JOURNAL OF PROPULSION AND POWER
Vol. 21, No. 2, March–April 2005

Ionic Propulsion Based on Heated Taylor Cones of Ionic Liquids

I. Romero-Sanz,* I. Aguirre de Carcer,† and J. Fernandez de la Mora‡
Yale University, New Haven, Connecticut 06520-8286

Electrical propulsion characteristics of emissions from heated Taylor cones in vacuo are investigated for the ionic liquid 1-ethyl-3-methylimidazoliumbis(perfluoroethylsulfonyl)imide. Low specific impulses are encountered at room temperature. However, the drop size decreases and the ion currents become very large at increasing temperatures, leading above 119°C to the appearance of a purely ionic regime with currents in excess of 4 μA. This mode of operation leads to thrusts approaching 1 μN per Taylor cone, at a specific impulse above 2000 s. The ion beam is dominated by the dimer ion (~80%), with a mass-over-charge ratio larger than 600 amu, substantially larger than possible with traditional ion sources. The purely ionic regime had been previously observed in room-temperature 1-ethyl-3-methylimidazolium$^+$-BF_4, but this is the first report where this regime exists over a wide range of currents. The levels of both thrust and specific impulse reported are considerably higher than those previously attained from single Taylor cones of organic electrolytes.

Nomenclature

g = gravity constant
I = current emitted by the spray
m = particle mass
Q = volumetric flow rate of electrosprayed liquid
q = charge on the drops (elementary charge for the ions)
u = particle velocity
V_0 = acceleration voltage
ρ = density of the liquid

I. Introduction

INTEREST in using charged drops produced from Taylor cones[1–3] for electrical propulsion dates back to the sixties,[4,5] but has been revitalized in recent years.[6,7] This has led to a search for propellant materials with performance superior to that of the traditionally used glycerol,[8] with an emphasis on those having substantially higher electrical conductivity and much lower viscosity.[9] Formamide offers some very interesting characteristics, though its finite vapor pressure calls for use of emitter tips only a few micrometers in diameter.[10] To overcome this volatility problem, we have recently reported on the use of room-temperature molten salts (ionic liquids) as alternative materials for forming Taylor cones in a vacuum.[11] These propellants combine the advantage of high electrical conductivity[12–15] with essentially zero vapor pressure, and this has stimulated similar investigations from other groups.[16,17] In particular, we have found that the ionic liquid EMI-BF_4 (EMI = 1-ethyl-3-methyl imidazolium$^+$), when electrosprayed in a vacuum at room temperature, exhibits a regime where it emits exclusively ions with no accompanying drops.[11] This finding suggests using Taylor cones of ionic liquids not only for colloidal, but also for ionic propulsion. The initial motivation for this shift was the promise of ionic liquids to yield ions with a mass/charge ratio intermediate between those already available from plasma sources ($m/z \sim 100$ amu) or colloidal devices ($m/z > 10^5$ amu). Figure 1 shows such ranges schematically, revealing a wide gap between about 10^5 amu and about 100 amu. This gap may currently be covered only partially and at limited propulsion efficiency in the mixed regime, where both ions and drops are produced. Here we will show that the low-mass end of the gap can also be covered at high propulsion efficiency with commercially available ionic liquids going up to about 600 amu (Phase I in the figure). The indicated Phase II extending to several kdalton is hypothetical, but not as far-fetched as may appear, because room-temperature ionic liquids with anion or cation masses in excess of 3 kdalton have already been reported. The propulsive interest of reaching this intermediate mass/charge range is well known, because the minimization of the weight of propellant calls for large specific impulse (small m/z), whereas the minimization of the associated weight of the power unit calls for a reduction in specific impulse. The optimal condition balancing these conflicting requirements is somewhere in between; hence the interest in a variety of missions to be able to cover the currently unavailable m/z range.

Our previous work with EMI-$BF_4$was limited in several respects. First, the modest currents (a few hundred nanoamperes) and mass flows yielded by a single Taylor cone of EMI-BF_4 in the purely ionic regime provided maximal thrusts less than 0.02 μN. Second, the emissions were dominated by the dimer ion BF_4–EMI_2^+, with a mass of 308.6 amu. Although this value is substantially better than can be reached at present with either plasma sources or liquid-metal ion sources, it is short of what can in principle be attained by ionic liquid propellants. Our present objective is therefore not only to test some of the heavier commercially available ionic liquids for their electrical propulsion characteristics, but also to achieve larger ion currents.

II. Experimental

The experimental apparatus is sketched in Fig. 2 and is similar to that previously described.[11] A conductive liquid is introduced into a high-vacuum system through a stainless steel capillary needle connected to an external vial. The liquid is then electrosprayed by applying a voltage difference between the needle and the extractor (grounded in this study). After the voltage is interrupted with a homemade switch at time $t = 0$, one can record the current received at the collector as a function of the time of flight (TOF) or t:

$$I = I(\mathrm{TOF}) = I(t) \tag{1}$$

Approximate values of the key propulsive parameters can be obtained from the time of flight curves, as in Gamero-Castaño and Hruby,[6] by assuming that there is no irreversible voltage drop in the process of forming the drops and the ions. Assuming that they are ejected with an energy qV_0, where V_0 is the needle voltage, energy conservation yields the distribution of the ratio m/q = mass/charge

Presented as Paper 2003-4846 at the AIAA/ASME/SAE/ASEE 39th Joint Propulsion Conference and Exhibit, Huntsville, AL, 20–23 July 2003; received 27 September 2003; revision received 25 August 2004; accepted for publication 25 August 2004.

*Graduate Student, Department of Mechanical Engineering. Member AIAA.
†Postdoctoral Associate, Department of Mechanical Engineering.
‡Professor, Department of Mechanical Engineering.

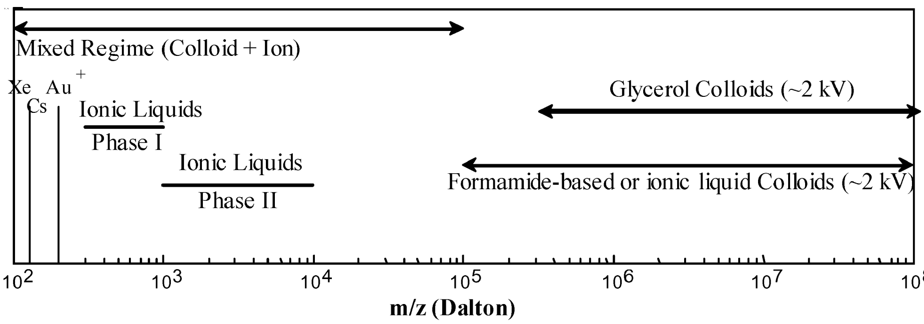

Fig. 1 Potential fuels for electrical propulsion as function of mass over charge ratio.

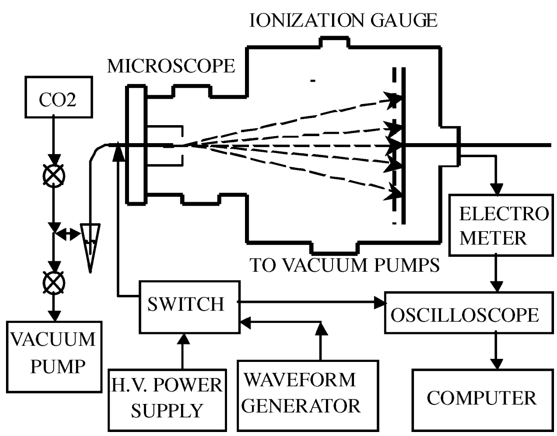

Fig. 2 Experimental apparatus.

[Eq. (2)], where L is the total flight length:

$$m/q = 2V_0(t/L)^2 \tag{2}$$

Considering a group of particles with arrival time in the interval δt, the associated current is obtained from the TOF measurement:

$$\delta I = \delta t[\mathrm{d}I(t)/\mathrm{d}t] \tag{3}$$

The corresponding mass flow and thrust can be then obtained as

$$\delta m' = -\delta I m/q = -\delta I \left(2V_0 t^2 \big/ L\right)^2 \tag{4}$$

$$\delta T = -\delta m' u = \delta I(2V_0 t/L) \tag{5}$$

Total values for both mass flow rate (m') and thrust (T) may therefore be obtained by integration from $t = 0$ to $t = \infty$ in Eqs. (4) and (5):

$$m' = \rho Q = -\frac{2V_0}{L^2}\int_0^\infty \frac{\mathrm{d}I}{\mathrm{d}t} t^2\,\mathrm{d}t = \frac{2V_0}{L^2}\int_0^\infty I(t)2t\,\mathrm{d}t \tag{6}$$

$$T = -\frac{2V_0}{L}\int_0^\infty \frac{\mathrm{d}I}{\mathrm{d}t} t\,\mathrm{d}t = \frac{2V_0}{L}\int_0^\infty I(t)\,\mathrm{d}t \tag{7}$$

Other propulsive parameters such as the specific impulse (I_{sp}) and the efficiency (η) can also be calculated:

$$I_{\mathrm{sp}} = T/m'g = u/g \tag{8}$$

$$\eta = T^2 \big/ 2m'V_0 I \tag{9}$$

Note that neither the ion energy, the mass flow rate, nor the thrust is measured directly, as this is primarily a qualitative exploration of whether the purely ionic regime is accessible in ionic liquids of increasing molecular weights.

The collector electrode was preceded by a 75% transparent metal screen, meant to avoid detection of the beam ions by induction prior to their arrival. This screen was biased negatively (generally at 9 V) to avoid escape of secondary electrons from the collector. All the currents reported in this paper and the derived quantities defined in Eqs. (1–9) are corrected for the 25% loss at the screen. The spraying needle used was made of stainless steel, with an inner diameter (184±20 μm) considerably larger than used before, in part forced by the high room-temperature viscosity of ionic liquids used. Two ionic liquids were tested, with properties reported in Table 1. We are not aware of published data for the viscosity of 1,2-dimethyl-3-propylimidazolium methide (DMPI-Me), nor of values of any of these properties at higher temperatures. Both liquids are commercially available from Covalent Associates Inc. (Woburn, MA). DMPI-methide turned out to be too viscous to be tested at room temperature, because the maximum pressure we could apply to the liquid reservoir yielded a flow rate smaller than the minimum required to stabilize the Taylor cone.

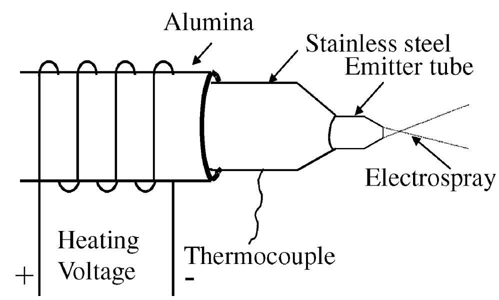

Fig. 3 Heated electrospray source.

Table 1 Physical properties at ambient conditions for the ionic liquids studied[a]

Liquid	m^+ (amu)	m^- (amu)	dimer$^+$ (amu)	ρ (g/cm^3)	γ (dyn/cm)	K (S/m)	μ (cP)
EMI-Beti	111.2	380.1	602.5	1.6	31.18	0.34	61
DMPI-Me	139.3	411.2	689.8	1.55	37.83	0.046	unknown

[a]EMI = 1-ethyl-3-methylimidazolium; DMPI = 1,2-dimethyl-3-propylimidazolium; Beti = $[(C_2F_5SO_2)_2N^-]$ = bis(perfluoroethylsulfonyl)imide; Me = Methide = tris(trifluoromethylsulfonyl) methide = $[(CF_3SO_2)_3C^-]$.

An important variation from Ref. 10 is that we may heat the emitting tip up to several hundred degrees Celsius by means of the small heating element in Fig. 3. Heating the Taylor cones is an essential feature of the present study, because the use of heavier and more viscous salts reduces their electrical conductivity (Table 1) well below the value for EMI-BF_4, giving little hope of reaching the purely ionic regime at room temperature.

The emitting capillary emerges at the end of the steel tube on the right of Fig. 3, where a K-type thermocouple is spot-welded. The alumina tube surrounding the steel tube is wound with heating nichrome wire covered with ceramic glue (Duralco 4700; Cotronics Co.) and powered with a variable-voltage transformer. The system is held by a Teflon cylinder on the left (not shown) that serves also as the support of an extractor electrode. The Teflon is attached to the flange coupling the source to the vacuum chamber.

By placing two thermocouples on the free end of the stainless steel tube, we have confirmed that the temperature to the right of the heating element is independent of position. Hence, the free end of the source is adiabatic and the temperatures in the meniscus and the thermocouple coincide.

III. Results

Figures 4a-4e summarize our results with Taylor cones of EMI$^+$-Beti$^-$ formed in a vacuum at varying liquid temperature. Each figure shows several traces corresponding to different propellant flow rates (quantified by the pressure pushing the liquid) and emitter voltages. The most relevant propulsive parameters derived from these $I(t)$ traces [according to Eqs. (2–9)] are collected in Table 2. Note that the table contains two main sources of ambiguity:

1) The large effect that a small current of large droplets has on the mass flow rate, the thrust, the specific impulse, and the propulsion efficiency.

2) The inaccuracy of the assumption that the ions and droplets all have an energy fixed by the needle voltage.

For these reasons, most of the numbers reported in the table should be interpreted more as approximate indicators than as precise performance parameters for thruster design. The large current fluctuations near $t = 0$, which are due to noise induced by the high-voltage switch on the electrometer, are removed for data analysis by treating the current as a constant ahead of the first step. In the purely ionic regime this initial noise occupies a fair fraction of the TOF trace, but the propulsive parameters are then defined just by the heights of the two steps and the masses of the two ions, both of which are either read from the graph or known independently.

At 22°C (Fig. 4a), one sees a first step at about 5 μs corresponding to ions, followed by abundant drops (100 to 400 μs). At 56°C (Fig. 4b), ions are already dominant. The main drops are also fairly small (flight times of ~30 μs), with an associated specific impulse of about 327 s. This is rather high for colloidal propulsion, particularly noting that the acceleration voltage is only 2 kV. With a postacceleration up to 5 kV the specific impulse would be 525 s. Unfortunately, a tail of much heavier drops leads to the considerably smaller overall specific impulses shown in Table 2. Note also that the ionic emission shows two steps. The dominant second step carries about 80% of the ion current and is associated with the dimer ion, which has an unusually large mass of 602.5 amu. In fact, there is only a factor of about 6 between the speed of these heavy ions and that of the drop step at 30 μs, so we are approaching conditions

Table 2 Propulsive parameters for EMI–Beti at different temperatures, needle voltages, and pressures driving the liquid[a]

Temp (°C)	Pressure (kPa)	I (nA)	Voltage (V)	m' (Kg/s)	Thrust (μN)	I_{sp} (s)	η %
22	1.87	204	2102	2.59E−09	0.95	37	40
	3.73	276	2123	1.19E−09	0.84	72	51
	6.13	412	2194	2.43E−09	1.40	59	44
	8.00	460	2528	7.49E−09	3.01	41	52
	1.76	572	2525	1.21E−08	4.25	36	52
56	6.40	850	2143	2.05E−09	1.55	77	32
	9.33	1700	1971	1.24E−09	1.33	109	21
	10.13	2400	2224	1.47E−09	1.80	125	21
	12.53	3375	2315	1.46E−09	2.71	189	31
	17.33	4050	2446	1.64E−09	2.67	166	24
119	**2.40**	**84**	**2184**	**4.30E−13**	**0.01**	**2947**	**98**
	3.20	**648**	**2062**	**4.81E−12**	**0.11**	**2227**	**86**
	4.80	2700	2143	1.25E−11	0.19	1559	25
	7.20	4500	2275	5.27E−11	0.79	1534	58
143	**3.20**	**1850**	**2022**	**1.69E−11**	**0.36**	**2182**	**96**
	4.00	**2950**	**2123**	**2.29E−11**	**0.46**	**2031**	**71**
	5.60	**4750**	**2649**	**3.96E−11**	**0.89**	**2283**	**96**
185	**4.80**	**3200**	**1880**	**2.53E−11**	**0.54**	**2157**	**94**
	5.33	**4150**	**2143**	**4.24E−11**	**0.83**	**1981**	**90**
	5.60	**5500**	**2133**	**4.65E−11**	**0.98**	**2152**	**88**

[a]Bold = pure ionic regime (drop-free). The liquid mass flow rate m', thrust, specific impulse I_{sp} and propulsion efficiency are computed from the time of flight curves as in Gamero and Hruby,[6] assuming that there is no irreversible voltage drop in the tip.

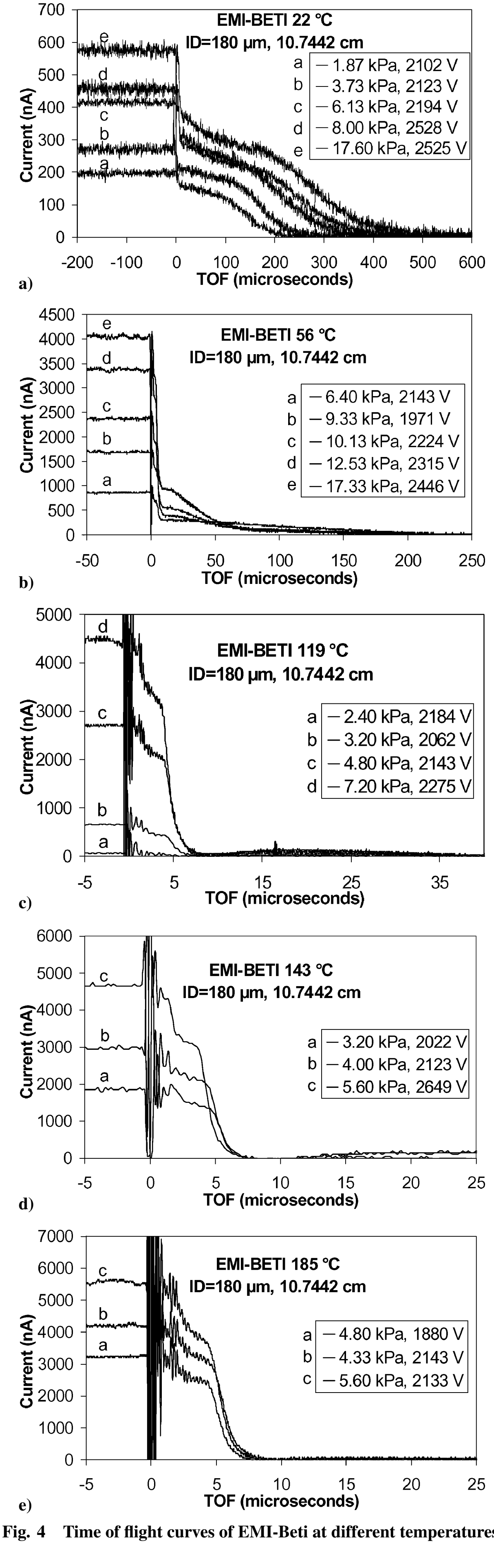

Fig. 4 Time of flight curves of EMI-Beti at different temperatures.

where the ions become so large and the drops so small that they begin to merge with each other. The purely ionic regime can first be seen at 119°C (Fig. 4c). As shown in Table 2, the lowest two traces, corresponding to the smallest currents, attain relatively high propulsion efficiencies, whereas the data at higher flow rates contain sufficient drops to decrease appreciably this figure of merit. At 143 and 185°C (Figs. 4d and 4e), the contributions from drops are minor at almost all flow rates. The fact that the purely ionic regime exists over a wide range of currents is an important variation from our earlier results with EMI-BF_4 at room temperature, where it was observed only at the minimum flow rate. Of even greater interest is that the combination of large current and large ion mass leads to a thrust level approaching 1 μN at a specific impulse larger than 2000 s, well above previously reported thrust for single Taylor cones of organic electrolytes or ionic liquids.

Similar preliminary measurements have been carried out with the DMPI-methide salt at 47, 77, and 119°C. The currents are below 600 nA, with modest ionic contributions at the two lowest temperatures. At 119°C the emissions are dominated by ions and reach near 2 μA. Although the purely ionic regime has not been attained at the temperatures investigated, the trends are similar to those of EMI-Beti. Operation at higher temperature was precluded by the appearance of bubbles on the meniscus. Originally it was unclear if this problem was due to the onset of thermal decomposition of the liquid, or rather to insufficient drying and degassing of the sample. Later work at Covalent Associates Inc. has established that the onset of DMPI-methide decomposition under a vacuum of 0.13 Torr (17.3 Pa) is 389°C, compared to 414°C at atmospheric pressure. Therefore, DMPI-methide should easily survive our conditions of temperature and pressure, and the bubbles must have been due to residual water and/or dissolved gas (Victor R. Koch, Covalent Associates, Inc., private communication). This conclusion is further strengthened by the high viscosity of this liquid (which drastically slows the liberation of bubbles) and the fact that it was degassed under vacuum only at ambient temperature.

IV. Conclusions

A study with two of the heaviest ionic liquids available commercially has revealed several features of considerable propulsive relevance.

1) The purely ionic regime is accessible for EMI–BETI under conditions leading primarily to dimer ions, at an m/z ratio in excess of 600 amu. This is a substantially higher m/z than previously available from liquid metals or plasma sources. The high ion currents observed ($\sim$4 μA) lead to thrust levels per Taylor cone approaching 1 μN, at specific impulses above 2000 s. This performance is much better than any previously reported based on Taylor cones of organic liquids.

2) Prior to reaching the purely ionic regime, EMI-Beti produces microampere current levels of unusually small drops (specific impulses in excess of 300 s) mixed with even larger ionic currents, leading to micronewton-level thrusts. Both the specific impulse and the thrust level per Taylor cone are considerably higher than previously attained by colloidal thrusters. This attractive performance is attained with relatively modest temperatures (56°C). Unfortunately the long tails of fewer large drops formed lead to a less satisfactory overall specific impulse in this mixed regime, and to low propulsion efficiency.

3) Controlling the temperature of the ionic liquids allows passing from a predominantly colloidal regime into a purely ionic regime with a single propellant. However, because the level of currents in the colloidal mode at room temperature is almost an order of magnitude smaller than in the ionic or mixed regimes at higher temperatures, near-colloidal operation does not offer a substantially higher thrust level, yet has a considerably smaller specific impulse and propulsion efficiency than the ionic regime.

4) A few preliminary results with the heavier salt DMPI-methide seem to indicate that even more massive and viscous molten salts than used here might be able to attain the purely ionic regime at temperatures within their thermal stability range.

After submission, a related study on EMI-BF_4 in the purely ionic regime appeared.[19]

Acknowledgments

This work has been supported in part by AFOSR Contract F-49620-01-1-1416 and by the Connecticut Analytical Corporation (NASA subcontract). We are most grateful to M. Gamero of Busek for his valuable contributions and for samples of the propellants tested. We have also benefited from useful discussions with V. Koch of Covalent Associates Inc. and J. Wilkes of the U.S. Air Force Academy.

References

[1]Taylor, G. I., "Disintegration of Water Drops in an Electric Field," *Proceedings of the Royal Society of London, Series A: Mathematical and Physical Sciences*, Vol. 280, No. 138, 1964, pp. 383–397.

[2]Taylor, G. I., "The Stability of a Horizontal Field Interface in a Vertical Electric Field," *Journal of Fluid Mechanics*, Vol. 2, No. 1, 1965, pp. 1–15.

[3]Cloupeau, M., and Prunet-Foch, B., "Electrostatic Spraying of Liquids: Main Functioning Mode," *Journal of Electrostatics*, Vol. 25, No. 2, 1990, pp. 165–184.

[4]Huberman, M. N., and Rosen, S. G., "Advanced High-Thrust Colloid Sources," *Journal of Spacecraft*, Vol. 11, No. 7, 1974, pp. 475–480.

[5]Kidd, P. W., and Shelton, H., "Life Test (4350 hrs.) of an Advanced Colloid Thruster Module," Paper AIAA 73-1077, 1973.

[6]Gamero-Castaño, M., and Hruby, V., "Electrospray as a Source of Nanoparticles for Efficient Colloid Thrusters," *Journal of Propulsion and Power*, Vol. 17, 2001, pp. 977–987.

[7]Martinez-Sánchez, M., Fernández de la Mora, J., Hruby, V., Gamero-Castaño, M., and Khayms, V., "Research on Colloid Thrusters," IEPC Paper 99-014, Oct. 1999.

[8]Krohn, V. E., "Glycerol Droplets for Electrostatic Propulsion," ARS Electric Propulsion Conference, Berkeley, CA, 1962.

[9]Gamero-Castaño, M., and Fernández de la Mora, J., "Direct Measurement of Ion Evaporation Kinetics from Electrified Liquid Surfaces," *Journal of Chemical Physics*, Vol. 113, No. 2, 2000, pp. 815–832.

[10]Bocanegra, R., Fernández de la Mora, J., and Gamero, M., "Ammonium Electrolytes Quench Ion Evaporation in Colloidal Propulsion," *Journal of Propulsion and Power*, Vol. 20, No. 4, 2004, pp. 728–735.

[11]Romero-Sanz, I., Bocanegra, R., Fernández 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.

[12]Wilkes, J. S., and Zawarotko, M. J., *Journal of the Chemical Society, Chemical Communications*, Vol. 13, July 1992, pp. 965–967.

[13]Fuller, J., Carlin, R. T., De Long, R. A., and Haworth, D., "Structure of 1-Ethyl-3-Methylimidazolium Hexafluorophosphate–Model for Room–Temperature Molten-Salts," *Journal of the Electrochemical Society, Chemical Communications*, Vol. 3, Feb. 1994, pp. 299–300.

[14]Ngo, H. L., LeCompte, K., Hargens, L., and McEwen, A. B., *Thermochemical Acta*, Vol. 357, Aug. 2000, pp. 97–102.

[15]Fuller, J., Carlin, R. T., and Osteryoung, R. A., "The Room Temperature Ionic Liquid 1-Ethyl-3-Methylimidazolium Tetrafluoroborate: Electrochemical Couples and Physical Properties," *Journal of the Electrochemical Society*, Vol. 144, No. 11, 1997, pp. 3881–3886.

[16]Lozano, P., "Studies on the Ion-Droplet Mixed Regime in Colloid Thrusters," Ph.D. Dissertation, Massachusetts Institute of Technology, Dec. 2002.

[17]Lozano, P., and Martinez-Sanchez, M., "Experimental Measurement of Colloid Thruster Plumes in the Ion-Droplet Mixed Regime," AIAA Paper 3814, 2002.

[18]Chiu, Y. H., Austin, B. L., Dressler, R. A., Levandier, D., Murray, P. T., Lozano, P., and Martinez-Sanchez, M., "Mass Spectrometric Analysis of Colloid Thruster Ion Emission from Selected Propellants," *Journal of Propulsion and Power* (to be published).

[19]Romero-Sanz, I., and Fernández de la Mora, J., "Spatial Structure and Energy Distribution of Electrosprays of Ionic Liquids in Vacuo," *Journal of Applied Physics*, Vol. 95, No. 4, 2004, pp. 2123–2129.