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Dual-Mode Propellant Properties and Performance Analysis of Energetic Ionic Liquids

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Imidazole-based energetic ionic liquids capable of dual-mode chemical monopropellant or bipropellant and electric electrospray rocket propulsion are investigated. A literature review of ionic liquid physical properties is conducted to determine an initial set of ionic liquids that show favorable physical properties for both modes, followed by numerical and analytical performance simulations. Of the ionic liquids considered in this study, [Bmim][dca], [Bmim][NO_3], and [Emim][$EtSO_4$] meet or exceed the storability properties of hydrazine and their electrochemical properties are comparable to [Emim][Im], the current state-of-the-art electrospray propellant. Simulations show that these liquids do not perform well as chemical monopropellants, having 10-22% lower specific impulse due to their lack of oxidizing species. The ionic liquids show acceptable bipropellant performance when burned with standard oxidizers, having specific impulse 6-12% lower than monomethylhydrazine and nitrogen tetroxide combination. Considering these ionic liquids as a fuel component in a binary monopropellant mixture with hydroxyl ammonium nitrate shows 1-3% improved specific impulse over some green monopropellants, while retaining a higher molecular weight, reducing the number of electrospray emitters required to produce a given thrust level. More generally, ionic liquids with oxidizing anions perform well as chemical monopropellants while retaining high molecular weight desirable for electrospray propulsion missions.

Nomenclature

E_{max}	=	maximum electric field
e	=	fundamental charge
F	=	thrust
g_o	=	acceleration of gravity
I_d	=	density specific impulse
I_{emit}	=	current flow per emitter
I_i	=	output current associated with charged particle emission
I_{sp}	=	specific impulse
K	=	electrical conductivity
MW	=	molecular weight
m_i	=	mass of particle *i*
$\dot{m}_{emit}$	=	mass flow rate per emitter
$\dot{m}_{tot}$	=	total mass flow rate
N_{emit}	=	number of emitters
P_c	=	chamber pressure
P_e	=	nozzle exit pressure
Q	=	volume flow rate
q	=	particle charge
R	=	gas constant
R_A	=	ion fraction
T_c	=	combustion temperature

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T_m	=	melting temperature
V_{acc}	=	electrostatic acceleration potential
V_e	=	exit velocity
x_i	=	mass fraction of species i
ΔH^0_f	=	heat of formation
δ_{av}	=	average specific gravity
ε	=	dielectric constant, or nozzle expansion ratio
ε_o	=	permittivity of free space
γ	=	ratio of specific heats, or surface tension
$\varphi(\varepsilon)$	=	proportionality coefficient
ρ	=	density
ρ_i	=	density of species i
ρ_n	=	density of species n

I. Introduction

THE purpose of a dual-mode spacecraft propulsion system is to improve spacecraft mission flexibility by utilizing both high-thrust chemical and high-specific impulse electric propulsion modes. A dual-mode system utilizing a single propellant for both modes would reduce system mass and volume, thereby providing maximum mission flexibility. This paper describes and examines requirements on the physical properties of various ionic liquids to assess their potential for use as propellants in a potential dual-mode system. Chemical propulsion performance of ionic liquids that have shown favorable properties toward both modes is then computed and compared to the current state-of-the-art in both bipropellant and monopropellant chemical propulsion.

The main benefit of a dual-mode system is increased mission flexibility through the use of both a high-thrust chemical thruster and a high-specific impulse electric thruster. By utilizing both thrust modes, the mission design space is much larger.[1] Missions not normally accessible by a single type of thruster are possible since both are available. The result is the capability to launch a satellite with a flexible mission plan that allows for changes to the mission as needs arise. Since a variety of high specific impulse and high thrust maneuvers are available in this type of system, this may also be viewed as a technology enabling launch of a satellite without necessarily determining its thrust history beforehand. Research has shown that a dual mode system utilizing a single ionic liquid propellant in a chemical bipropellant or monopropellant and electrical electrospray mode has the potential to achieve the goal of improved spacecraft mission flexibility.[2-4] Furthermore, utilizing a single ionic liquid propellant for both modes would save system mass and volume to the point where it becomes beneficial when compared to the performance of a system utilizing a state-of-the-art chemical and electric thruster with separate propellants, despite the performance of the ionic liquid being less than that of each thruster separately. While a bipropellant thruster would provide higher chemical performance, a monopropellant thruster provides the most benefit because the utilization of a bipropellant thruster in this type of system could inherently lead to unused mass of oxidizer since some of the fuel is used for the electrical mode.[3]

An ionic liquid is essentially a molten, or liquid, salt. All salts obtain this state when heated to high enough temperature; however, a special class of ionic liquids is known as room temperature ionic liquids (RTIL's) that remain liquid well below room temperature. Ionic liquids have been known since the early 20th century; research in the field, however, has only recently begun to increase, with the number of papers published annually increasing from around 120 to over 2000 in just the last decade.[5] As a result, many of the ionic liquids that have been synthesized are still being researched, and data on their properties is not yet available. Current research has aimed at synthesizing and investigating energetic ionic liquids for propellants and explosives, and current work has highlighted the combustibility of certain ionic liquids as they approach decomposition temperature.[6,7] This leads to the possibility of using an ionic liquid as a storable spacecraft propellant.

Hydrazine has been the monopropellant of choice for spacecraft and gas generators because it is storable and easily decomposed to give good combustion properties.[8] However, hydrazine is also highly toxic and recent efforts have been aimed at replacing hydrazine with a high-performance, non-toxic monopropellant. The energetic salts hydroxyl ammonium nitrate (HAN), ammonium dinitramide (ADN), and hydrazinium nitroformate (HNF) have received attention as potential replacements.[8-12] All of these have melting points above room temperature, and it is therefore necessary to use them in an aqueous solution to create a storable liquid propellant. Typically, these are also mixed with a compatible fuel component to provide improved performance. The main limitation to the development of these as monopropellants has been excessive combustion temperatures.[12,13] Sweden, however, has recently flight tested an ADN-based thruster capable of handling combustion temperatures exceeding 1900 K.[12]

Electrospray is a propulsion technology in which charged liquid droplets are extracted from an emitter via an applied electric field.[14] Electrospray liquids with relatively high vapor pressure boil off the emitter and produce an uncontrolled, low performance emission. Ionic liquids are candidates for electrospray propulsion due to their negligible vapor pressure and high electrical conductivity.[15] Ionic liquid emissions can range from charged droplets to a purely ionic regime (PIR) similar to that of field emission electric propulsion with specific impulses in the range of 200-3000 seconds for current propellants.[14] The ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Emim][Im]) was selected as the propellant for the ST7 Disturbance Reduction System mission, and represents the only application of electrospray, or colloid, thrusters to date.[16] Several other imidazole-based ionic liquids have been suggested for research in electrospray propulsion due to their favorable physical properties.[17]

The following sections analyze the potential of ionic liquids to be used as spacecraft propellants in a dual-mode system. Section II identifies the physical properties required for acceptable performance in both modes, and ionic liquids that meet these criteria. Section III investigates the expected chemical performance of these ionic liquids as both mono- and bipropellants. Section IV examines the electrospray performance of the ionic liquid propellants. The results of the preceding sections are discussed, and criteria for future dual-mode propellant developments are presented in Section V. Section VI presents conclusions based on the entirety of analyses.

II. Ionic Liquid Physical Properties

Fundamental physical properties required of ionic liquids to perform as both mono- or bipropellant and electrospray propellant in a spacecraft environment are identified. These properties are compared to those of the current state-of-the-art propellants to assess the feasibility of using these ionic liquids for the intended application.

A. Thermochemical Properties

The thermochemical properties required to initially analyze the ability of ionic liquids to perform as spacecraft propellants include the following: melting temperature, density, and heat of formation.[8] Both high density and low melting temperature are common to both propulsive modes in the dual-mode system because they do not have a significant effect on the operation of each thruster, but represent the storability of propellants only. A low melting temperature is desired so that the power required to keep the propellant in liquid form is minimal. Hydrazine has a melting temperature of 2^{o} C, so it is reasonable to assume that new propellants must fall near or below this value. Density is an additional storability consideration. A high density is desired to accommodate a large amount of propellant in a given volume on a spacecraft. The chemical propellant must also be easily ignitable and give good combustion properties. The heat of formation of the compound is required to estimate the equilibrium composition, and subsequently compute the estimated chemical performance, namely specific impulse. A high heat of formation results in a greater energy release upon combustion, therefore a higher combustion temperature, and subsequently a higher specific impulse.

B. Electrochemical Properties

The electrochemical properties important for electrospray propulsion include both surface tension and electrical conductivity. Liquids with high surface tension and conductivity have been shown to be capable of operating near or in the purely ionic regime (PIR), characterized by the highest attained performance for electrospray propulsion. This has been shown both theoretically and experimentally,[17-19] and is related to the maximum electric field on the meniscus of the liquid on the emitter[16.17]

$$E_{\max} = \varphi(\varepsilon)\gamma^{1/2}\varepsilon_0^{-2/3}(K/Q)^{1/6} \quad (1)$$

Additionally, Fernandez De La Mora[17,19] has shown that the smallest flow rate that can form a stable Taylor cone scales as $1/K$, hence[17]

$$E_{\max} \sim \gamma^{1/2}K^{1/3} \quad (2)$$

This relation is a measure of the ability of an ionic liquid to form a Taylor cone with emission near or at the PIR regime, and does not necessarily translate to thruster performance. The thrust and specific impulse for an electric propulsion system by an individual particle are calculated as[8,14]

$$F = I_i(m_i/q)\sqrt{2V_{acc}(q/m_i)} \quad (3)$$

$$I_{sp} = (1/g_0)\sqrt{2V_{acc}(q/m_i)} \quad (4)$$

Previous research has shown that an excessively high specific impulse for electrospray propulsion is not practical for typical satellite maneuvering operations.[3] Higher molecular weight propellants, such as 1-butyl-3-methylimidazolium dicyanamide ([Bmim][dca]), are desirable due to the higher thrust produced by emission of heavier ions or droplets. Therefore, ionic liquids with electrical conductivity and surface tension close to the current state-of-the-art electrospray propellants and high molecular weight are considered.

C. Physical Properties of Ionic Liquids Used in this Study

The number of ionic liquids available for study is numerous; therefore, this study has initially been restricted to only imidazole-based ionic liquids. The main reason for selecting imidazole-based ionic liquids is their capability as electrospray propellants, particularly those based on the $[Emim]^+$ cation.[17] A recent patent on this particular type of dual-mode system lists several potential ionic liquid propellants, most of which are imidazole-based.[20] These are used in the initial screening for chemicals of interest; however, many ionic liquids do not have enough published physical property data to make reasonable estimates of initial system feasibility. In particular, heat of formation is not available for many of the ionic liquids considered initially. In the end, three ionic liquids are selected for further study based on availability of property data: 1-butyl-3-methylimidazolium nitrate ($[Bmim][NO_3]$), [Bmim][dca], and 1-ethyl-3-methylimidazolium ethyl sulfate ($[Emim][EtSO_4]$). Representative physical property data for these ionic liquids are shown in Table 1; variance in this data will be addressed in the next section. The properties of hydrazine and [Emim][Im] are shown for comparison of thermochemical and electrochemical properties, respectively.

Table 1. Physical Properties of Ionic Liquids

Propellant	Formula	ρ [g/cm^3]	T_m [^{o}C]	ΔH_f^o [kJ/mol]	K [S/m]	γ [dyn/cm]	MW [g/mol]
$[Bmim][NO_3]$	$C_8H_{15}N_3O_3$	1.157 [21]	<10 [21]	-261.4 [22]	0.82 [23]		201.23
[Bmim][dca]	$C_{10}H_{15}N_5$	1.058 [24]	-10 [24]	206.2 [25]	1.052 [26]	46.6 [27]	205.26
$[Emim][EtSO_4]$	$C_8H_{16}N_2O_4S_1$	1.236 [28]	-37 [29]	-579.1 [30]	0.382 [31]	45.4 [32]	236.29
[Emim][Im]	$C_8H_{11}F_6N_3O_4S_2$				0.91 [33]	36.9 [34]	391.13
Hydrazine	N_2H_4	1.005 [8]	2 [8]	109.3 [35]			32.05

The density, electrical conductivity, and surface tension reported in the table are at a temperature of 298 K for all liquids listed, except for the electrical conductivity of $[Bmim][NO_3]$, where the only data point given in literature is at a temperature of 379 K. All of the ionic liquids have density greater than that of hydrazine. The melting temperature of [Bmim][dca] and $[Emim][EtSO_4]$ is less than that of hydrazine. $[Bmim][NO_3]$ has a slightly higher melting temperature, but the exact melting temperature is not reported. The value shown in Table 1 represents the fact that liquid viscosity measurements are reported for as low as 10 ^{o}C in literature.[22,36] Both the electrical conductivity and surface tension of [Bmim][dca] is above that of [Emim][Im], making it a very viable electrospray propellant candidate. The electrical conductivity of $[Emim][EtSO_4]$ is below that of [Emim][Im]; however, preheating the electrospray emitter to a value of 50 ^{o}C would raise its electrical conductivity to a value above that of [Emim][Im].[33] Also, the surface tension of $[Emim][EtSO_4]$ is higher than that of [Emim][Im]. Eq. (2) indicates that for favorable electrospray operation the electrical conductivity may be slightly less if the surface tension is higher. Using Eq. (2) as an estimate, with the surface tension of $[Emim][EtSO_4]$, the electric field on the meniscus is equal to that of [Emim][Im] with an electrical conductivity of 0.67. This value is exceeded with an emitter preheat of 40^{o}C.[33] As stated, the electrical conductivity reported for $[Bmim][NO_3]$ is at a temperature of 379 K, making it slightly less feasible to use as an electrospray propellant since it will have to be heated to over 100^{o}C to achieve an electric field meniscus nearly equal to [Emim][Im]. Surface tension for $[Bmim][NO_3]$ is not reported; however, it can be reasonably inferred based on trends reported in literature. A longer alkyl chain in imidazole-based ionic liquids has been reported to result in decreased surface tension.[37] $[Emim][NO_3]$, the lower alkyl chain derivative of $[Bmim][NO_3]$ has a surface tension of 82.7 dyne/cm.[38] The value reported for the lower alkyl chain derivative of [Bmim][dca] is 1-ethyl-3-methylimidazolium dicyanamide, [Emim][dca] is 64 dyne/cm.[39] Following these trends, the surface tension for $[Bmim][NO_3]$ should fall below that of $[Emim][NO_3]$, but above that of [Bmim][dca]; therefore, the surface tension of $[Bmim][NO_3]$ should be higher than that of [Emim][Im], and may allow for a slightly lower electrical conductivity.

D. Variance of Physical Property Data in Literature

Representative physical property data for candidate ionic liquid propellants has been shown and analyzed in the previous section; however, the multiple values reported in literature are found to deviate slightly from the values listed in Table 1. Therefore, a full literature review is presented to determine how this affects the conclusions in this study.

Of the ionic liquids presented in this study, [Bmim][NO_3] has the least, and also the most questionable, published physical property data currently available. The densities reported in literature are in good agreement, with reported values ranging from 1.157-1.159 g/cc.[21,36,40] This 0.2% difference is not significant for this study. The reported value for electrical conductivity is the result of molecular dynamics simulations.[23] Currently, there are no data available for experimental conductivity measurements of [Bmim][NO_3]; however, Kowsari[23] reports that their simulated conductivity results are less than obtained from experimental results of ionic liquids they studied which had published experimental results available.

[Bmim][dca] has more experimental data available in literature. Density measurements range from 1.058-1.063 g/cc.[24,26,41-43] This is a 0.3% difference, but again is not significant for the purposes of this study. Electrical conductivity measurements show a slight variance, ranging from 1.052-1.139 S/m.[26,41,44] Zech[26] suspects halide impurities result in a higher measured electrical conductivity for this ionic liquid, and expects the value of pure [Bmim][dca] to be even lower than his measured value of 1.052 S/m. Values obtained for surface tension also show a slight variance: 45.81-48.6 dyne/cm.[27-45] Klomfar[27] measured surface tension using both the Wilhelmy plate and du Nuoy ring methods and found values of 45.81 and 45.88 dyne/cm, respectively, suggesting that the variance in surface tension is likely also due to impurities. Since the lowest values for surface tension and electrical conductivity found in literature are still above that of [Emim][Im], the conclusion that [Bmim][dca] is a good candidate for electrospray propulsion remains unchanged.

For a variety of reasons, [Emim][$EtSO_4$] has been intensely studied over the past five years.; as such, a plethora of published data is available. Density, as with the other two ionic liquids, shows good agreement: 1.236-1.242 g/cc.[28,46] Since over 30 sources that have experimentally measured density were found over the course of this study, only the highest and lowest values obtained are included. Again, this amounts to only 0.5% difference between the highest and lowest values, and is therefore not significant for purposes of this study. Surface tension, like [Bmim][dca], has a slight variance amongst published data. Values range from 45.43-48.79 dyne/cm,[32,47,48] but again do not affect the conclusions because these values are still well above that of [Emim][Im]. Other than the value listed in the table, an electrical conductivity of 0.398 S/m is published in literature,[48] which does not affect the conclusions significantly.

III. Chemical Performance Analysis

The three aforementioned liquids are feasible candidates for both chemical and electrical propulsion purely based on their reported physical properties. A chemical rocket performance analysis is conducted to determine if they have potential as chemical mono- or bipropellants. Equilibrium combustion analysis is conducted using the NASA Chemical Equilibrium with Applications (CEA) computer code.[35] In each case, the temperature of the reactants is assumed to be 298 K. Where applicable, specific impulse is calculated by assuming frozen flow at the throat[8]

$$I_s = \sqrt{\left(\frac{2\gamma}{\gamma-1}\right)\left(\frac{RT_c}{MW}\right)\left(1-\left(\frac{P_e}{P_c}\right)^{\frac{(\gamma-1)}{\gamma}}\right)} \tag{5}$$

$$\frac{1}{\varepsilon} = \left(\frac{\gamma+1}{2}\right)^{\frac{1}{\gamma-1}}\left(\frac{P_e}{P_c}\right)^{\frac{1}{\gamma}}\sqrt{\frac{\gamma+1}{\gamma-1}\left(1-\frac{P_e}{P_c}\right)^{\frac{\gamma-1}{\gamma}}} \tag{6}$$

Given a combustion pressure and nozzle expansion ratio, Eqs. (5) and (6) are then only functions of the combustion gas temperature and products, which are given in the CEA output. When condensed species are found to be present in the equilibrium combustion products, a shifting equilibrium assumption through the nozzle must be applied instead to account for the multi-phase flow. For each simulation hereafter a chamber pressure of 300 psi and nozzle expansion ratio of 50 are assumed. These represent typical values for on-orbit engines.[49] The ambient pressure is taken as vacuum, therefore the specific impulse computed is the absolute maximum for the given design conditions. As an additional measure of chemical performance, the density specific impulse is computed simply from[8]

$$I_d = \delta_{av} I_{sp} \tag{7}$$

A. Monopropellant Performance

The CEA computer code is utilized to determine the expected performance of the ionic liquids as monopropellants with the assumptions and conditions described above. The reaction is then decomposition of the ionic liquid into gaseous products. The computed specific impulse and density impulse values are shown in Table 2. CEA predicts condensed carbon in the exhaust species for the ionic liquids; therefore, the specific impulse shown in the table is for shifting equilibrium. For comparison, the performance of ADN-based monopropellant FLP-103 (63.4% ADN, 25.4% water, 11.2% methanol) is also computed. The specific impulse computed in this analysis for FLP-103 agrees precisely with the theoretical calculations performed by Wingborg, et.al.[50] at the same design conditions and a frozen flow assumption, as CEA was also utilized in that study for performance prediction. The specific impulse for hydrazine is taken from Ref. 51 and is its theoretical maximum where the catalyst bed has been designed to allow for no ammonia to dissociate. None of the ionic liquids show performance comparable to that of hydrazine, with [Bmim][NO_3] coming closest at a value of 17.9% lower specific impulse. The performance of the ionic liquids is slightly more promising in terms of density specific impulse. [Bmim][dca], [Bmim][NO_3], and [Emim][$EtSO_4$] fall 22.5%, 5.4%, and 10.5%, respectively, below that of hydrazine. None of the ionic liquids compete with the theoretical density specific impulse of advanced monopropellant FLP-103, which is predicted to be 22.5% higher than hydrazine.

Table 2. Chemical Performance of Ionic Liquids

Propellant	I_{sp} [s]	I_d [s]
[Bmim][NO_3]	211	244
[Bmim][dca]	189	200
[Emim][$EtSO_4$]	186	231
FLP-103	254 (Equilibrum)	333
	251 (Frozen)	329
Hydrazine	257	258

Analysis of the equilibrium combustion products, Table 3, indicates a large amount of solid carbon in the theoretical exhaust gases, indicating incomplete combustion, and leading to the poor performance of the ionic liquids. [Bmim][dca] has no oxidizing components in its anion and as expected it has the highest mole fraction of carbon of the three ionic liquids. The other two liquids have 15% less carbon in the exhaust due to the oxygen present in their anions, which tends to form the oxidized species CO, H_2O, and CO_2. Decomposition of [Emim][$EtSO_4$] shows a higher mole fraction of H_2O and CO_2 compared to that of [Bmim][NO_3] due to the additional oxygen atom in the anion with the same carbon content. Each of the ionic liquids is predicted to form roughly 10% CH_4, a product that could be combusted further with additional oxidizer. Additionally, some of the hydrogen is used to form H_2S due to the presence of the sulfur atom in the anion, another product that with additional oxidizer will combust further.

Table 3. Equilibrium Decomposition Products of Ionic Liquids

Product Species	Mole Fraction [Bmim][NO_3]	[Bmim][dca]	[Emim][$EtSO_4$]
C	0.35	0.50	0.35
N_2	0.10	0.15	0.07
H_2	0.27	0.24	0.19
H_2O	0.07	0.00	0.11
CO	0.09	0.00	0.07
CO_2	0.02	0.00	0.05
CH_4	0.09	0.11	0.09
H_2S	0.00	0.00	0.07

B. Bipropellant Performance

Bipropellant performance is computed by considering the ionic liquids as fuels burned with standard storable oxidizers. The oxidizers selected for this study are the following: inhibited red fuming nitric acid (IRFNA), nitrogen tetroxide (NTO), and hydroxyl ammonium nitrate (HAN). Both IRFNA and NTO are available in the CEA reactant library. HAN ($N_2H_4O_4$) is input with a heat of formation of -79.68 kcal/mol.[52] The computed specific impulse is compared to the typical bipropellant combination of monomethylhydrazine (MMH) and NTO. The initial conditions are the same as described in the monopropellant analysis, and frozen flow is assumed for all simulations. Specific impulse is plotted as a function of equivalence ratio for equivalence ratios of 0.6 to 2.6. Results are shown in Fig. 1.

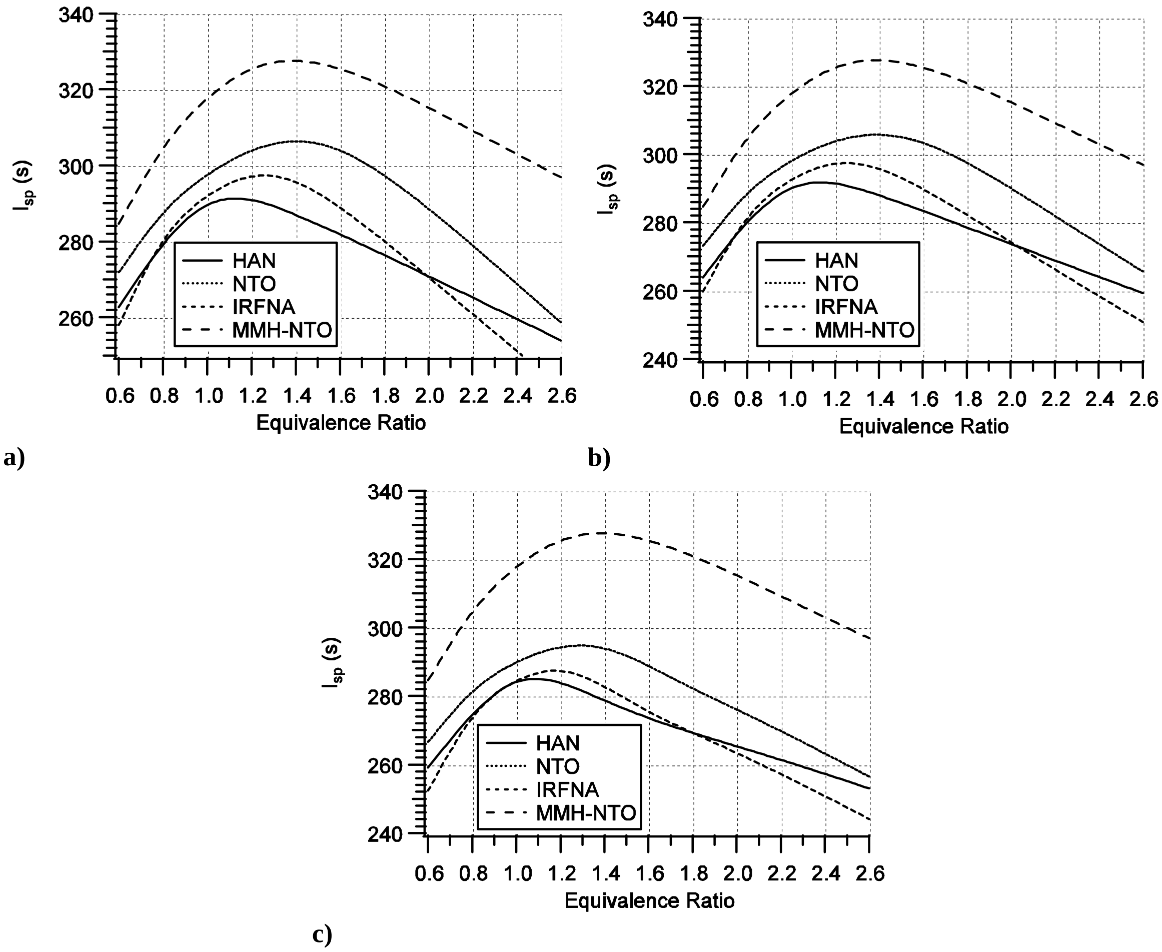

Figure 1. Bipropellant Performance of a) [Bmim][dca], b) [Bmim][NO_3], and c) [Emim][$EtSO_4$]. *Specific impulse as a function of equivalence ratio for ionic liquid fuels combined with standard oxidizers.*

All of the ionic liquid fuels show similar trends. Performance for each of the ionic liquids is highest when burned with NTO, followed by IRFNA and then HAN. When burned with NTO, the specific impulse is 6.5%, 7%, and 10% below that of the MMH-NTO combination for [Bmim][dca], [Bmim][NO_3], and [Emim][$EtSO_4$], respectively. The maximum specific impulse of the ionic liquid fuels when burned with IRFNA is 8%, 9%, and 12% lower than that of MMH-NTO for [Bmim][dca], [Bmim][NO_3], and [Emim][$EtSO_4$], respectively. The lowest performing oxidizer with the ionic liquids is HAN, which has a specific impulse 11% below MMH-NTO for both [Bmim][dca] and [Bmim][NO_3] fuels, and a specific impulse 13% below MMH-NTO when paired with [Emim][$EtSO_4$].

C. Ionic Liquids in Binary Mixtures as Monopropellants

The possibility of using ionic liquids as fuel components in a binary monopropellant mixture is considered. This may, in fact, be possible due to the ionic liquids capability as solvents, particularly [Bmim][dca] and [Bmim][NO_3], as their anions have H-bond accepting functionality.[44,53] HAN, also, is noted for its solubility in water, which led to its initial application as a liquid gun propellant.[54] Furthermore, [Bmim][dca] has been tested for hypergolicity with HAN oxidizer, and, notably, it showed no visible signs of reactivity at room temperature.[55] A monopropellant mixture of the ionic liquids with HAN, or another oxidizer salt, may be created which would be thermally stable at room temperature, and ignited thermally or catalytically.

CEA is again employed with the same conditions applied previously, and with shifting equilibrium assumption. Specific impulse is calculated as a function of percent HAN oxidizer by weight in the binary mixture. This is shown in Fig. 2. The highest performance is seen at mixture ratios near the stoichiometric value, around 80%, and represents values nearer to bipropellant performance. However, this performance is not feasible when considering current monopropellant thruster technology. The main issue facing monopropellant development is the fabrication of catalyst material that can withstand the high combustion temperatures. A typical hydrazine thruster may operate at temperatures exceeding 1200 K;[8] however, Sweden has recently developed a monopropellant thruster capable of operation with ADN-based propellant at combustion temperatures exceeding 1900 K.[12] Considering 1900 K to be the current technology limit on monopropellant combustion temperature, the ionic liquids [Bmim][dca], [Bmim][NO_3], and [Emim][$EtSO_4$] exceed this value at roughly a 69%, 61%, and 59% binary mixture with HAN by weight, respectively, as shown in Fig. 3. From Fig. 2, these mixture ratios correspond to a specific impulse of 263, 263, and 255 seconds for [Bmim][dca], [Bmim][NO_3], and [Emim][$EtSO_4$], respectively. This is promising as the specific impulse of the binary mixtures is higher than the ADN-based FLP-103 (Table 1) at the same design conditions.

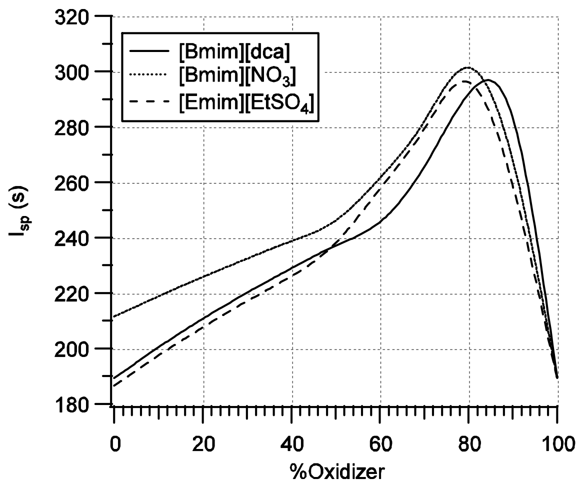

Figure 2. Specific Impulse as a Function of Percent Oxidizer. *Specific impulse of ILs in binary mixture with HAN oxidizer.*

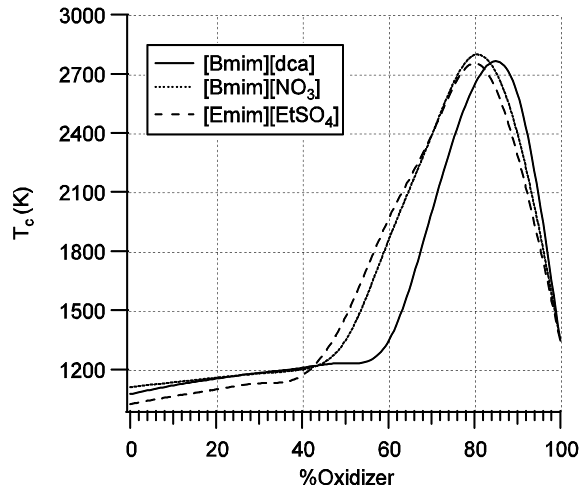

Figure 3. Combustion Temperature as a Function of Percent oxidizer. *Combustion temperature of ILs in binary mixture with HAN oxidizer.*

Additional conclusions can be made by further consideration of the equilibrium combustion products associated with the ionic liquid binary mixtures in Fig. 4. For [Bmim][dca], as the percent by weight of HAN oxidizer is increased, the solid carbon species decreases as both CO and H_2 increase and reach a maximum at 58% oxidizer. Further HAN addition leads to formation of complete combustion products CO_2 and H_2O at the highest combustion temperatures. The same trend is observed in the other ionic liquids, with the exception of the solid carbon disappearing at 44% oxidizer for [Bmim][NO_3] and at 41% oxidizer for [Emim][$EtSO_4$]. The sulfur atom in the [Emim][$EtSO_4$] fuel functions to form oxidized sulfur species SO_2, which peaks at roughly 2% near the stoichiometric mixture ratio.

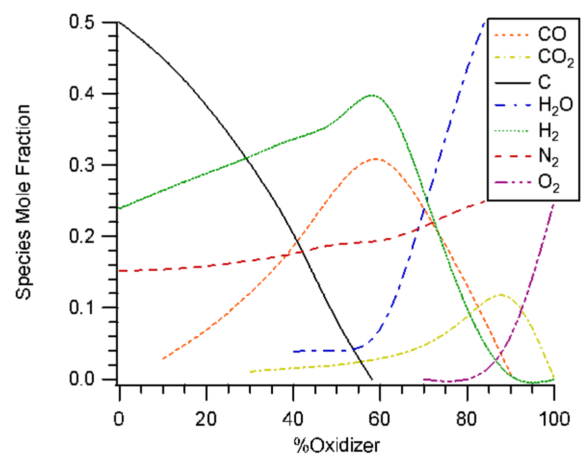

Figure 4. Major Combustion Products. *Mole fractions of exhaust species of binary mixtures of [Bmim][dca] with HAN oxidizer.*

For further comparison, the specific impulse of the binary mixtures of ionic liquids as a function of percent HAN oxidizer is computed assuming frozen flow; therefore, only mixture ratios that do not yield solid carbon are included. This is shown in Fig. 5. At the aforementioned mixture ratios yielding a 1900 K combustion temperature, the specific impulse is now 251 seconds for [Bmim][dca] and [Bmim][NO_3], and 249 seconds for [Emim][$EtSO_4$] which are roughly equal to that of FLP-103. As mentioned, a [Bmim][dca] mixture requires at least 58% HAN to form completely gaseous products. At this mixture ratio, the specific impulse is 213 seconds, 15% below that of FLP-103. For [Bmim][NO_3], the specific impulse at a 44% mixture of HAN oxidizer is 212 seconds, and for [Emim][$EtSO_4$] at a 41% mixture of HAN the specific impulse is 200 seconds. So, at the minimum oxidizer amount required for conversion of the predicted solid carbon to gaseous combustion products, the specific impulse of a mixture with an ionic liquid fuel is 15-20% below that of advanced monopropellant FLP-103, but at a much lower combustion temperature of roughly 1300 K in each case.

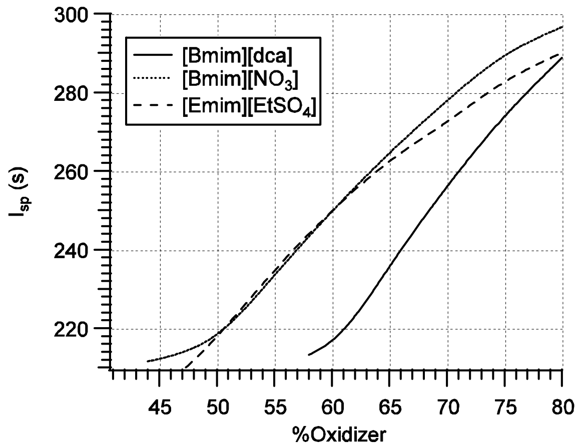

Figure 5. Specific Impulse as a Function of Percent Oxidizer. *Specific impulse of IL/HAN binary mixture under frozen flow assumption.*

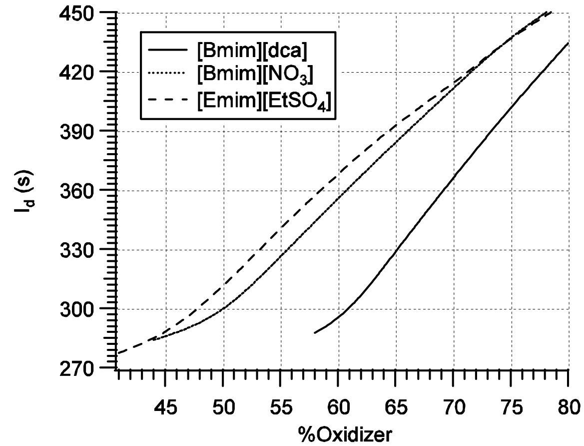

Figure 6. Density Specific Impulse as a Function of Percent Oxidizer. *Density specific impulse of IL/HAN binary mixture under frozen flow assumption.*

The main performance gain in the current generation of proposed green monopropellants is their superior density to traditional hydrazine monopropellant. As mentioned, ADN-based propellant FLP-103 is predicted to have a density specific impulse 22.5% higher than that of hydrazine, as calculated by Eq. (7). The density of a mixture of liquids can be estimated by assuming volume is additive,

$$\frac{1}{\rho_n} = \sum\left(\frac{x_i}{\rho_i}\right) \tag{8}$$

Eq. (8) is a conservative estimate since it does not take into account intermolecular attraction between the constituent liquids. The density specific impulse can then be computed for a desired mixture ratio using Eq. (7). The results for each ionic liquid fuel as a function of percent HAN oxidizer are shown in Fig. 6. Again looking at the mixture ratio that produces a 1900 K combustion temperature, the density specific impulse is 358, 362, and 362 seconds for [Bmim][dca], [Bmim][dca], and [Emim][EtSO$_4$], respectively. This corresponds to an improvement in density specific impulse of 8-9% over FLP-103 advanced monopropellant. Considering the minimum oxidizer amount required to form completely gaseous products, the density specific impulse for [Bmim][dca], [Bmim][NO$_3$], and [Emim][EtSO$_4$] binary mixtures is 287, 284, and 277 seconds, a 7-10% improvement over hydrazine.

IV. Electrospray Performance Analysis

The three candidate ionic liquids are acceptable candidates for bipropellant chemical propulsion and may even exceed the performance of state-of-the-art monopropellants when considered as a fuel component in a binary mixture with HAN oxidizer. To fully assess the dual-mode capability of each ionic liquid, the electrospray performance must also be considered. Electrospray performance can be estimated by considering emission in the purely ionic regime (PIR).[2-4,14] For ionic liquids, PIR emission consists of both pure ions and droplets with ions attached to *N* number of neutral pairs. Typically, ionic liquids that achieve PIR emit mostly ions (*N*=0) and ions attached to a single neutral pair (*N*=1), although small amounts of the third ion state (*N*=2) are also detected.[14] The actual ratio of *N*=0 to *N*=1 states in an electrospray emission is determined experimentally and can be varied depending on flow rates and extraction voltages. For example, the ionic liquid [Emim][Im] has been used in an almost pure droplet emission mode for the ST7 DRS mission,[14] whereas pure ion emission has also been reported.[56] It is therefore necessary to consider the entire range of possible emissions in the first two ion states when analyzing new potential electrospray propellants.

Electrospray performance in the PIR regime can be estimated by the following methods. The specific impulse for an emission consisting of the first two ion states is given by[2-4]

$$I_{sp} = \frac{V_{e,N=0}R_A + V_{e,N=1}(1-R_A)}{g_0} \tag{9}$$

where R_A is the fraction of the flow that is pure ions. For an electrostatic device, the following relations hold.[8] The velocity of a charged particle accelerated through a net potential is given by

$$V_e = \sqrt{\frac{2e\Delta\phi}{m}} \tag{10}$$

The power supplied to the system is related to thrust and specific impulse by

$$\eta_{sys} P_{in} = \frac{1}{2} T I_{sp} g_0 \tag{11}$$

Thrust is therefore a constant function of specific impulse for a constant power level and efficiency. The total mass flow rate required to produce the given thrust is calculated by

$$F = \dot{m}_{tot} I_{sp} g_0 \tag{12}$$

where the total mass flow rate is the sum of the mass flow from all emitters

$$\dot{m}_{tot} = N_{emit} \dot{m}_{emit} \tag{13}$$

The mass flow produced by a single emitter is related to the current produced by a single emitter by

$$\dot{m}_{emit} = \frac{I_{emit} m}{e} \tag{14}$$

A. Electrospray System Parameters

The relations described in Eqs. (9)-(14) are used to estimate the electrospray propulsion performance of the three ionic liquid fuels analyzed in the previous sections. In order to isolate the effect of the propellant alone on performance, constant system parameters are selected for all calculations: 200 W power level, 25% system efficiency, 1 µA current per emitter, and AC operation mode. The 200 W power level is chosen because electrospray technology is currently being selected for utilization in missions typical of 200 W low-power Hall thrusters. The system efficiency is arbitrarily selected as representative of what current electrospray systems might be capable of, considering the relative immaturity of the technology,[2-4] and that current hall thruster systems are roughly 50% efficient.[57] Similarly, current electrospray technology has demonstrated current levels of up to 1 µA with a single emitter. Improvements in the current electrospray technology level will affect all propellants the same,[2-4] provided it is not the physical properties of the propellant that drive the technology improvement; therefore, for this analysis it is prudent to use constant system parameters with respect to estimated current technology levels. The final consideration made is with respect to the operation mode of the thruster. An alternating polarity (AC) mode has been selected because both positive and negative ions are extracted. This is most likely the mode in which future electrospray systems will operate because all of the propellant is extracted, it provides a net neutral beam, and it generally avoids the problem of electrochemical fouling. The result of AC operation is an averaged thrust and specific impulse of the emitted cations and anions.

B. Electrospray Performance of Single Ionic Liquids

The electrospray performance of the three ionic liquid fuels alone is computed through the aforementioned analysis techniques and conditions. This represents the electrospray performance of the ionic liquids as they would be used in a bipropellant dual-mode system. Throughout the analysis, the ionic liquids [Emim][Im] and HAN have been shown for comparison. From Eqs. (9)-(14), it is seen that the electrospray performance when all system parameters are held constant is a function of the propellant mass alone. The cation and anion masses for each propellant used in this study are given in Table 4.

Table 4. Mass Data for Ionic Liquid Propellants.

Propellant	Chemical Formula		MW [g/mol]	
	Cation	Anion	Cation	Anion
[Bmim][dca]	$C_8H_{15}N_2$	C_2N_3	139	66
[Bmim][NO_3]	$C_8H_{15}N_2$	NO_3	139	62
[Emim][$EtSO_4$]	$C_6H_{11}N_2$	$C_2H_5SO_4$	111	125
[Emim][Im]	$C_6H_{11}N_2$	$C_2NF_6S_2O_4$	111	280
HAN	NH_3OH	NO_3	34	62

The specific impulse of each propellant is calculated as a function of net accelerating voltage from 200-2000V, and for ion fractions of 0-1. The results for [Bmim][dca] are shown in Fig. 7. From the figure, it is clear that the specific impulse increases as ion fraction decreases because more massive droplets are emitted in the first solvated state. Additionally, the specific impulse increases with an increase in net accelerating voltage. All of the ionic liquid propellants show the same trends. For [Bmim][dca], the specific impulse at the low end of the range shown is 1100 seconds for emission of only N=1 states at an accelerating voltage of 200 V. For ion emission only and at an extraction voltage of 2000 V, the specific impulse is 6600 seconds. The specific impulse range for each propellant for extraction voltages from 200-2000V is shown in Table 5. [Bmim][dca] and [Bmim][NO_3] have similar ranges because they only differ slightly in molecular weight. HAN achieves the highest specific impulse because it is the lowest molecular weight of the propellants selected. The highest molecular weight propellant, [Emim][Im], has a range of 4800 seconds, while HAN has a range of 7800 seconds. The range of the other propellants falls in order of molecular weight as seen in Table 5, indicating that lower molecular weight propellants can be throttled more easily than higher molecular weight propellants.

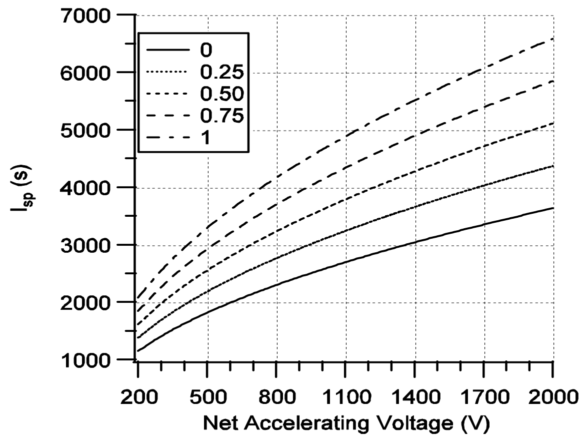

Figure 7. Electrospray Specific Impulse. *Specific impulse of [Bmim][dca] as a function of net accelerating voltage in an electrospray system.*

Table 5. Range of Specific Impulse of Ionic Liquid Propellants.

Propellant	I_{sp} (s)
[Bmim][dca]	1100-6600
[Bmim][NO_3]	1100-6700
[Emim][$EtSO_4$]	1000-5800
[Emim][Im]	800-5000
HAN	1700-9500

One of the major limitations on electrospray propulsion currently is the number of emitters required to produce thrust levels high enough to be useful in actual satellite operations. Fig. 8a shows the number of emitters required to produce a given thrust level for each propellant when emitting only the first solvated state (*N*=1), and Fig. 8b shows the same for pure ion emission (*N*=0). As expected, for a constant current per emitter, the heavier propellants require less emitters to produce a given thrust level, and droplet (*N*=1) emission also requires less emitters due to heavier species being extracted. For every thrust level and ion fraction, [Bmim][dca], [Bmim][NO_3], and [Emim][$EtSO_4$] require 91%, 94%, and 66% more emitters, respectively, than [Emim][Im]; however, the number of emitters required is 53%, 52%, and 59% less than HAN, respectively. For each propellant, at a constant thrust level, the number of required emitters is always 66% less when emitting *N*=1 species compared to pure ion emission (*N*=1).

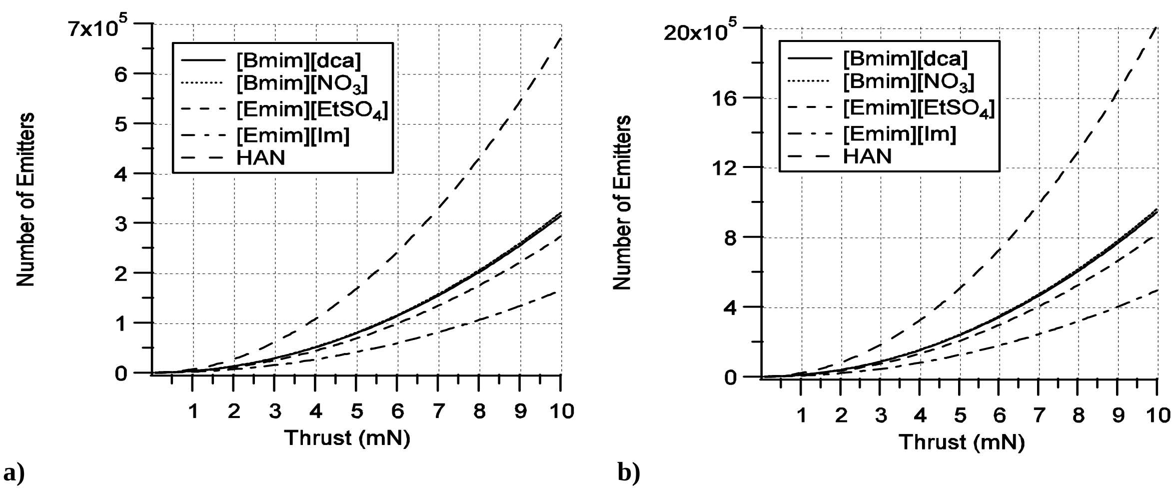

Fig. 8 Number of Emitters Required for a) R_A=0 and b) R_A=1. *Number of electrospray emitters required to produce a given thrust level for each IL propellant.*

More conclusions can be drawn by considering the net accelerating voltage required to produce a given thrust level. For an electrostatic thruster device, the thrust is a constant function of specific impulse, and does not depend on the propellant choice (Eq. (11)). Since this is the case, the specific impulse required to produce a given thrust can be dialed in by changing the net accelerating voltage for a given propellant. Fig. 9 shows the net accelerating voltage required to produce a specific impulse that produces a given thrust at constant power level. For each case, the lower molecular weight propellants require less net accelerating voltage, and emission of pure ions also results in less net accelerating voltage. HAN requires 53%, 52%, and 60% less net accelerating voltage than fuels [Bmim][dca], [Bmim][NO_3], and [Emim][$EtSO_4$], respectively. The same fuels require 47%. 48%, and 39% less accelerating voltage than [Emim][Im].

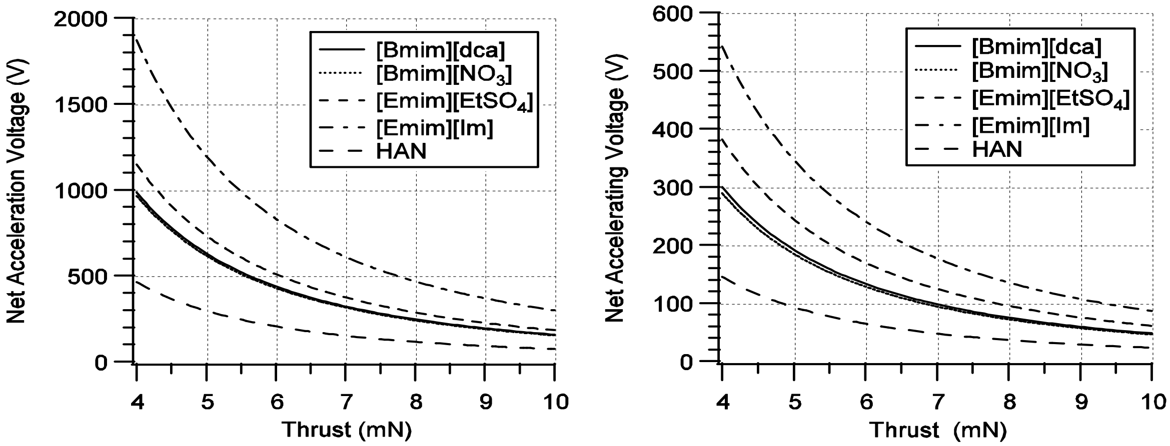

Figure 9. Net Accelerating Voltage Required for a) R_A=0 and b) R_A=1. *Net accelerating voltage required to produce a given thrust level for each IL propellant in an electrospray system.*

C. Electrospray Performance of Ionic Liquids in Binary Mixtures

In the preceding sections, ionic liquid binary mixtures have been suggested as a potential route toward development of a true dual-mode propellant. It was shown that the chemical performance of these propellants may theoretically exceed that of some state-of-the-art monopropellants. The electrospray performance is more difficult to analyze because electrospray research on ionic liquids has focused on single ionic liquids. Mixtures of liquids have been studied as electrospray propellants, but most were simply solutions consisting of a salt and an electrically insulating solvent.[14] Garoz[58] studied a mixture of two ionic liquids, but did not study the composition of the droplets in the plume. A mixture of two ionic liquids may yield emissions more complicated than a single liquid since two liquids could be ionized and extracted. Extraction of pure ions would yield four possible emitted species: two cations and two anions. Extraction of higher solvated states may yield many more possible emitted species since the two salts essentially dissociate in solution and remain in chemical equilibrium, although the solution remains neutral. For example, the only N=1 solvated state of the cation of [Bmim][dca] is $[Bmim]^+$-[Bmim][dca]; however, extraction of the $[Bmim]^+$ cation in an N=1 solvated state from a mixture of HAN and [Bmim][dca] could yield $[Bmim]^+$-[Bmim][dca], $[Bmim]^+$-HAN, or even $[Bmim]^+$-$[Bmim]^+$-$[NO_3]^-$. Although this poses an interesting research question, analysis of binary mixtures as electrospray propellants for this study is restricted to the extraction of pure ions only. As shown in the preceding section, the trends should still hold.

The number of emitters required and required extraction voltage to produce an electrospray thrust level of 5 mN is computed as a function of percent oxidizer in the binary monopropellant mixture. The results are shown in Figs. 10 and 11. The same trends are shown as with the single ionic liquids: higher molecular weight mixtures require less emitters and higher net accelerating voltage to produce a given thrust level. For emission of pure ions, [Emim][Im] requires 125000 emitters to produce 5 mN of thrust, and HAN requires 500000. From the chemical performance analysis, the binary mixture of fuels [Bmim][dca], [Bmim][NO_3], and [Emim][$EtSO_4$] with HAN oxidizer reached a combustion temperature, and thus performance, roughly equal to ADN-based monopropellant FLP-103 at 69%, 61%, and 59% oxidizer. From Fig. 10, this equates to 26%, 30%, and 37% less emitters than required for pure HAN, but pure [Emim][Im] requires 66%, 64%, and 60% less emitters than the ionic liquid fuels, respectively. From Fig. 11, the required net accelerating voltage is 22%, 27%, and 41% higher than for pure HAN, but 67%, 66%, and 62% lower than [Emim][Im], respectively. From the chemical performance analysis, the minimum amount of oxidizer required for elimination of solid exhaust species is 58%, 44%, and 41% for each fuel respectively. At these mixture ratios, the required number of emitters is now 32%, 38%, and 46% less than required for pure HAN. The net accelerating voltage required is 24%, 30%, and 40% higher than for pure HAN.

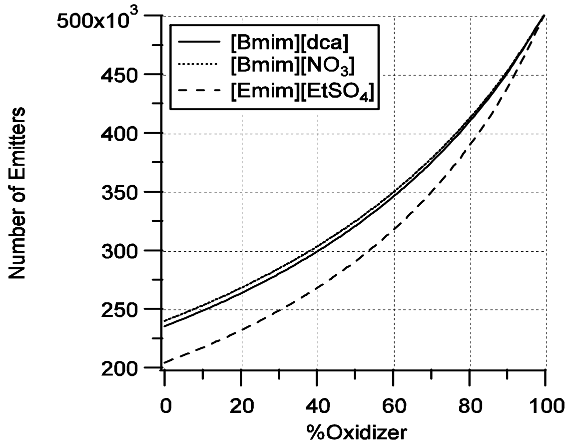

Figure 10. Number of Emitters. *Number of electrospray emitters required to produce 5 mN of thrust as a function of percent HAN oxidizer for IL binary mixtures.*

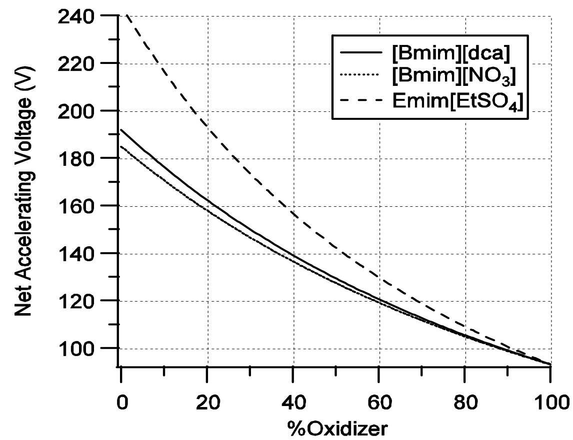

Figure 11. Net Accelerating Voltage. *Net accelerating voltage required to produce 5 mN of thrust in an electrospray system as a function of percent HAN oxidizer for IL binary mixtures.*

V. Discussion

The results of the chemical performance analysis are promising because the ionic liquids show better performance as bipropellants when burned with HAN, and acceptable performance when paired with standard oxidizers NTO and IRFNA. Even more promising for dual-mode propulsion is their performance as fuel components in a high-molecular weight binary monopropellant mixture, which may theoretically exceed the performance of some state-of-the-art advanced monopropellants. The electrospray performance of these ionic liquids is promising and may yield higher performance than the current state of the art, but also may be limited by current technology levels. The results of the preceding sections are discussed and overall feasibility of imidazole-based ionic liquids as dual-mode propellants is assessed.

A. Imidazole-Based Ionic Liquids as Monopropellants

Considering solely a thermal decomposition of the ionic liquids as monopropellants shows poor performance in terms of specific impulse, but slightly more acceptable performance in terms of density specific impulse as all of the ionic liquids in the study have greater density than hydrazine. However, this must be re-examined considering the fact that a shifting equilibrium assumption was employed due to the solid carbon present in the exhaust. Typically, shifting equilibrium specific impulse is an over-estimate of actual specific impulse. Sutton[8] suggests that this is a 1-4% over-estimate. If this is taken as 4%, the highest performing ionic liquid, [Bmim][NO_3], now falls 9% below hydrazine in terms of density specific impulse and 22% below hydrazine in terms of specific impulse. The solid carbon formation in the exhaust gases leads to the poor performance directly. Furthermore, solid exhaust particles are also objectionable in many spacecraft applications because they degrade functional surfaces such as lenses and solar cells,[8] and could cause a cloud of orbital debris. The solid carbon formation is a direct result of the lack of oxidizer present in the anion compared to the large organic alkyl substituted chains in the cation for the imidazole-based ionic liquids. While these high molecular weight organic chains are favorable for electrospray propulsion application, they are detrimental to the chemical aspect of a dual mode system. The highest performing ionic liquid is [Bmim][NO_3], which contains three oxygen atoms that form small amounts of water and carbon monoxide that lead to its higher performance. Despite having an additional oxygen atom, the large negative heat of formation of [Emim][$EtSO_4$] produces a lower overall energy release, and therefore leads to its poor performance. [Bmim][dca] performs slightly better than [Emim][$EtSO_4$] because it has a large, positive heat of formation despite containing zero oxidizing components.

B. Imidazole-Based Ionic Liquids as Bipropellants

Utilizing imidazole-based ionic liquids as bipropellants when burned with standard storable oxidizers is more promising. For all of the ionic liquids, NTO outperforms IRFNA. This is typical of most propellants since NTO has a higher heat of formation. The greatest performance of the ionic liquids is obtained by [Bmim][dca] for each oxidizer. [Bmim][NO_3] has the second highest performance for all oxidizers, followed by [Emim][$EtSO_4$]. The trend, therefore, seems to be that higher performance is obtained through decreasing oxidizer content in the anion. Again, this is due to the high heat of formation obtained by utilizing solely fuel components in the ionic liquid. The highest performing ionic liquid bipropellants will therefore contain no oxidizing elements, as with [Bmim][dca]. Although the performance falls below the current state-of-the-art bipropellants when the ionic liquids are burned with standard oxidizers NTO and IRFNA, this slightly lower performance may be deemed acceptable, particularly in favor of the mission flexibility offered by the dual-mode system. HAN is the lowest performing oxidizer, but may offer additional flexibility compared to NTO and IRFNA since it has the potential to be used for electrospray propulsion. Additionally, the performance values shown in Fig. 1 for HAN oxidizer are unobtainable limits, since HAN is actually a solid at room temperature. Considering aqueous HAN with 5% additional water, however only lowers the computed specific impulse by roughly 2%, although the water may pose an issue for electrospray propulsion and will be discussed further in the electrospray section.

In order to use these ionic liquids as bipropellants, they must also be readily ignitable. For spacecraft, the preferred ignition method is by hypergolic reaction. [Bmim][dca] has been investigated as a hypergolic fuel, and results are reported in literature.[55.59.60] It was observed to readily ignite with nitric acid, and although reactivity was reported for NTO, it did not ignite. In general, ionic liquids with the nitrate anion have not shown hypergolic behavior with standard storable oxidizers.[60] Since [Bmim][dca] shows the highest bipropellant performance of the investigated ionic liquids, favorable electrospray properties, as well as hypergolic ignition capabilities, it represents a strong candidate for further research. The prospect of utilizing [Bmim][dca] as a spacecraft bipropellant fuel and electrospray propellant appears feasible.

C. Binary Mixtures of Imidazole-Based Ionic Liquids as Monopropellants

Imidazole-based ionic liquids as fuel components in a binary mixture with HAN oxidizer may be a viable option for dual-mode monopropellants. The specific impulse computed via the shifting equilibrium assumption at a combustion temperature of roughly 1900 K for the ionic liquid monopropellant blends is 1-4% higher than that of FLP-103, and roughly equal to that of FLP-103 with a frozen flow assumption. This is a feat considering the predicted combustion temperature for FLP-103 is actually 2000 K. The reason for the improved performance of the ionic liquid monopropellant blends is the combustion products that are formed. At the conditions producing a 1900 K chamber temperature, the binary ionic liquid mixtures form incompletely oxidized species CO, H_2, and N_2, as shown in Fig. 4. By contrast, the ADN-based monopropellants such as FLP-103 have been specifically designed to provide a complete combustion with major products CO_2, H_2O, and N_2.[10] Examination of Eq. (5) shows that lower molecular weight exhaust products yield higher specific impulses. The lower molecular weight combustion products of the binary ionic liquid mixtures lead to higher specific impulse despite slightly lower combustion temperature compared to FLP-103. In terms of density specific impulse, the binary mixtures of ionic liquids are 8-9% greater than FLP-103 for the frozen flow assumption, which yielded roughly equal specific impulse. The main consideration here is the ingredients in each mixture. The density of the fuel component, methanol, in FLP-103 is 0.79 g/cc.[50] The ionic liquid fuels have a much higher density, making their use as fuel components in a monopropellant mixture attractive. Additionally, FLP-103 contains a large amount of water, which also lowers the density of the mixture.

These types of binary mixtures have been shown to be advantageous in terms of performance, but practically they must be chemically compatible and also be thermally stable and readily ignitable. As mentioned previously, mixtures of [Bmim][dca] with HAN have notably shown no visible reactivity, leading to the possibility that they may indeed be thermally stable at room temperature. However, this represents somewhat of an unknown presently as this has not been measured quantitatively. Literature suggests that mixtures of ammonium salts with dicyanamide anions may not be compatible.[61-63] [Bmim][NO_3] or [Emim][$EtSO_4$] may be compatible with HAN, but HAN may not be miscible in either liquid, requiring a third liquid solvent which may be undesirable. Furthermore, it is also unknown whether these mixtures will ignite by reasonable thermal or catalytic means. These ignition methods represent the most common and reliable means of igniting a monopropellant and verification of this is a major milestone in any monopropellant development effort.

D. Imidazole-Based Ionic Liquids as Electrospray Propellants

In terms of electrospray performance, the ionic liquid fuels investigated show potential to be higher performing than the current state-of-the-art in electrospray propellants; however, they may present a challenge in terms of the current technology levels. The ionic liquid fuels investigated in this study have the potential to have higher performance, and also greater flexibility, than the current state-of-art electrospray propellant [Emim][Im]. This is a direct result of the lower molecular weight of the investigated ionic liquids compared to [Emim][Im]. However, low molecular weight may be a detriment to electrospray propulsion. Considering the number of emitters required to produce thrust levels typical of electric propulsion missions shows this effect. To produce 5 mN of thrust with emission of pure ions, [Bmim][dca], [Bmim][NO_3], and [Emim][$EtSO_4$] require 200000-235000 emitters compared to 125000 for [Emim][Im]. If the current technology limit is taken as 13000 emitters per cm^2,[64] this equates to a total area of 15-18 cm^2 for the ionic liquid fuels compared to 9.5 cm^2 for [Emim][Im]. By comparison, the 200 W SPT-35 Hall thruster has an area of 9.6 cm^2 and produces a thrust of 11 mN.[65] Purely ionic emission of HAN requires a total area almost four times larger of 38.5 cm^2 to produce 5 mN of thrust. From Figs. 9 and 10, it is seen that lower molecular weight propellants require a lower net accelerating voltage. However, considering that typical extraction voltages range from roughly 1.5-2.5 kV,[14] the lower molecular weight propellants will actually require a deceleration grid. The magnitude of the deceleration increases with decreasing molecular weight to actually throttle to the specific impulse required to produce a given thrust level at constant power. Improvements in electrospray technology will help reduce the required number of emitters to produce a given thrust level; however, the heavier ionic liquid propellants will always require less emitters, and therefore less massive electrospray systems as a whole.

The performance of imidazole-based ionic liquids as electrospray propellants has been computed using a simplified model for electrostatic thrusters. For purely ionic emission, the charge of the particles should be equal to the fundamental charge; however, ions attached to one or more neutral pairs will undoubtedly have a less efficient charge due to the presence of some finite dielectric neutral liquid. Chiu[66] reports nearly purely ionic emission for the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF_4]) at an accelerating voltage of 1.5 kV. Examination of the time of flight curves from Chiu's[66] experiments shows that roughly 60% of the species emitted were pure ions. Some N=2 species were detected, but were negligible compared to the N=0 and N=1 states. Using Eqs. (9) and (10) yields a specific impulse of 4600 seconds for these conditions. From the experimental results, Chiu[66] calculated a specific impulse of 4000 sec. So, while the simple electrostatic relationships overestimate the performance, they provide a reasonable estimate for emitted species of the first two solvated states. Regardless of this fact, the basic trends shown in this analysis should hold; however, the performance obtained for the lower ion fractions may be overly optimistic.

E. Binary Mixtures of Ionic Liquids as Electrospray Propellants

The chemical performance of ionic liquids in binary mixtures is promising; however achieving good performance with current technology in the electrospray mode may present more of a challenge. The reason is the same as discussed above: the low molecular weight of the propellants. This issue is compounded by adding ionic oxidizers, such as HAN, which have a much lower molecular weight than even the ionic liquid fuels investigated in this paper. To achieve chemical performance equal to ADN-based FLP-103, the number of emitters required to produce 5 mN of thrust is 370000, 352000, and 315000 emitters when using [Bmim][dca], [Bmim][NO_3], and [Emim][$EtSO_4$] as fuels, respectively. Therefore, to achieve equal chemical and electrospray performance, [Emim][$EtSO_4$] requires 15% less emitters than [Bmim][dca], thereby saving roughly 15% mass in terms of the emitter hardware. It is therefore more ideal for dual-mode propellants to use fuels with high molecular weight, but that have oxidizing elements, as equal performance may be obtained in both modes, but with a reduction in electrospray hardware.

F. Considerations for Dual-Mode Propellant Design

Imidazole-based ionic liquids with energetic anions were investigated here due to their already proven feasibility as electrospray propellants. Due to the fact that these ionic liquids contain a large amount of organic fuel in their cations, good performance as monopropellants is not easily attainable. Using these types of ionic liquids as bipropellants is feasible, but at lower performance than state-of-the-art bipropellant systems. The preferred ionic liquid bipropellants will be those with no oxidizer present in the energetic anion group, such as the dicyanamide anion investigated previously. [Bmim][dca] shows favorable bipropellant performance as well as favorable electrochemical properties. Additionally, it has been proven experimentally to be hypergolic with nitric acid. Because its electrospray capability has not been tested experimentally, it is difficult to determine if this is definitively a good dual-mode propellant, but the results show that with relatively minimal increases in electrospray technology it may be beneficial. In terms of propellant formulation, advances in dual-mode bipropellants should include attempts to find fuels with higher heats of formation and higher molecular weights, while not compromising the minimum physical properties required to actually electrospray the propellant. Additionally, the ideal in dual-mode bipropellants will be hypergolic with another ionic liquid oxidizer, such that both can be electrosprayed.

The ultimate goal of this type of dual-mode system will be the utilization of a single liquid as a monopropellant and electrospray propellant. As mentioned previously, this represents the most flexible configuration for mission design, and for small satellites may be ideal where volume is limited and may not allow for an additional propellant tank and other hardware. Based on the results, the current adequately characterized imidazole ionic liquids will not provide good performance as monopropellants due to the fact that they are very fuel rich. If it is possible to combine two ionic liquids into a binary mixture that represents a storable monopropellant, this class of ionic liquids may present some potential. Based on the results from the three ionic liquids studied here, ionic liquids that have more oxidizer can produce equal performance to that of more fuel rich ionic liquids in binary mixtures in both modes. However, since typical oxidizers are much lower in molecular weight than the ionic liquid fuels, the fact that less additional oxidizer is necessary results in improved electrospray capabilities.

Actually forming a mixture of two ionic liquids in solution that are chemically compatible may be difficult. Typically, green monopropellants such as FLP-103 and other HAN-based formulations include a fuel component and a solvent, typically water, to hold these in solution. For dual-mode monopropellant mixtures, it may be most desirable to reduce the amount of solvent used as much as possible. The reason is this: volatile solvents, such as water, limit the electrospray capabilities of the propellant since these substances will boil off in vacuum and essentially be unusable for propulsive purposes. Additionally, this could also affect the formation of a stable Taylor cone. Therefore, the most ideal dual-mode monopropellant mixture will include a binary mixture of fuel and oxidizer that are miscible without the need for a volatile solvent.

The ultimate in dual-mode propellants, however, may be a single liquid which would provide enough oxidizer in the anion to combust to gaseous products CO, H_2, and N_2, while still retaining reasonable electrospray properties. Such an ionic liquid has been dubbed an oxygen-balanced ionic liquid. This idea of an oxygen-balanced ionic liquid is not new, as attempts have been made to synthesize such a liquid for energetic use.[67,68] The ionic liquids synthesized by Tao, et, al.[67] were based on lanthanide nitrate complex anions and either triazole- or tetrazole-based cations. The ionic liquids synthesize by Christe and Drake[68] were imidazole-based. A few of these ionic liquids were reportedly stable, for example 1-ethyl-3-methylimidazolium tetranitratoaluminate ($C_6H_{11}N_6AlO_{12}$). These are not ideal spacecraft monopropellants as their combustion forms a significant amount of solid products, such as Al_2O_3. Solid combustion products are objectionable in many spacecraft applications, as mentioned previously.[8] Furthermore, it is unknown to this point whether these propellants have the electrochemical properties required for electrospray propulsion. However, to illustrate what may be possible, the molecular weight of 1-ethyl-3-methylimidazolium tetranitratoaluminate is 386 g/mol, comparible to [Emim][Im]. For future design considerations of dual-mode monopropellants, the effect of adding oxidizing species to the anion on the surface tension and electrical conductivity of ionic liquids must be quantified, and elimination of metallic elements in the anion must be achieved.

VI. Conclusions

Imidazole based ionic liquids have been examined as potential candidates for dual-mode chemical mono- or bipropellant and electrospray propulsion. Physical properties required of ionic liquids for dual-mode spacecraft propulsion were identified to be high density, low melting temperature, high electrical conductivity, high surface tension, and high molecular weight. These properties should be comparable to current state-of-the-art propellants hydrazine and [Emim][Im] for the chemical and electrical modes, respectively. Three ionic liquids were identified that exceed or are close to meeting the physical property criteria: [Bmim][dca], [Bmim][NO_3], and [Emim][$EtSO_4$].

Theoretical chemical performance is calculated for these ionic liquids using the NASA CEA computer code and performance equations. Considering these ionic liquids as monopropellants shows that they do not perform well compared to hydrazine. The bipropellant performance shows slightly more promise, as the ionic liquids when burned with NTO oxidizer showed 6.5-10% lower performance than the MMH-NTO bipropellant combination. Considering the ionic liquids as fuel components in a binary monopropellant mixture with 60-70% HAN oxidizer shows performance exceeding that of ADN-based monopropellants. Ionic liquids with more oxidizing elements in the anion require less additional HAN oxidizer to form gaseous CO, and thus achieve an acceptable level of performance.

Examination of the electrospray performance of these ionic liquids shows that they may compete with current state-of-the-art propellants with improvements in technology. High molecular weight propellants reduce the number of required electrospray emitters, while also requiring accelerating voltages nearer to typical extraction voltages. The addition of a lower molecular weight oxidizer to an imidazole-based ionic liquid fuel increases the number of emitters required, but is necessary to obtain good chemical performance. Ionic liquid fuel components with oxidizing components in the anion require less additional oxidizer to achieve similar chemical performance, thereby reducing the number of required emitters for electrospray propulsion. By extension, oxygen-balanced ionic liquids may be the ultimate in dual mode propulsion as they have the required oxidizer to combust into complete products, while most likely retaining high molecular weight favorable to electrospray propulsion.

Due to their fuel rich nature, imidazole based ionic liquids are suitable candidates for bipropellant propulsion. [Bmim][dca] has been proven to be hypergolic with WFNA and shows potential for electrospray propulsion. [Bmim][dca] is therefore a good candidate for a bipropellant dual-mode system. The dual-mode configuration allowing for the most flexibility, however, includes a chemical monopropellant thruster. Binary mixtures of high molecular weight ionic liquid fuels and oxidizer may be a potential route to a dual-mode monopropellant since good performance can be attained in both modes. The biggest challenge to achieve this may be identifying oxidizer and fuel combinations that are miscible, as addition of a volatile solvent, such as water, is detrimental to electrospray propulsion. The ideal dual-mode propellant will be an oxygen-balanced liquid that does not combust into solid products. Furthermore, it must not sacrifice electrochemical properties of high electrical conductivity and high surface tension. At this time, there is not enough information available to determine the feasibility of realizing this type of propellant.

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