.314592
H	-3.97336	-1.4552	3.453365
C	-3.31886	-2.25909	5.216214
H	-3.82079	-1.45974	5.768532
H	-3.48872	-3.19517	5.76645
C	-1.81671	-1.96887	5.170121
H	-1.62138	-1.00875	4.687142
H	-1.3944	-1.93353	6.182608
H	-1.29264	-2.75398	4.611097
N	-2.77725	0.773716	3.151367
O	-1.60647	1.200321	2.977862
O	-3.39209	0.217548	2.18791
O	-3.33727	0.866044	4.27291
N	-1.46782	-0.16522	-0.23657
H	-2.13844	0.130245	0.478182
H	-1.85581	-1.01617	-0.63891
C	-0.21581	-0.49878	0.446435
H	0.535514	-0.76464	-0.30989
H	0.129104	0.408068	0.950487
C	-0.33532	-1.62192	1.478457
H	-0.66133	-2.55313	0.997637
H	0.622569	-1.81051	1.979256
H	-1.07282	-1.34319	2.233505

[HSO$_4$]$^-$ +[EA-H]

S	-4.582948723	-1.447673952	0.733092723
O	-5.09757587	-0.461008364	-0.241537718
O	-4.246722311	-2.740123253	0.112337037
O	-5.299356204	-1.51441422	2.003653352
O	-3.099481624	-0.799677726	1.207281962
H	-2.622996239	-0.643508933	0.383157263
N	-7.355413321	-0.776447684	-2.226833456
H	-6.937672663	-0.857118841	-3.151038043
H	-6.584696146	-0.57860435	-1.583698172
C	-7.936723413	-2.069945673	-1.85946248
H	-8.23344344	-2.003442346	-0.807414849
H	-8.857607528	-2.215952908	-2.440557105
C	-7.01306667	-3.276222566	-2.049456534
H	-6.102871141	-3.165715883	-1.453835415
H	-7.514593461	-4.205800427	-1.751733195
H	-6.728371246	-3.369502877	-3.10517537

[EA]$^+$ +[EA-H]

C	2.2799560327	0.4104485175	-0.4826948198
H	3.0267074039	1.2059286598	-0.5615910676
H	2.1521445466	-0.0208574164	-1.4797005997
C	2.7414132735	-0.6463632131	0.5087293555
H	3.7071807265	-1.0549655731	0.2044251467
H	2.8603743939	-0.2186561557	1.5088038173
H	2.0329172693	-1.4785661809	0.5710308907
H	0.7126976083	1.7389187749	-0.6837058665
N	0.9625852016	0.9670794328	-0.0641614436
H	-0.1619638200	-0.1591195858	-0.0441558565
C	-2.2678940635	-0.3779533418	-0.5061768275
H	-2.9682027597	-1.2050648700	-0.6335415521
H	-2.1010205319	0.0889871441	-1.4787769539
C	-2.7627257420	0.6220045252	0.5239446245
H	-2.0601111045	1.4497115467	0.6468447082
H	-3.7184597695	1.0357071323	0.1967256614
H	-2.9211282034	0.1433374588	1.4945742151
H	-0.6399999357	-1.6886549995	-0.7122383467
N	-0.9476847301	-0.9498645266	-0.0760121009
H	1.0744333480	1.3946920554	0.8564262610
H	-1.0295691438	-1.3697193845	0.8529307546

$[EA]^+$ +2[EA-H]

C	-2.796341685	-3.591492753	-0.866253381
H	-2.768270802	-4.601139698	-1.289639164
H	-3.253384578	-2.936970221	-1.614209078
C	-3.615061563	-3.591770088	0.415624661
H	-4.622517329	-3.968512064	0.225753296
H	-3.154961125	-4.235471443	1.171549225
H	-3.706567063	-2.583958696	0.832843851
H	-0.870125413	-3.158944541	-1.450840574
N	-1.427016776	-3.079608064	-0.599970495
H	-0.613588448	0.072826986	0.202032377
C	-2.613983043	0.299687821	-0.452981542
H	-3.527246859	-0.296840487	-0.398249306
H	-2.280242383	0.318296846	-1.492990961
C	-2.834495991	1.702554792	0.087745649
H	-1.917650259	2.294732069	0.034798232
H	-3.601654927	2.209193807	-0.501199439
H	-3.174530704	1.673717227	1.12698621
H	-1.467611523	-1.430264175	-0.002225006
N	-1.55575408	-0.416355868	0.320566176
H	-0.976261234	-3.70874281	0.065143545
H	-1.788295124	-0.418384221	1.315632933
C	1.918510873	-0.189224683	-0.576028924
H	2.882750367	0.269286048	-0.819620387
H	1.520726704	-0.621666809	-1.499228157
C	2.109379043	-1.268402568	0.479413032
H	2.827244852	-2.016929715	0.136109942
H	2.495131815	-0.839560621	1.409208672
H	1.166267016	-1.777567496	0.701480867
H	0.885702524	1.579652004	-0.782044903
N	0.942132766	0.823156345	-0.100126936
H	1.318014949	1.259733073	0.742249584

$[EA]^+$ +[EA-H] +[C_2H_5OH]

C	2.31793355	-0.258364679	-0.155340195
H	3.131514865	0.438161891	-0.366828467
H	2.095722955	-0.815480803	-1.067984354
C	2.659838296	-1.186117157	0.998039897
H	3.544016962	-1.774814062	0.746288909
H	2.883191809	-0.618635371	1.906139807
H	1.838968715	-1.87658921	1.207069892
H	0.896348977	1.235422701	-0.596701466
N	1.096867375	0.546629496	0.158079086
H	0.234716156	-0.09318872	0.256426888

C	-2.217544318	-0.376335402	-0.543985396
H	-3.100712559	-1.011766506	-0.666614987
H	-1.812015004	-0.176851203	-1.540150783
C	-2.604161142	0.925658176	0.140675039
H	-1.745984847	1.599122344	0.226859663
H	-3.379349241	1.441049218	-0.430793182
H	-2.998309052	0.737792979	1.14408436
H	-0.986164818	-1.987035724	-0.172913443
N	-1.1608161	-1.069829636	0.237947137
H	1.226038978	1.056016792	1.034043006
H	-1.525343219	-1.26557371	1.170771681
C	0.74544134	4.690496415	-2.302732141
C	-0.158797591	3.588196288	-1.790021745
H	0.266174524	5.662823998	-2.161899879
H	1.698287881	4.690745712	-1.768519997
H	0.94173655	4.567501832	-3.372360877
O	0.458139514	2.283781908	-1.920720338
H	-0.355598698	3.704111591	-0.72198318
H	-1.118255698	3.579158737	-2.315800691
H	0.78228384	2.207362106	-2.825514247

$[EA]^+$ +$[HNO_3]$

C	2.2371812497	0.4686142983	-0.5660763451
H	3.2368660100	0.8771678941	-0.7187825007
H	1.5887250107	0.7854962516	-1.3835729813
C	2.2482667641	-1.0388781944	-0.3981542800
H	2.6414089478	-1.4944808644	-1.3087901127
H	2.8886783000	-1.3446719679	0.4337321400
H	1.2387341575	-1.4237100954	-0.2370617103
N	1.6861637467	1.1188504862	0.6820953033
H	0.7093672038	0.8123437268	0.8473533172
H	2.2384906423	0.8572799457	1.5036602975
H	1.6916720222	2.1403033577	0.6164410231
O	-1.0211487879	0.1946383408	1.0783573698
N	-1.6176225779	-0.1420860255	0.0672060099
O	-1.2182445221	-0.1100028034	-1.0817347365
O	-2.8762560615	-0.6080457676	0.3059652510
H	-3.2238621050	-0.8303485828	-0.5780780453

$[EA]^+$ +2$[HNO_3]$

C	0.755314415	-5.934815062	-1.036285557
H	1.698002361	-5.57556343	-1.451676393

H	-0.046747995	-5.749066459	-1.751721436
C	0.829368887	-7.396027704	-0.632068685
H	1.039887785	-8.000038321	-1.516639058
H	1.625691109	-7.568097012	0.096174739
H	-0.121280249	-7.733575836	-0.212298618
N	0.461613334	-5.085702153	0.17377517
H	-0.443971495	-5.355983109	0.589935731
H	1.194661972	-5.21841313	0.889642426
H	0.419246497	-4.091157091	-0.059988437
O	-2.081320613	-6.00798423	1.304784589
N	-2.854951088	-6.466859082	0.481402475
O	-2.714711801	-6.531903018	-0.725766139
O	-4.00600761	-6.96381954	1.026844653
H	-4.514705881	-7.285606249	0.259637654
N	2.956730701	-5.158010668	2.955435758
O	3.969323521	-5.751277624	3.661017745
H	4.130977887	-5.141037942	4.404230895
O	2.513587316	-4.102980982	3.359571176
O	2.617430945	-5.794721359	1.970441313

[EA]$^+$ +[C$_2$H$_5$OH]

N	-0.68831161	-2.921820954	0.2802661
H	-0.512092907	-2.772885167	1.276873152
H	-1.231713963	-3.785288471	0.200909245
C	0.606239978	-3.046643994	-0.478769758
H	0.332045663	-3.149317686	-1.529652299
H	1.13009333	-2.099408119	-0.345533782
C	1.417355523	-4.226659857	0.02345792
H	0.877011832	-5.167634077	-0.111562255
H	2.347214362	-4.290855976	-0.544573933
H	1.676465779	-4.111535216	1.079477477
H	-1.278637322	-2.124303003	-0.084533029
C	-0.454504914	0.70436825	-0.289840319
C	-1.899267245	0.505353557	-0.690079162
O	-2.142889887	-0.92391485	-0.804890098
H	-3.047707537	-1.052810517	-1.112765341
H	0.217661206	0.288246359	-1.044715362
H	-2.577696489	0.922049381	0.058571796
H	-2.100174252	0.96907189	-1.658576939
H	-0.241198119	1.772177065	-0.202781993
H	-0.248813429	0.248171386	0.683758579

[EA]$^+$ +[HNO$_3$] +[C$_2$H$_5$OH]

C	-0.399428931	-2.86222407	0.138621575
H	0.101780439	-3.785846022	-0.155505389
H	-1.476912945	-3.034329456	0.150276649
C	0.106950658	-2.339290467	1.471080457
H	-0.095348717	-3.080949937	2.246247592
H	1.186220819	-2.167209447	1.44097564
H	-0.395902419	-1.408326636	1.742273931
N	-0.141581186	-1.848493032	-0.941539216
H	-0.637129194	-0.938461661	-0.730679118
H	0.855410134	-1.624748304	-0.997723418
H	-0.442309092	-2.186898821	-1.857718038
O	2.018439284	0.10645148	-0.210621986
N	2.070824981	1.292916778	0.035167225
O	1.206577848	2.140158313	-0.11663259
O	3.272391405	1.703490057	0.553561763
H	3.158586882	2.662172437	0.68894741
C	-3.526898886	-0.370242241	-0.215327649
C	-2.681685083	0.883719143	-0.270611741
O	-1.289592254	0.482538505	-0.25168715
H	-0.725696244	1.267591421	-0.275572317
H	-3.313702891	-0.93919118	0.693765405
H	-2.880755857	1.452459931	-1.18309617
H	-2.874148782	1.51924086	0.597669375
H	-4.586541077	-0.104776084	-0.205563513
H	-3.35147889	-1.000621569	-1.092638727

[Emim]$^+$ +[C$_2$H$_5$OH]

N	-1.1282183	-0.792519525	-0.430441504
N	-2.194826006	0.89687938	0.429171808
C	-1.01993321	0.503415686	-0.092830876
H	-0.125588709	1.102928622	-0.23255983
C	-3.067479612	-0.166091657	0.423998078
H	-4.079045683	-0.083318017	0.791357008
C	-2.391151746	-1.235465358	-0.115416394
H	-2.711384295	-2.249639907	-0.299422254
C	-2.500940868	2.256774373	0.89123505
H	-3.241200214	2.705710436	0.228620013
H	-1.581388183	2.840504079	0.869868945
H	-2.881318357	2.207595995	1.911329864
C	-0.030263869	-1.608250499	-0.989363559
H	-0.421611451	-2.102092493	-1.881782715
H	0.745780664	-0.901051411	-1.287682141
C	0.483271454	-2.607619989	0.037521135

H	0.849880518	-2.090451647	0.927789747
H	1.308428401	-3.177679997	-0.396429156
H	-0.296570351	-3.312542473	0.335442527
C	4.122513971	0.510763009	-0.302838299
C	2.875123308	1.162032937	0.263431911
H	4.875654302	0.394759909	0.481406915
H	3.890797102	-0.475230523	-0.712885161
H	4.557294668	1.125593803	-1.096564314
O	1.83700073	1.295201521	-0.729691353
H	2.436464965	0.543910571	1.050906039
H	3.103113386	2.143672092	0.691768425
H	2.200997384	1.822941081	-1.449489906

[Emim]$^+$ +[EA-H]

N	0.340485528	3.484221389	0.487159252
H	0.823343397	3.526357968	1.384489814
H	1.088325738	3.319511179	-0.186313954
C	-0.24717367	4.81118681	0.219858663
H	-0.767367002	4.756170177	-0.744185257
H	-1.014716177	4.991474526	0.980831084
C	0.745574605	5.969657359	0.199828004
H	1.504477558	5.814822953	-0.573755811
H	0.239572611	6.917890688	-0.003948537
H	1.255465878	6.056633315	1.163839357
N	-1.434969609	1.553739028	-1.618475465
N	-1.803439763	1.230988643	0.502629064
C	-2.12784177	1.988282522	-0.554109461
H	-2.832832913	2.805436214	-0.552338696
C	-0.857597964	0.315824012	0.117841699
H	-0.436220304	-0.400543316	0.806363379
C	-0.627549598	0.514200118	-1.223985186
H	0.013956688	-0.013329754	-1.912909131
C	-2.228463214	1.489442461	1.880371209
H	-2.326579471	0.536637196	2.399723639
H	-3.194635208	1.993097803	1.861547517
H	-1.480179746	2.118455656	2.363643848
C	-1.513104184	2.120588058	-2.978578191
H	-1.809255099	1.312601063	-3.652068826
H	-2.317625616	2.859158054	-2.959126855
C	-0.188099172	2.746819194	-3.389646254
H	0.090896436	3.546572843	-2.699844642
H	-0.286745263	3.172714503	-4.391001572
H	0.612137304	2.003619341	-3.415538692

[Emim]$^+$ +[HNO$_3$]

N	9.928869533	-1.683660734	0.481435937
N	8.534360543	-1.346218282	2.121598768
C	9.681930339	-1.94920673	1.773426845
H	10.30213502	-2.548382852	2.422828469
C	8.026697362	-0.695331997	1.024457076
H	7.107971494	-0.130231694	1.066445083
C	8.907353119	-0.908907715	-0.012076516
H	8.892171142	-0.55451467	-1.031314576
C	7.886486274	-1.442720383	3.435881982
H	7.602294811	-0.442067034	3.760616846
H	8.599844941	-1.866350776	4.14218676
H	7.009831134	-2.084750897	3.350411995
C	11.08258897	-2.190390221	-0.291127679
H	11.627182	-1.320446485	-0.666264253
H	11.72303367	-2.712108914	0.423285795
C	10.62898094	-3.112324266	-1.413812998
H	10.05858532	-3.95420167	-1.017129562
H	11.50873533	-3.495894782	-1.935933987
H	10.01148007	-2.578924334	-2.14026511
N	6.631556808	-3.742033062	0.439299369
O	6.015348878	-4.412873758	-0.601262179
H	5.066756103	-4.243535637	-0.458499621
O	5.915022365	-3.108028833	1.194528658
O	7.836333833	-3.863784277	0.458022898

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