Drying methods for [Emim]+ based ionic liquid electrospray propellants

Christopher T. Lyne[1] and Joshua L. Rovey[2]
University of Illinois at Urbana-Champaign, Urbana, IL, 61801, USA

Steven P. Berg[3]
Froberg Aerospace, LLC, Wilmington, North Carolina, 61820, USA

Ionic liquids (ILs) have become popular propellants for electrospray propulsion applications over the last two decades. ILs consisting of the imidazolium-based cation [Emim]+ (1-ethyl-3-methylimidazolium) paired with various anions are especially popular, despite their tendency to absorb water from the ambient atmosphere. Absorbed water can lead to poor electrospray performance and can reduce shelf life in some ionic liquids; thus, quantifying and reducing water content is important. Here we quantify the drying rate of three [Emim]+-based IL electrospray propellants by vacuum, and by direct contact with molecular sieves. We study [Emim]+ paired with [Im]-, [BF$_4$]-, and [EtSO$_4$]- anions and find that the final water content of dried [Emim][Im] is approximately 5-30 times lower than that of [Emim][EtSO$_4$] under the same drying conditions. Our results show that water content after drying ranks [Emim][Im] < [Emim][BF$_4$] < [Emim][EtSO$_4$], matching trends in the literature. We find that vacuum drying at 1.5 Torr is more effective than direct contact with 3Å molecular sieves for [Emim][Im] and [Emim][BF$_4$], resulting in a final water content 2-3 times lower. For [Emim][EtSO$_4$], vacuum drying and drying by molecular sieves were equally effective.

Nomenclature

Abbreviation	Full Name	Other Common Abbreviations[**]
[Emim]+	1-ethyl-3-methylimidazolium	EMI, [C$_2$mim], [C$_1$C$_2$Im]
[Bmim]+	1-butyl-3-methylimidazolium	[C$_4$mim]
[Im]-	bis(trifluoromethylsulfonyl)imide	[Tf$_2$N], [NTf$_2$], BTI, TFSI
[BF$_4$]-	Tetrafluoroborate	-
[EtSO$_4$]-	ethyl sulfate	[ESO$_4$], [EtOSO$_3$], [C$_2$OSO$_3$]
IL	Ionic Liquid	RTIL (room temperature ionic liquid)
KF	Karl Fischer	

[**]Refer to Appendix A for a more thorough discussion of chemical abbreviations, naming, and notation.

---

[1] NASA Space Technology Research Fellow, Department of Aerospace Engineering, AIAA Student Member.
[2] Associate Professor, Department of Aerospace Engineering, AIAA Associate Fellow.
[3] CEO, AIAA Senior Member.

I. Introduction

Over the past two decades, ionic liquids (ILs) have gained popularity as electrospray propellants. IL propellants based on the [Emim]$^+$ (1-ethyl-3-methylimidazolium) cation are especially common. For example, [Emim][Im] has been used as an electrospray propellant for the disturbance reduction system on the Lisa Pathfinder mission [1,2]. [Emim][BF$_4$] can produce electrospray plumes almost entirely comprised of ions and ion clusters, operating in the so-called pure ion regime [3]. [Emim]$^+$-based ILs have also been used in more exotic applications. For example, [Emim][EtSO$_4$] mixed with hydroxylammonium nitrate (HAN) has been studied as a propellant for monopropellant-electrospray multimode propulsion, in which a monopropellant thruster and an electrospray thruster share a single propellant supply [4–8].

One disadvantage of using [Emim]$^+$-based ILs (and many other ILs) as electrospray propellants is that they tend to be hygroscopic, absorbing water from their surroundings. The presence of water or other volatiles in propellant can disrupt electrospray emission, especially for capillary electrospray sources [9], resulting in unstable emission and shortened thruster lifetime. Water content can change the physiochemical properties of ILs, including the electrical conductivity, density, viscosity, and electrochemical window [10]. Water can also reduce propellant shelf life. Some anions, such as [BF$_4$]$^-$ and [EtSO$_4$]$^-$, have been shown to chemically degrade in the presence of water (hydrolyze) [11,12]. For example, the [PF$_6$]$^-$ anion hydrolyzes into hydrofluoric acid (HF), a highly corrosive and toxic substance [13].

An extensive body of literature is dedicated to techniques for dehydrating chemicals, including organic solvents (see [14] for a brief review) and ionic liquids (see section II.B). In the electrospray propulsion literature, vacuum drying is perhaps the most common method used. More broadly, two of the simplest methods used are to evaporate water from the sample (using heat or vacuum) or to use sorbents (desiccants) to 'soak up' and trap the water. For this work, we focus on these two basic methods because we believe they are the easiest to implement within the electrospray propulsion community.

Here, we evaluate two simple and widely available drying methods – drying by vacuum or desiccants – for removing water from [Emim]$^+$-based IL electrospray propellants. We studied three ionic liquids: [Emim][Im], [Emim][BF$_4$], and [Emim][EtSO$_4$]. IL samples were prepared with a water content of 1% wt. H$_2$O, then dried for 24 or 72 hours. Their initial and final water contents were measured using coulometric Karl Fischer titration. Our data provide a quantitative, side by side measurement of water removal from [Emim]$^+$-based ILs relevant to electrospray propulsion. We find that the anion plays a significant role in determining the IL water content after drying, with [Emim][Im] sometimes reaching a water content an order of magnitude lower than [Emim][EtSO$_4$]. Our data also provide a quantitative comparison between vacuum drying and drying by direct contact with molecular sieves, revealing that vacuum is generally more effective than sieves under the conditions tested.

II. Background

The following sections give relevant background on (A) absorption of water by ILs and its effects, (B) drying methods for ILs, and (C) Karl Fischer titration fundamentals. Background on IL chemical structures, names, abbreviations, and notation can be found in Appendix A.

A. Effect of Water on [Emim]$^+$ based Ionic Liquids

There is a significant body of work showing that the tendency of [Emim]$^+$-based ILs to absorb and retain water is determined primarily by the anion [13,15,16]. For example, Cuadrado-Prado et al. found that water absorption by [Emim][EtSO$_4$] from ambient air is more rapid and less easily reversed than water absorption by [Emim][BF$_4$] [16]. Freire et al. also studied imidazolium-based ILs and found that miscibility with water is primarily determined by the anion [17]. They found that miscibility decreases with imidazolium alkyl chain length, but the effect is less significant than the choice of anion. They conclude that imidazolium based ILs with [BF$_4$]$^-$ interact more strongly with water than those with [Im]$^-$

. Huddleston et al. also studied the effects of the anion and the imidazolium alkyl chain length on IL water absorption [13]. They measured the equilibrium water content of ILs in direct contact with water at 25 °C and found that [Bmim][Im] equilibrated to 3280 ppm H_2O while [Bmim][BF$_4$] was fully miscible with water. After vacuum drying for 4 hours at 70 °C, [Bmim][Im] had a remaining water content nearly ten times lower than [Bmim][BF$_4$] (474 ppm H_2O vs 4530 ppm H_2O). This implies that imidazolium based ILs with the [BF$_4$]$^-$ anion will absorb and retain more water than those with the [Im]$^-$ anion. From this review of the literature, we expect that the water content of the ILs used in this study after drying will be ordered: [Emim][Im] < [Emim][BF$_4$] < [Emim][EtSO$_4$].

In addition to determining the rate of water absorption and the equilibrium water content in imidazolium based ILs, the anion primarily determines the stability of the IL in the presence of water. Freire et al. documented the hydrolysis (chemical degradation in the presence of water) of the [BF$_4$]$^-$ and [PF$_6$]$^-$ anions in imidazolium based ILs [11]. Furthermore, the hydrolysis of fluorinated species such as [BF$_4$]$^-$ and [PF$_6$]$^-$ can produce HF and other hazardous products [13].

Besides affecting the shelf life of ILs, water content can also result in significant changes to the physical and chemical properties. Widegren et al. measured the electrical conductivity of several ILs and found that the conductivity of [Bmim][Im] increases by 36% when the water mass fraction is increased from 1×10^{-5} (10 ppm) to 8.85×10^{-3} (8850 ppm) [18]. In some ILs, water has been shown to decrease density and viscosity, and change the electrochemical window [10]. The impact of water content on the physiochemical properties of ILs, along with the ability of many ILs to readily absorb water from the atmosphere, make drying and handling procedures an important aspect of working with IL electrospray propellants.

B. Brief Review of Drying Methods

The detrimental effects of water as an impurity is not limited to ionic liquids, and an extensive body of work is dedicated to dehydrating solvents (see the brief review in [14], for example). Table 1 shows some of the methods used in the literature for dehydrating ILs and other solvents.

One of the most common techniques for removing water is by evaporation, sometimes at reduced pressure (i.e., vacuum drying). Evaporation of water at elevated temperatures and ambient pressure is feasible for drying some ILs if they have sufficient thermal stability. [Emim][Im] can be distilled at 300 °C and recondensed apparently without degradation [19]. But not all ILs share that thermal stability, so elevated temperatures cannot always be used. [Emim][Im] and [Emim][BF$_4$] have been effectively dried at lower temperatures (70 – 80 °C) under vacuum [10,13].

Another popular way to remove water is using sorbents, which are also called desiccants when used for water. They work by trapping water either on the surface (adsorption) or within the sorbent (absorption). Desiccants can be used to dry liquids by direct contact. For example, ethanol for biofuel is often dehydrated using packed beds of molecular sieves. Desiccants can also be used to maintain a dry atmosphere around a hygroscopic liquid. For example, Gamero-Castaño has used Drierite to desiccate a hermetic container surrounding a vial of [Emim][Im] electrospray propellant, avoiding direct contact between the IL and the desiccant [20].

Other drying methods are also used. Reactive metal compounds can be used to remove water from certain solvents, but they are hazardous to work with [14]. Another method is to bubble dry gas through the liquid, also known as sparging. This technique has been used to reduce water levels in [Emim][BF$_4$] to ≤ 10 ppm after 50 minutes of sparging with ultrahigh purity argon at 70 °C [10]. Water electrolysis is an interesting possibility for removing water from ILs [23], but we found relatively few published articles discussing it. Freeze drying has also been used for [Emim][BF$_4$] [22], but it typically requires specialized equipment that is not widely available.
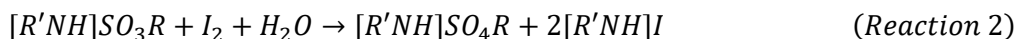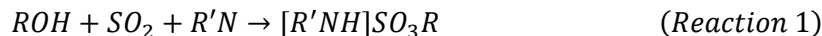
Table 1: Sample of drying methods used in the literature for ionic liquids and other solvents.

Drying Method	Liquid Being Dried	Ref
Sorbents / Desiccants		
Alumina, Silica, Activated Carbon	[Emim][BF$_4$]	[21]
Silica, Alumina, Molecular Sieves	Various Organic Solvents	[14]
Reactive Metals / Metal Hydrides		
Potassium Hydroxide (KOH)	methanol, ethanol	[14]
Sodium (Na) w/ Benzophenone indicator	toluene, tetrahydrofuran	[14]
Vacuum		
At 70 °C	[Emim]$^+$, [Bmim]$^+$ with [BF$_4$]$^-$, [Im]$^-$	[13]
At 80 °C	[Emim][BF$_4$], [Bmim][BF$_4$]	[10]
Freeze drying	[Bmim][BF$_4$]	[22]
Water electrolysis	ILs with [Im]$^-$, [BF$_4$]$^-$ anions	[23]
Sparging with inert gas	[Emim][BF$_4$], [Bmim][BF$_4$]	[10]

C. Karl Fischer Titration Fundamentals

Karl Fischer (KF) titration is an analytical method that is commonly used to quantify moisture content in liquid and solid samples. KF titration can use a variety of reagents depending on the sample chemistry. The generalized reaction sequence for KF titration is given by Reaction 1 and Reaction 2, in which Iodine (I$_2$) consumes water in a 1:1 molar ratio [24,25].

A note on chemical notation: The symbol R denotes any group that is attached to the molecule by a carbon or hydrogen in the group. For example, R could represent a simple methyl group (-CH$_3$) that is attached to the rest of the molecule by the carbon atom, thus making ROH methanol. R' simply denotes another R-group, but not necessarily the same one that is denoted by R. For more information about chemical notation and abbreviations, refer to Appendix A.

$$ROH + SO_2 + R'N \rightarrow [R'NH]SO_3R \qquad (Reaction\ 1)$$

$$[R'NH]SO_3R + I_2 + H_2O \rightarrow [R'NH]SO_4R + 2[R'NH]I \qquad (Reaction\ 2)$$

The reaction begins when the alcohol ROH reacts with sulfur dioxide SO_2 and a base $R'N$ to form an alkylsulfite salt $[R'NH]SO_3R$. That alkylsulfite anion SO_3R is then oxidized to alkyl sulfate SO_4R by iodine I_2, consuming water H_2O. Reaction 2 produces two stable products- an alkylsulfate salt $[R'NH]SO_4R$ and a hydroiodic acid salt $2[R'NH]I$. Karl Fischer reagents are commercially available from Hydranal and Aquastar for a variety of KF titration techniques. One part reagents are available that contain alcohol ROH, a base $R'N$, and sulfur dioxide SO_2 in solution, greatly simplifying the KF titration process for the end user. Modern KF reagents often use methanol (CH$_3$-OH) as the alcohol, and imidazolium as the base.

Typically, the alcohol ROH, base $R'N$, and sulfur dioxide SO_2 are present in excess. Therefore, the availability of H_2O and I_2 control the reaction. Once a sample containing water is added, I_2 controls the reaction, consuming water in a 1:1 ratio. In volumetric KF titration, iodine is added by dripping a solution containing iodine into the titrator vessel. Iodine is added until the titration endpoint is detected, typically by bipotentiometric means wherein a constant current is passed through the titrator bath and the voltage required to drive that current is measured. The titration endpoint is indicated by the presence of excess iodine, which reduces the required electrode voltage.

For samples with a low water content, from 1 ppm to about 5% wt., coulometric Karl Fischer titration is more appropriate [26]. In coulometric KF, iodine is produced by an electrochemical reaction that converts iodide (I$^-$) into iodine (I$_2$) at the generator anode (Reaction 3). The amount of iodine produced

4

is directly related to the charge that flowed through the generator (i.e., the generator current integrated over time).

$$2I^- \rightarrow I_2 + 2e^- \hspace{2cm} (Reaction\ 3)$$

The choice of KF reagent will depend on the chemistry of the sample to be analyzed. For example, some amines undergo side reactions with methanol that prevent the titration from reaching a stable endpoint. This is true for hydroxylammonium nitrate, an energetic salt that is used in a variety of IL rocket propellants. For this case, we have successfully used an ethanol-based KF reagent (Hydranal Coulomat E) to avoid the side reaction between methanol and hydroxylamine and reliably measure water content.

III. Methods

A. Karl Fischer Titration

Coulometric Karl Fischer titration was performed to measure sample water content throughout this work. A Hanna Instruments HI904 coulometric titrator was used with the methanol-based reagent Hydranal Coulomat AG. Bipotentiometric endpoint detection was used with a polarization current of 2 µA and an endpoint voltage of 100 mV. Unless otherwise noted, each sample was titrated in 'triplicate', meaning that each sample was titrated three times and each measurement was recorded. The scatter between the three triplicate measurements is used for error bars throughout this work. Ionic liquid samples were drawn into a 1 mL syringe and injected into the titrator vessel through a septum to avoid exposing the KF reagent to ambient humidity. Sample mass was recorded by measuring the syringe mass before and after sample injection using a laboratory mass balance with a precision of 10 µg.

Titration validation was performed using Hydranal Water Standard 1.0 (1.001 mg/g H_2O) to determine the minimum sample size required for accurate KF measurements. Figure 1 shows the measurement error as a function of sample water content. We found errors of ±1.5% for samples with >= 80 µg H_2O. Accordingly, all water content measurements reported here for ionic liquids were performed on samples containing at least 80 µg of water.
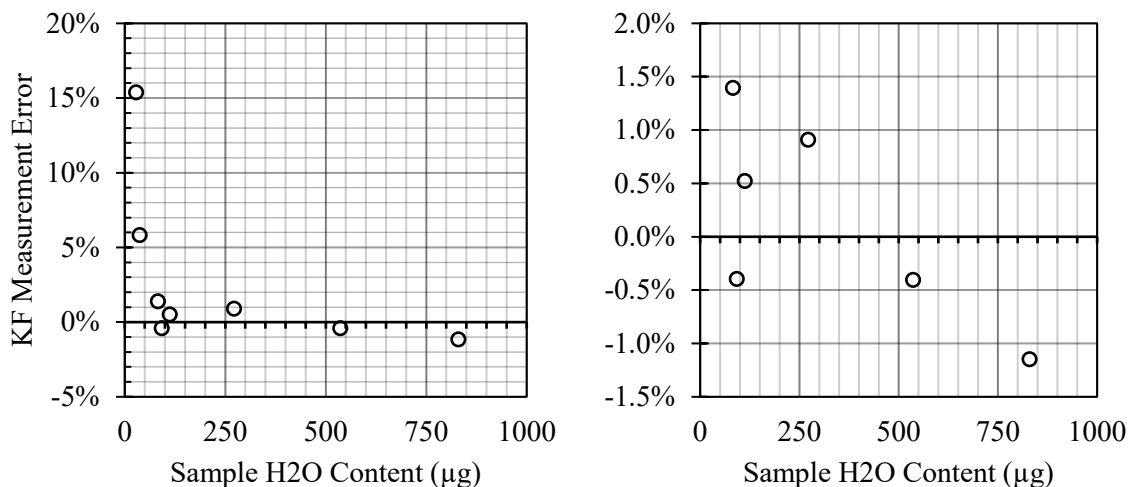

Figure 1: Results for Hydranal water standards (1.001 mg H_2O per g) titrated the coulometric KF reagent Hydranal AG. Measurement error indicates the difference between the water content found using KF titration and the certified water content of the water standard. When measuring samples with less than 50 µg total water content the measurement error rises above 5% (Left). For sample water content of 82 µg or more, the measurement error falls in the range of ±1.5% (Right).

5

B. Sample Preparation and Handling

IL Sample Preparation

The ionic liquids used in this work were purchased commercially. [Emim][Im] with a purity of >98% was obtained from TCI America through Fisher Scientific. [Emim][BF₄] with a purity of >98% was obtained from Sigma Aldrich. [Emim][EtSO₄] with >95% purity was obtained from Sigma Aldrich. The as-received [Emim][EtSO₄] had a strong odor and was degassed using a rotary evaporator prior to use. This degassing step removed the odor, and presumably removed the volatile impurities that caused it. To provide a consistent initial water content for drying, deionized water was added to each IL until the water content reached 1% H_2O by mass. These mixtures (1% wt. H_2O, 99% wt. IL) were used as the starting samples for all drying results presented in this work.

IL Sample Handling

A glovebox (Cleatech, LLC) fed with a dry air supply was used for handling the ILs, preparing samples, and weighing the injected sample mass for titration. The dry box was kept at a relative humidity between 4% and 10% and at room temperature. Although this provided a less humid atmosphere than the ambient air, these ILs are still capable of absorbing water from the dry box air. Handling procedures minimized the exposure of IL samples to dry box air by using 'air-free' handling techniques using syringes, non-coring syringe needles, and septum tops that allow for samples to be injected or withdrawn from a test tube without exposing the contents to ambient air.

C. Drying Methods

We investigated the effectiveness of two drying methods, vacuum drying and direct contact with molecular sieves, to dry several [Emim]⁺-based ionic liquid electrospray propellants. The following subsections detail the procedures used for each drying method. Note that in all cases, the starting sample was 2.5 g of IL with an initial water content of 1% wt. H_2O (10,000 ppm).

Method 1: Drying by Vacuum

For each ionic liquid and planned drying time, 2.5 g of IL with 1% wt. H_2O content was added to a 12 mm by 75 mm borosilicate glass test tube, then a rubber cap was used to seal each test tube. The samples were then loaded into a test tube rack and placed into a vacuum chamber in front of a large viewport. The test tube caps were removed, and the vacuum chamber was closed. The chamber was pumped down using an Edwards RV8 rotary vane pump, which has a peak pumping speed of 6 cfm (2.8 lpm). The chamber pressure reached 3 Torr in approximately 5 minutes, then slowly decreased until reaching an ultimate pressure of 1.5 Torr. After 24 hours, the vacuum chamber was repressurized using ultra high purity argon. The chamber was opened, and the test tubes were quickly capped. The samples were removed from the vacuum chamber and transported to the dry air glovebox. Each sample was then drawn into a syringe and the water content was measured using KF titration. Each sample was titrated in triplicate. This process was repeated with a 72 hour drying time.

Method 2: Drying by 3Å Molecular Sieves

Molecular sieves are a type of sorbent that are often used to remove water (i.e., a desiccant) from solvents, gases, or other media. Molecular sieves remove water and other impurities by trapping molecules in sub-nanometer 'pores'. The pore size determines the maximum size of molecule that can be trapped. For example, 3Å sieves can effectively trap water molecules, while rejecting larger molecules such as ethanol. Molecular sieves can typically be regenerated and reused by desorbing water, for example using vacuum or dry gas.

We chose to investigate drying by direct contact between molecular sieves and the ILs. We should note that there is evidence of contamination of ILs in direct contact with some sorbents. Specifically, alumina, silica, and carbon sorbents in direct contact with [Emim][BF₄] have been shown to modify its thermal stability [21]. Our goal here is simply to study the efficacy of drying by direct contact with molecular sieves, and we do not consider possible contamination or its effects.

6

We used 3Å molecular sieves (3 Angstrom pore size) that were spherical beads 1-2 mm in diameter (Alfa Aesar L05335). Samples were prepared for each combination of ionic liquid and drying time as follows. First, 1 g of 3Å molecular sieves were added to a 12 mm by 75 mm borosilicate glass test tube. Then, 2.5 g of ionic liquid with 1% wt. H_2O content was added to the test tube. The test tube was then sealed using a rubber cap and stored in the dry air glovebox at a relative humidity of 4% - 10%. At the end of the drying time the contents of the test tube were withdrawn into a syringe, and the water content measured by KF titration. Each sample was titrated in triplicate, except for the [Emim][Im] sample dried for 24 hours using molecular sieves, in which the whole sample was titrated in a single measurement.

The water adsorption capacity of the molecular sieves used here is given by the vendor as 20% to 30%, meaning that 200 mg to 300 mg of water can be trapped per gram of sieves. A quick calculation shows that the initial water content of our IL samples at 1% wt. H_2O is (2.5 g)(0.01) = 25 mg H_2O total water content. Since 1 gram of molecular sieves were added to each 2.5 g IL sample, we see that the initial water content (25 mg) is well under the sieve water capacity (200 mg to 300 mg). We therefore conclude that 1 gram of molecular sieves per 2.5 gram IL sample is sufficient to study their drying effects.

IV. Results

The drying data (Figure 2 and Table 2) show the final water content reached for each drying method and duration starting from a nominal water content of 1% wt. H_2O (10,000 ppm).
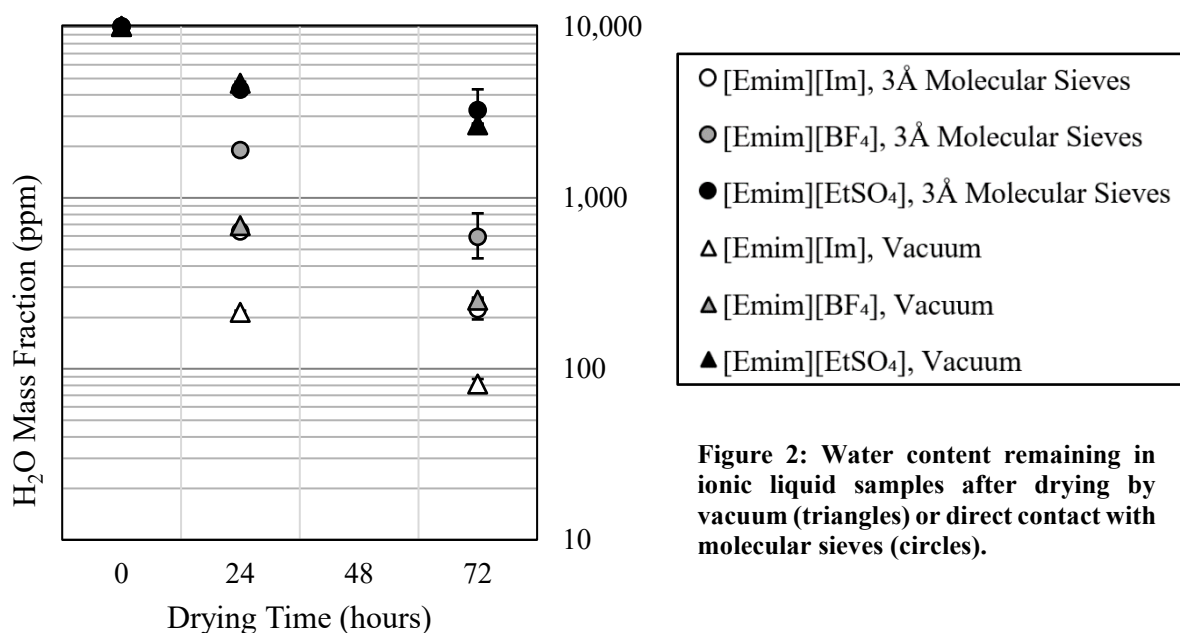

Figure 2: Water content remaining in ionic liquid samples after drying by vacuum (triangles) or direct contact with molecular sieves (circles).

Table 2: Water content of IL samples starting from a nominal water content of 1% wt. H_2O (10,000 ppm).

		H_2O Mass Fraction (ppm)		
Ionic Liquid	Drying Method	0 hours	24 hours	72 hours
[Emim][Im]	Vacuum	10,205	214	81
[Emim][Im]	3Å Sieves		636	223
[Emim][BF$_4$]	Vacuum	10,016	687	252
[Emim][BF$_4$]	3Å Sieves		1904	591
[Emim][EtSO$_4$]	Vacuum	10,075	4671	2670
[Emim][EtSO$_4$]	3Å Sieves		4288	3254

V.   Discussion

Vacuum drying proved to be more effective than molecular sieves for [Emim][Im] and [Emim][BF$_4$] under the test conditions, leaving 2 to 3 times less water remaining after drying. For [Emim][EtSO$_4$], molecular sieves are about as effective as vacuum drying. After 24 hours of drying, the vacuum dried [Emim][EtSO$_4$] sample had a higher water content than the sieve dried sample (4671 ppm vs 4288 ppm), but that trend reverses for the 72 hour samples (2670 ppm vacuum dried vs 3254 ppm sieve dried). Note that a change surface area exposed to vacuum will change the rate of drying. Likewise, using more molecular sieves (e.g., 2 g per 2.5 g of IL) would likely result in faster drying.

There is another, more practical drawback to using molecular sieves as a desiccant for viscous ILs: After drying by contact with molecular sieves (1 g sieves per 2.5 g IL), we estimate that 0.5 g to 1.0 g of IL remained on the surface of the sieves and could not be extracted. It may be possible to recover this 'lost' IL, for example by using a volatile solvent to wash the sieves and then removing the solvent by distillation, but such recovery is beyond the scope of this work. While molecular sieves seem impractical for initial drying of electrospray propellants, they may be practical for point-of-use drying. For example, they could be put into a packed bed desiccator in an electrospray feed system immediately before a capillary electrospray source. As it passed through the desiccator, the propellant would be dried of any remaining moisture. It is also possible that molecular sieves can be used to extend the shelf life of water-sensitive ILs by preventing hydrolysis, although the possibility of contamination from direct contact between the sieves and IL should be investigated.

As expected from a review of the literature, the water content of ILs after drying ranked [Emim][Im] < [Emim][BF$_4$] < [Emim][EtSO$_4$]. After 72 hours under vacuum, [Emim][Im] retained only 81 ppm H$_2$O, less than [Emim][BF$_4$] (252 ppm) and [Emim][EtSO$_4$] (2670 ppm). This difference, spanning nearly two orders of magnitude, underscores the importance of the anion in water absorption and retention. These results suggest that designers should consider the hygroscopic properties when selecting ILs for water-sensitive applications such as electrospray propulsion, along with other properties such as electrical conductivity and surface tension. In the case of [Emim]$^+$-based ILs (and the [C$_2$mim] family more broadly), the anion hydrophobicity is the primary determinant of how strongly the IL interacts with water. Miscibility with water can be a good proxy for anion hydrophobicity. For example, [Bmim][BF$_4$] is miscible with water, while [Bmim][Im] is not [17]. Other properties that can be used to estimate IL-water interaction strength include hydrophilicity, hygroscopic grade, and solubility in water for other ILs containing a given anion. The tendency of an anion to hydrolyze, or degrade in the presence of water, is also relevant and often available in the literature. The electrospray researcher can consider such data, if available, when assessing candidate electrospray propellants.

VI.   Conclusions

We measured water content in three ionic liquids – [Emim][Im], [Emim][BF$_4$], and [Emim][EtSO$_4$] – before and after drying by vacuum or direct contact with molecular sieves. We found that the water content after drying ranked [Emim][Im] < [Emim][BF$_4$] < [Emim][EtSO$_4$], matching trends in the literature. Furthermore, the range of final water contents for a given drying method and time spanned nearly two orders of magnitude between the different ILs. For example, the 72 hour vacuum dried [Emim][Im] reached a water content about 33 times lower than [Emim][EtSO$_4$] under the same conditions. This significant difference shows that the tendency to absorb and retain water (hygroscopic grade) should be considered alongside other properties, such as electrical conductivity and surface tension, when selecting an IL electrospray propellant. Hygroscopic grade may be especially important for ILs sensitive to hydrolysis, such as those with [BF$_4$]$^-$ or [EtSO$_4$]$^-$ anions. Our results also suggest that current drying methods used for IL electrospray propellants (i.e., vacuum drying) may be inadequate for dehydrating some ILs (e.g., [Emim][EtSO$_4$]) while being sufficient for others (e.g., [Emim][Im]). However, the maximum water content that a capillary electrospray can tolerate while remaining stable is

not currently known and must be established before making definitive conclusions about the adequacy of vacuum drying for preparing IL electrospray propellants.

We find that drying by molecular sieves is 2 to 3 times less effective than vacuum drying under the tested conditions for [Emim][Im] and [Emim][BF$_4$], and equally effective for [Emim][EtSO$_4$]. The loss of IL caused by direct contact between the molecular sieves and the IL, and their potential to contaminate the IL, make molecular sieves unappealing as a method of conditioning (drying) IL electrospray propellants prior to storage or use. Molecular sieves may find other uses, however, when vacuum drying is not suitable. For example, molecular sieves could be used to dry the environment surrounding a sensitive IL (no direct contact with the IL) or in a packed bed desiccator in a feed system.

VII.   Acknowledgements

VIII.   Appendix A: Ionic liquid terminology and molecular structures

Table 3 lists common cations and anions found in ionic liquid electrospray propellants. Abbreviations for these molecules vary across the literature. Common abbreviations are listed below the full chemical name of each ion, along with the works in which those abbreviations were used.

Ion Name and Abbreviations	References	Molecular Structure
1-ethyl-3-methylimidazolium:		
EMI, EMI$^+$	[20,27–32]	
Emi	[33]	
[Emim],[emim]$^+$, EMIM	[10,16,34–37]	
[C$_2$mim], [C$_2$mim]$^+$, C$_2$MIM	[13,16–19,21,38–40]	
[C$_1$C$_2$Im]	[12]	
1-butyl-3-methylimidazolium:		
[C$_4$mim], [C$_4$mim]$^+$	[17,18,21,38–40]	
Bmim, [bmim]$^+$, bmim, BMIM	[9,10,16,22,33,37,41]	
bis(trifluoromethylsulfonyl)imide:		
Im, [Im], [Im]$^-$	[20,27,28,30,35,36]	
[NTf$_2$], [NTf$_2$]$^-$	[12,19,21,38,42]	
[Tf2N], [Tf2N]$^-$, Tf2N	[13,18,32,37,39,40]	
[N(SO$_2$CF$_3$)$_2$], [N(SO$_2$CF$_3$)$_2$]$^-$, N(SO$_2$CF$_3$)$_2$	[13,17]	
tetrafluoroborate:		
BF$_4$, [BF$_4$]$^-$	[10,12,13,16,17,22,29,31–33,36,37,39,40,42]	
ethyl sulfate:		
[EtSO$_4$]$^-$	[12,34,38]	
[ES]$^-$	[16]	
[EtOSO$_3$]$^-$	[38]	
[C$_2$OSO$_3$]	[39]	

9

Many electrospray propellants are based on cations in the 1-alkyl-3-methylimidazolium family. These cations have an alkyl chain, such as -methyl ($-CH_3$), -ethyl ($-C_2H_5$), or -butyl ($-C_4H_9$), attached to an imidazole ring. For example, $[Emim]^+$ (see figure in table above) has an ethyl group attached to the nitrogen in position 1 (at the bottom), while $[Bmim]^+$ has a butyl group attached there instead. Chemists often abbreviate the 1-alkyl-3-methylimidazolium family as $[C_nmim]^+$, where n denotes the number of carbons in the alkyl chain. The electrospray literature often uses $[Emim]^+$ or EMI rather than $[C_2mim]^+$, and $[Bmim]^+$ rather than $[C_4mim]^+$.

The anions discussed here, [Im]-, [BF4]-, and [EtSO4] also have different naming conventions across the literature. The electrospray propulsion literature often uses $[Im]^-$ to denote the bis(trifluoromethylsulfonyl)imide anion, while chemists prefer abbreviations more clearly conveying molecular structure, such as $[NTf_2]^-$, $[Tf_2N]^-$, and less commonly $[N(SO_2CF_3)_2]^-$. The ethyl sulfate anion is also abbreviated differently across the literature. We found that $[EtSO_4]^-$ is most common, while $[EtOSO_3]$ and $[C_2OSO_3]$ are preferred by some authors. There is no apparent disagreement over how to abbreviate the tetrafluoroborate anion, probably due to its simple structure, and $[BF_4]^-$ is used across the literature.

Brackets are usually used with polyatomic ions, usually with a superscript to denote its charge. For example, $[C_2mim]^+$ (or $[Emim]^+$), $[BF_4]^-$, and Cl- are appropriate abbreviations. In ionic liquids the charge signs are typically omitted when a cation is paired with an anion (e.g., $[C_4mim][PF_6]$) [43].

IX. Bibliography

[1] Demmons, N., Hruby, V., Spence, D., Roy, T., Ehrbar, E., Zwahlen, J., Martin, R., Ziemer, J., and Randolph, T. ST7-DRS Mission Colloid Thruster Development. *44th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, 2008*. AIAA 2008-4823. https://doi.org/10.2514/6.2008-4823.

[2] Ziemer, J. K., Marrese-Reading, C. M., Arestie, S. M., Conroy, D. G., Leifer, S. D., Ortega, A. L., Demmons, N. R., Wirz, R. E., and Gamero-Castaño, M. Incorporating Lessons Learned into LISA Colloid Microthruster Technology Development. *AIAA Propulsion and Energy Forum and Exposition, 2019*. AIAA 2019-3814.

[3] Romero-Sanz, I., Bocanegra, R., Fernandez de la Mora, J., and Gamero-Castaño, M. "Source of Heavy Molecular Ions Based on Taylor Cones of Ionic Liquids Operating in the Pure Ion Evaporation Regime." *Journal of Applied Physics*, Vol. 94, No. 5, 2003, pp. 3599–3605. doi:10.1063/1.1598281.

[4] Berg, S. P., Rovey, J., Prince, B., Miller, S., and Bemish, R. Electrospray of an Energetic Ionic Liquid Monopropellant for Multi-Mode Micropropulsion Applications. *51st AIAA/SAE/ASEE Joint Propulsion Conference, 2015*. AIAA 2015-4011. https://doi.org/10.2514/6.2015-4011.

[5] Wainwright, M. J., Rovey, J. L., Miller, S. W., Prince, B. D., and Berg, S. P. "Hydroxylammonium Nitrate Species in a Monopropellant Electrospray Plume." *Journal of Propulsion and Power*, Vol. 35, No. 5, 2019, pp. 922–929. doi:10.2514/1.B37471.

[6] Berg, S. P., and Rovey, J. L. "Decomposition of Monopropellant Blends of Hydroxylammonium Nitrate and Imidazole-Based Ionic Liquid Fuels." *Journal of Propulsion and Power*, Vol. 29, No. 1, 2013, pp. 125–135. doi:10.2514/1.B34584.

[7] Rasmont, N., Broemmelsiek, E. J., and Rovey, J. L. "Linear Burn Rate of Green Ionic Liquid Multimode Monopropellant." *Combustion and Flame*, Vol. 219, 2020, pp. 212–224. doi:10.1016/j.combustflame.2020.04.014.

[8] Rovey, J. L., Lyne, C. T., Mundahl, A. J., Rasmont, N., Glascock, M. S., Wainwright, M. J., and Berg, S. P. "Review of Multimode Space Propulsion." *Progress in Aerospace Sciences*, Vol. 118, 2020, p. 100627. doi:10.1016/j.paerosci.2020.100627.

[9] Lyne, C. T., Rovey, J., and Berg, S. P. Monopropellant-Electrospray Multimode Thruster Testing Results: Electrospray Mode. *AIAA Propulsion and Energy Forum, 2021*. AIAA 2021-3439. https://doi.org/10.2514/6.2021-3439.

[10] Jarosova, R., and Swain, G. M. " Rapid Preparation of Room Temperature Ionic Liquids with Low

Water Content as Characterized with a t A- C:N Electrode .” *Journal of The Electrochemical Society*, Vol. 162, No. 8, 2015, pp. H507–H511. doi:10.1149/2.0191508jes.

[11]   Freire, M. G., Neves, C. M. S. S., Marrucho, I. M., Coutinho, J. A. P., and Fernandes, A. M. “Hydrolysis of Tetrafluoroborate and Hexafluorophosphate Counter Ions in Imidazolium-Based Ionic Liquids.” *Journal of Physical Chemistry A*, Vol. 114, No. 11, 2010, pp. 3744–3749. doi:10.1021/jp903292n.

[12]   Jacquemin, J., Goodrich, P., Jiang, W., Rooney, D. W., and Hardacre, C. “Are Alkyl Sulfate-Based Protic and Aprotic Ionic Liquids Stable with Water and Alcohols? A Thermodynamic Approach.” *Journal of Physical Chemistry B*, Vol. 117, No. 6, 2013, pp. 1938–1949. doi:10.1021/jp312241h.

[13]   Huddleston, J. G., Visser, A. E., Reichert, W. M., Willauer, H. D., Broker, G. A., and Rogers, R. D. “Characterization and Comparison of Hydrophilic and Hydrophobic Room Temperature Ionic Liquids Incorporating the Imidazolium Cation.” *Green Chemistry*, Vol. 3, No. 4, 2001, pp. 156–164. doi:10.1039/b103275p.

[14]   Williams, D. B. G., and Lawton, M. “Drying of Organic Solvents: Quantitative Evaluation of the Efficiency of Several Desiccants.” *Journal of Organic Chemistry*, Vol. 75, No. 24, 2010, pp. 8351–8354. doi:10.1021/jo101589h.

[15]   Takamuku, T., Kyoshoin, Y., Shimomura, T., Kittaka, S., and Yamaguchi, T. “Effect of Water on Structure of Hydrophilic Imidazolium-Based Ionic Liquid.” *Journal of Physical Chemistry B*, Vol. 113, No. 31, 2009, pp. 10817–10824. doi:10.1021/jp9042667.

[16]   Cuadrado-Prado, S., Domínguez-Pérez, M., Rilo, E., García-Garabal, S., Segade, L., Franjo, C., and Cabeza, O. “Experimental Measurement of the Hygroscopic Grade on Eight Imidazolium Based Ionic Liquids.” *Fluid Phase Equilibria*, Vol. 278, No. 1–2, 2009, pp. 36–40. doi:10.1016/j.fluid.2008.12.008.

[17]   Freire, M. G., Santos, L. M. N. B. F., Fernandes, A. M., Coutinho, J. A. P., and Marrucho, I. M. “An Overview of the Mutual Solubilities of Water-Imidazolium-Based Ionic Liquids Systems.” *Fluid Phase Equilibria*, Vol. 261, No. 1–2, 2007, pp. 449–454. doi:10.1016/j.fluid.2007.07.033.

[18]   Widegren, J. A., Saurer, E. M., Marsh, K. N., and Magee, J. W. “Electrolytic Conductivity of Four Imidazolium-Based Room-Temperature Ionic Liquids and the Effect of a Water Impurity.” *Journal of Chemical Thermodynamics*, Vol. 37, No. 6, 2005, pp. 569–575. doi:10.1016/j.jct.2005.04.009.

[19]   Earle, M. J., Esperança, J. M. S. S., Gilea, M. A., Canongia Lopes, J. N., Rebelo, L. P. N., Magee, J. W., Seddon, K. R., and Widegren, J. A. “The Distillation and Volatility of Ionic Liquids.” *Nature*, Vol. 439, No. 7078, 2006, pp. 831–834. doi:10.1038/nature04451.

[20]   Gamero-Castaño, M., and Cisquella-Serra, A. “Electrosprays of Highly Conducting Liquids: A Study of Droplet and Ion Emission Based on Retarding Potential and Time-of-Flight Spectrometry.” *Physical Review Fluids*, Vol. 6, No. 1, 2021, p. 13701. doi:10.1103/PhysRevFluids.6.013701.

[21]   Clare, B. R., Bayley, P. M., Best, A. S., Forsyth, M., and MacFarlane, D. R. “Purification or Contamination? The Effect of Sorbents on Ionic Liquids.” *Chemical Communications*, No. 23, 2008, pp. 2689–2691. doi:10.1039/b802488j.

[22]   Bou Malham, I., Letellier, P., Mayaffre, A., and Turmine, M. “Part I: Thermodynamic Analysis of Volumetric Properties of Concentrated Aqueous Solutions of 1-Butyl-3-Methylimidazolium Tetrafluoroborate, 1-Butyl-2,3-Dimethylimidazolium Tetrafluoroborate, and Ethylammonium Nitrate Based on Pseudo-Lattice Theory.” *Journal of Chemical Thermodynamics*, Vol. 39, No. 8, 2007, pp. 1132–1143. doi:10.1016/j.jct.2007.01.007.

[23]   Islam, M. M., Okajima, T., Kojima, S., and Ohsaka, T. “Water Electrolysis: An Excellent Approach for the Removal of Water from Ionic Liquids.” *Chemical Communications*, No. 42, 2008, pp. 5330–5332. doi:10.1039/b811174j.

[24]   Aquastar. Karl Fischer Titration Basics. https://www.emdmillipore.com/US/en/lab-technical-resources/karl-fischer-faqs/w5yb.qB.0VgAAAFE3oMWq.DH,nav.

[25]   Honeywell.   Hydranal   Manual   For   Karl   Fischer   Titration. https://lab.honeywell.com/content/dam/rc/en/resources/resource-library/hydranal-manuals/pmt-rc-661-hydranal-manual.pdf.

11

[26]   Hanna Instruments. *Titration Theory Principles HI 904 Karl Fischer Coulumetric Titrator, Rivision 1.0*. 2013.

[27]   Gamero-Castaño, M. "Characterization of the Electrosprays of 1-Ethyl-3-Methylimidazolium Bis(Trifluoromethylsulfonyl) Imide in Vacuum." *Physics of Fluids*, Vol. 20, No. 3, 2008. doi:10.1063/1.2899658.

[28]   Grustan-Gutierrez, E., and Gamero-Castaño, M. "Microfabricated Electrospray Thruster Array with High Hydraulic Resistance Channels." *Journal of Propulsion and Power*, Vol. 33, No. 4, 2017, pp. 984–991. doi:10.2514/1.B36268.

[29]   Courtney, D. G., Dandavino, S., and Shea, H. "Comparing Direct and Indirect Thrust Measurements from Passively Fed Ionic Electrospray Thrusters." *Journal of Propulsion and Power*, Vol. 32, No. 2, 2016, pp. 392–407. doi:10.2514/1.B35836.

[30]   Thuppul, A., Wright, P. L., Collins, A. L., Ziemer, J. K., and Wirz, R. E. Lifetime Considerations for Electrospray Thrusters. *Aerospace*. 8. Volume 7.

[31]   Krejci, D., Mier-Hicks, F., Thomas, R., Haag, T., and Lozano, P. "Emission Characteristics of Passively Fed Electrospray Microthrusters with Propellant Reservoirs." *Journal of Spacecraft and Rockets*, Vol. 54, No. 2, 2017, pp. 447–458. doi:10.2514/1.A33531.

[32]   Krpoun, R., and Shea, H. R. "Integrated Out-of-Plane Nanoelectrospray Thruster Arrays for Spacecraft Propulsion." *Journal of Micromechanics and Microengineering*, Vol. 19, No. 4, 2009. doi:10.1088/0960-1317/19/4/045019.

[33]   Alexander, M. S., Stark, J., Smith, K. L., Stevens, B., and Kent, B. "Electrospray Performance of Microfabricated Colloid Thruster Arrays." *Journal of Propulsion and Power*, Vol. 22, No. 3, 2006, pp. 620–627. doi:10.2514/1.15190.

[34]   Berg, S. P., and Rovey, J. L. "Assessment of Multimode Spacecraft Micropropulsion Systems." *Journal of Spacecraft and Rockets*, Vol. 54, No. 3, 2017, pp. 592–601. doi:10.2514/1.A33649.

[35]   Chiu, Y. H., Gaeta, G., Levandier, D. J., Dressler, R. A., and Boatz, J. A. "Vacuum Electrospray Ionization Study of the Ionic Liquid, [Emim][Im]." *International Journal of Mass Spectrometry*, Vol. 265, No. 2–3, 2007, pp. 146–158. doi:10.1016/j.ijms.2007.02.010.

[36]   Chiu, Y., and Dressler, R. A. "Chapter 10 Ionic Liquids for Space Propulsion." pp. 138–160.

[37]   Bini, R., Bortolini, O., Chiappe, C., Pieraccini, D., and Siciliano, T. "Development of Cation/Anion 'Interaction' Scales for Ionic Liquids through ESI-MS Measurements." *Journal of Physical Chemistry B*, Vol. 111, No. 3, 2007, pp. 598–604. doi:10.1021/jp0663199.

[38]   Nieto de Castro, C. A., Langa, E., Morais, A. L., Lopes, M. L. M., Lourenço, M. J. V, Santos, F. J. V, Santos, M. S. C. S., Lopes, J. N. C., Veiga, H. I. M., Macatrão, M., Esperança, J. M. S. S., Marques, C. S., Rebelo, L. P. N., and Afonso, C. A. M. "Studies on the Density, Heat Capacity, Surface Tension and Infinite Dilution Diffusion with the Ionic Liquids [C4mim][NTf2], [C4mim][Dca], [C2mim][EtOSO3] and [Aliquat][Dca]." *Fluid Phase Equilibria*, Vol. 294, No. 1, 2010, pp. 157–179. doi:https://doi.org/10.1016/j.fluid.2010.03.010.

[39]   Singh, T., and Kumar, A. "Static Dielectric Constant of Room Temperature Ionic Liquids: Internal Pressure and Cohesive Energy Density Approach." *The Journal of Physical Chemistry B*, Vol. 112, No. 41, 2008, pp. 12968–12972. doi:10.1021/jp8059618.

[40]   Zhou, J., Sui, H., Jia, Z., Yang, Z., He, L., and Li, X. "Recovery and Purification of Ionic Liquids from Solutions: A Review." *RSC Advances*, Vol. 8, No. 57, 2018, pp. 32832–32864. doi:10.1039/C8RA06384B.

[41]   Berg, S. P., and Rovey, J. L. "Assessment of Imidazole-Based Ionic Liquids as Dual-Mode Spacecraft Propellants." *Journal of Propulsion and Power*, Vol. 29, No. 2, 2013, pp. 339–351. doi:10.2514/1.B34341.

[42]   Huang, M. M., Jiang, Y., Sasisanker, P., Driver, G. W., and Weingärtner, H. "Static Relative Dielectric Permittivities of Ionic Liquids at 25 °c." *Journal of Chemical and Engineering Data*, Vol. 56, No. 4, 2011, pp. 1494–1499. doi:10.1021/je101184s.

[43]   Sherman, R. Chapter 3 - Carbon Dioxide Snow Cleaning Applications. In (R. Kohli and K. L. B. T.-D. in S. C. and C. A. of C. T. Mittal, eds.), Elsevier, pp. 97–115.