

# Electrostatic influence on charge to mass spectrum in mixed ion/droplet mode: implications for colloid thruster design.

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The use of ionic liquids has been identified for potential propellants in colloid thruster systems. Detailed understanding and characterization of the properties of these liquids when they are electrosprayed is however critical to evaluate the propulsion efficiency achievable. The most important parameter to characterize is the charge to mass ratio for the electrospray, the distribution function for this spectrum together with any sensitivity the spectrum has upon electrostatic conditions in the electrospray. Results are presented here, obtained using a high resolution, high charge to ratio mass limit mass spectrometer, which reveal the richness of the electrosprayed spectrum for one ionic liquid, 1-ethyl-3-methyl imidazolium tetrafluoroborate. It is observed that the spectrum is sensitive to electrostatic conditions. It is observed that near onset conditions the spray is more ionic in nature, although the emission of the single monomer ion is difficult to obtain. At low electric stress the spectrum is dominated by singly charged cluster ions, some of these being quite sizable, being identified up to the 55-mer state. The droplet charge to mass ratio is sensitive to electric stress, with the average droplet having a charge to mass ratio of approximately 8000, when in the spray mode dominated by droplets. It is concluded that for high propellant utilization efficiency, a thruster using this propellant would be best suited to operating in the predominantly droplet mode.

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## I. Introduction

Colloid thrusters are the subject of increasing interest to the propulsion community due to their potential to provide high thrust density at high specific impulse and low specific power. These devices potentially can produce thrust in the range  $\mu\text{N}$  to  $\text{mN}$ , with high accuracy. This level of thrust is of relevance to many up-coming science missions, particularly those requiring formation flying.

The ability to achieve high specific impulse, comparable to that customarily associated with conventional Kaufmann type ion engines has been recognized since the potential to adopt ionic liquids as a propellant in these devices. Ionic liquids – essentially room temperature liquids containing pure salts, were first identified some years ago as potential propellants for colloid micro thrusters. It appears that depending upon the configuration adopted it is possible to achieve different modes of electrospray. Three modes have been defined: purely ionic emission, pure droplet emission and a mixed mode. The determination of these modes has been made in conventional time-of-flight chambers wherein the signal of an electrospray is interrupted instantaneously and the subsequent spray current is measured at some location down stream. The variation of current with time is then used to determine the mass to charge ratio ( $m/z$ ) of the species forming the spray. Whilst this is a powerful technique to determine some elements of the spectrum, particularly in revealing the presence of monomer ions, dimers and even trimer ions, the sensitivity of such instruments is such that there is only limited ability to evaluate the detailed  $m/z$  spectrum of larger cluster ions and droplets, as the spray mode changes from the ion mode into the mixed mode.

Detailed knowledge of the  $m/z$  spectrum in a colloid thruster is of significant importance however since it affects directly the beam and propellant utilization efficiency, in addition to the effective specific impulse. An appropriate instrument to reveal the  $m/z$  is of course a mass spectrometer. However given the large  $m/z$  expected of the droplet component even in an ionic liquid propellant, the mass spectrometer requires the capability to be able to determine the  $m/z$  at values greater than  $10^4$ .

In this paper we report the results we have obtained using one such liquid, 1-ethyl-3-methyl imidazolium tetrafluoroborate EMI  $\text{BF}_4$ . This liquid is readily available commercially, and has a measured conductivity greater than  $1\text{S/m}$ . As such it appears to meet the requirements for behaving in an ionic manner and has been identified to be a potential propellant for colloid thrusters.

## II Experimental Configuration

The instrument we have used is a Qstar instrument (QToF). This has a triple quadrupole system followed by a high resolution time-of-flight system. The maximum  $m/z$  of the instrument is 40,000 and has a resolution of 10,000. In the experiments reported here the electrospray was formed at atmospheric pressure, in positive ion emission mode. The samples of EMI  $\text{BF}_4$  were loaded into a stainless steel capillary emitter (New Objective, MA) that taper to an inner diameter of  $4\mu\text{m}$ . Total emission current on the emitter was monitored directly on the emitter. The applied voltage to the emitter could be varied in order to change the electrospray conditions. In these measurements, reported here, we did not include the flow rate determination whilst spraying, although this can be achieved using the standard procedure we first identified in an earlier paper<sup>1</sup>. These more detailed results are subject of a further publication currently in preparation.

## III Results

An example of a mass to charge spectrum for EMI  $\text{BF}_4$  is shown in Figure 1. For these particular results the separation between the emitter tip and the skimmer entrance to the mass spectrometer was a few millimetres. Whilst this distance can be varied to optimise the spray property measurement for the sequence of results reported here, the distance was retained at a fixed value, in order to determine the relative importance of different features in the spray spectrum.

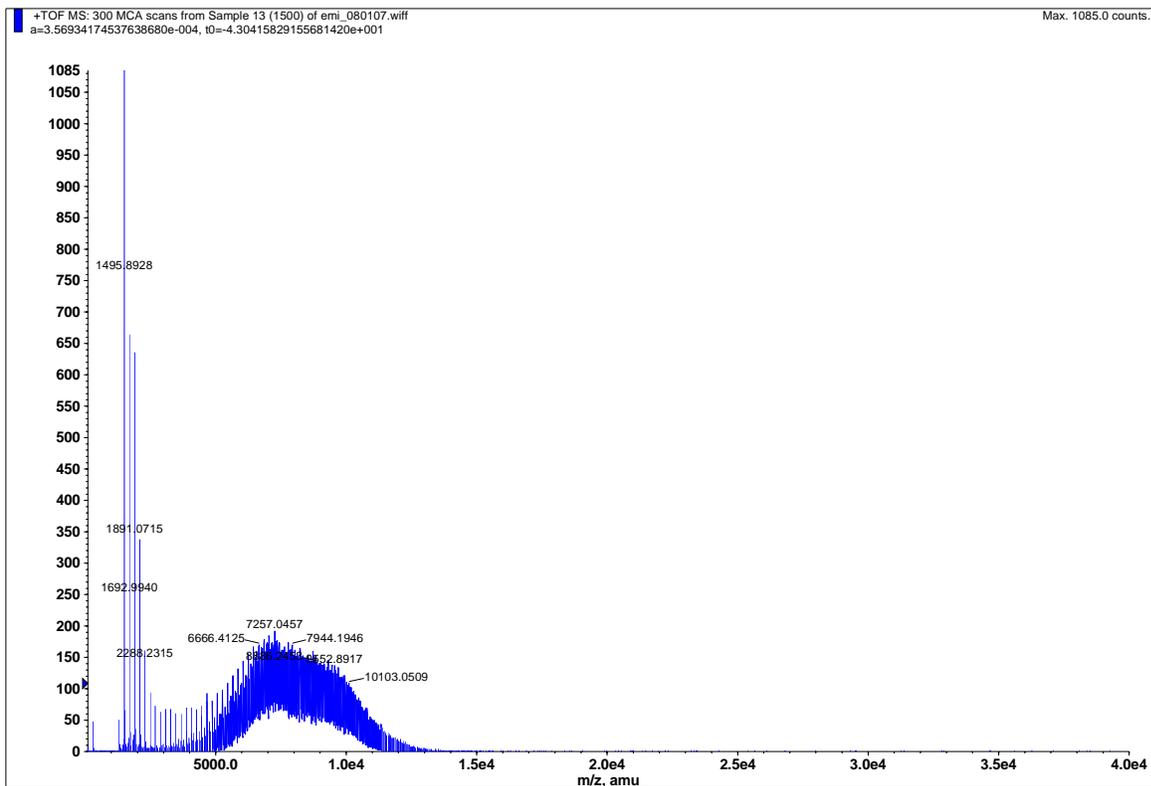


Figure 1 Electrospray m/z spectrum of EMI BF<sub>4</sub> at an applied source voltage of 1500 Volts

There are two principal features to be noted in Figure 1: a series of individual large peaks in the spectrum, the lowest of these is at a mass to charge ratio of approximately 111 (AMU/EMU) – the singly charged pure ion EMI<sup>+</sup>, and a broader continuous distribution that appears to have a peak at an m/z value of ~8000.

A more detailed spectrum of one of the second lowest m/z peak is shown in Figure 2. This now clearly identifies the singly charged solvated ion of (EMI BF<sub>4</sub>)EMI<sup>+</sup>, with two isotopic components being clearly identified at 308.84 and 310.84, being associated with respectively the Boron 10 and Carbon 13 isotopes. The relative intensity of these peaks also confirms this identification. This spectrum clearly shows the power of the QStar instrument in resolving features in the spectrum.

In order to identify the sensitivity of the spectrum to electrospray conditions, the voltage was varied on the emitter, with a fixed emitter skimmer spacing, and both the total current and the spectra recorded over the range from electrospray onset until unstable spray conditions were observed. The spray current, as measured on the emitter as a function of voltage is shown in Figure 3.

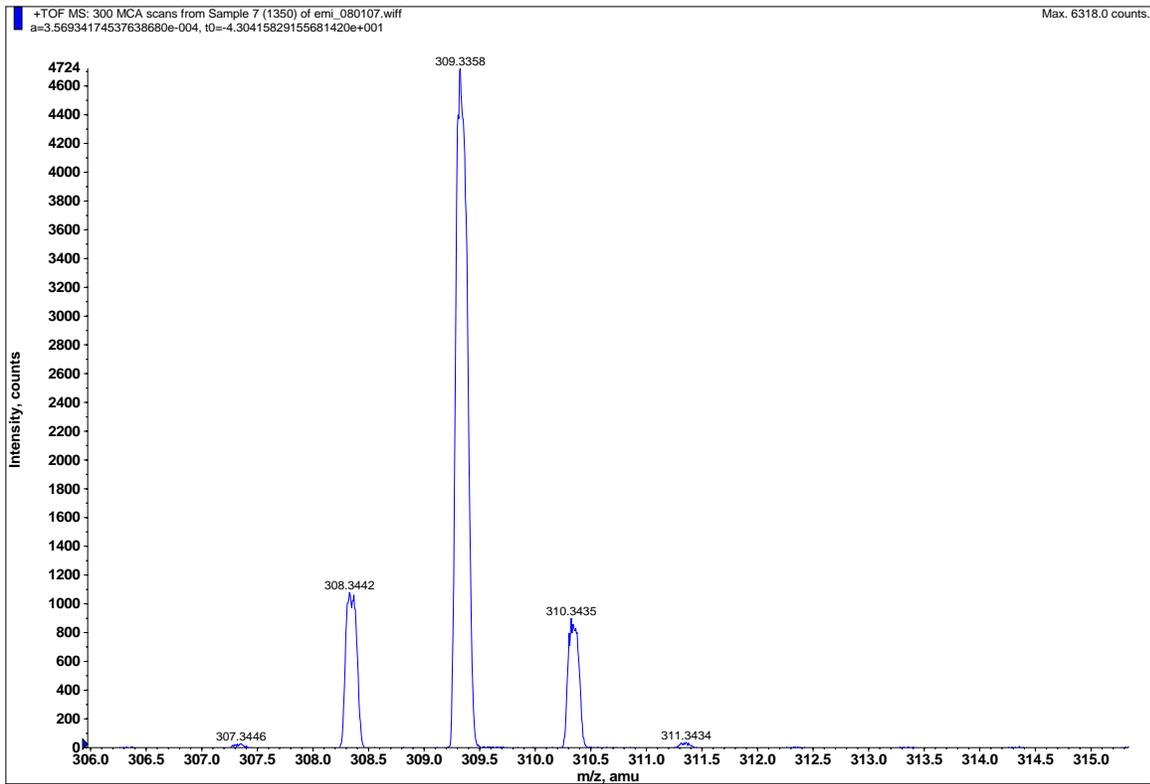


Figure 2 Detailed m/z spectrum revealing the dimer ion  $(EMI\ BF_4)EMI^+$ , with resolution of individual isotopes

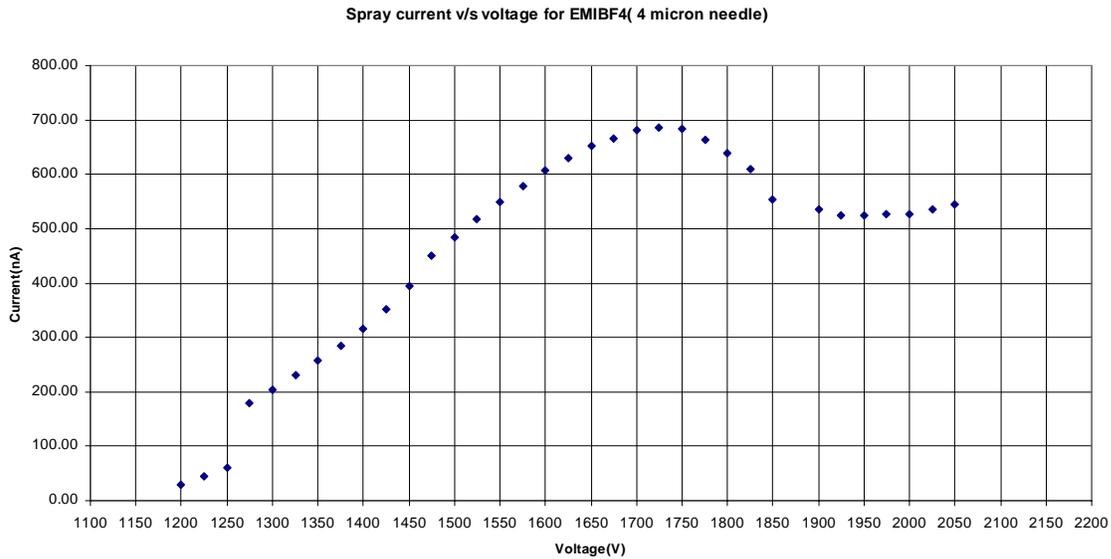


Figure 3. Total electrospray current as measured as a function of emitter voltage

There is a clear variation of current with voltage. Initially a low current is observed. There is then a distinct jump in current, observed for these conditions between 1250 and 1275 volts. There is then a near linear variation in voltage until a peak current is detected, after which the current falls to a new (high) minimum value. After this minimum and until unstable spray conditions, the current again rises with applied voltage.

Detailed evaluation of the spectrum reveals that at low voltages the spectrum appears to contain a significant ion component however it is difficult to isolate a voltage at which a pure singly charged ion exists. The purest ion mode for this set was observed at 1275 volts and the spectrum is recorded in figure 4. It appears however that even under these conditions the spectrum is very rich with many species being present.

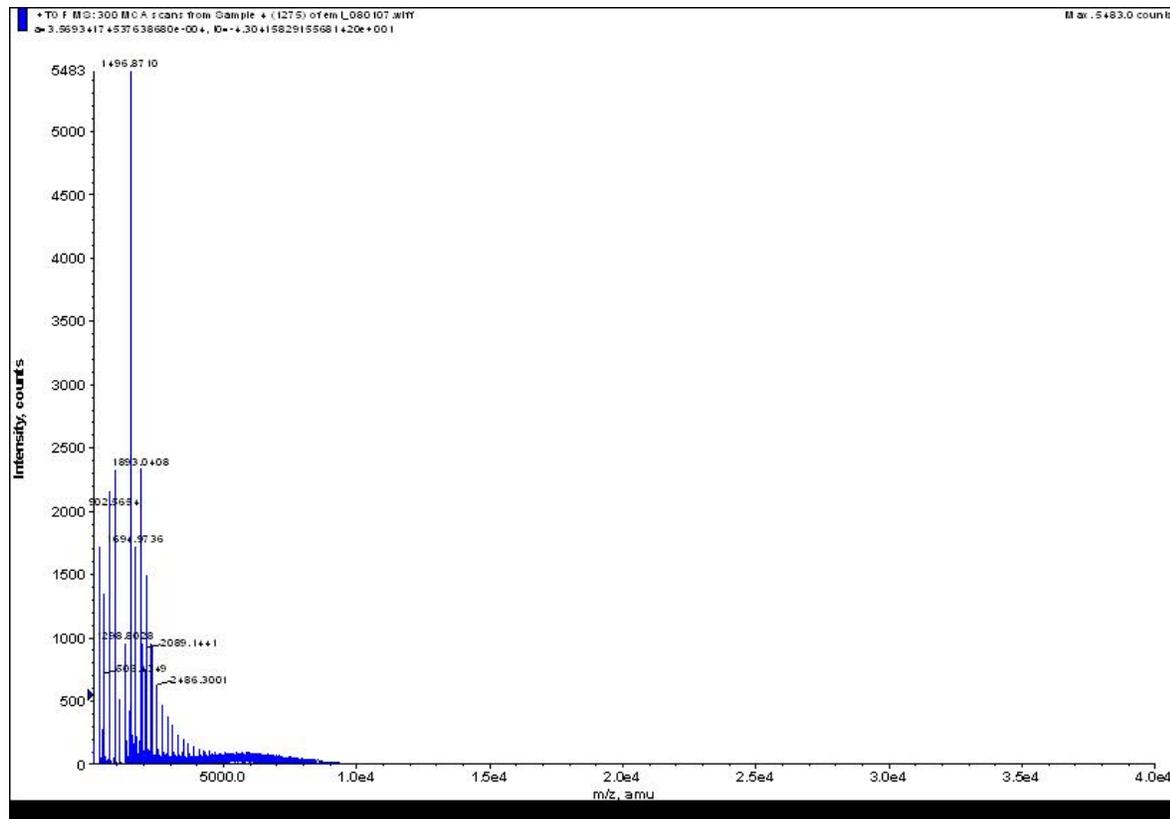


Figure 4. The  $m/z$  spectrum of  $\text{EMI BF}_4$  obtained at 1275 volts

As the voltage is increased the continuous droplet spectrum, as shown earlier in Figure 1 with the applied voltage of 1500 volts, becomes more apparent and dominant. However there are still many individual lines observable in this spectrum. These may clearly be seen in Figure 5, obtained at an applied voltage of 1350 volts. These have been identified as singly charged cluster species, with species as large as  $(\text{EMI BF}_4)_{55}\text{EMI}^+$ .

As noted however as the applied voltage is increased the droplet spectrum dominates. The mean value for  $m/z$  for the droplet distribution however is also seen to change. Indeed this mean value increases from approximately 5500 at 1275, rising to a maximum value just above 8000. This variation is shown in Figure 6.

#### IV Discussion

It is apparent from these observations that when an electrospray is operated with no applied pressure, and is controlled by voltage extraction alone, as in the results reported here, the nature of charged species seen in the spray is dependent upon the actual voltage selected. In the design of a colloid thruster system, based upon simple extraction voltage control of flow rate, a suitable operating point must be established. There are two key features of concern: i) the extent of the spread in  $m/z$  and ii) the presence of high energy impacts between species in the spray. The implications on thruster efficiency will be most affected by the second feature, the presence in the beam of species having very different speeds, with the potential for charge exchange reactions to occur. The concern resulting from this feature is the potential for the production of neutral species within the acceleration region. Such species may most readily be produced by species having very low charge, such as the singly charged cluster ions and larger droplets. The opportunity for this to arise is at the lower voltages, dominated by a variety of cluster ions, although still with some droplets present. It is therefore concluded that operating in the predominant droplet mode

may be more appropriate than in the mode wherein ions are also present, even though, due to the low value of  $m/z$ , such a system would offer higher specific impulse.

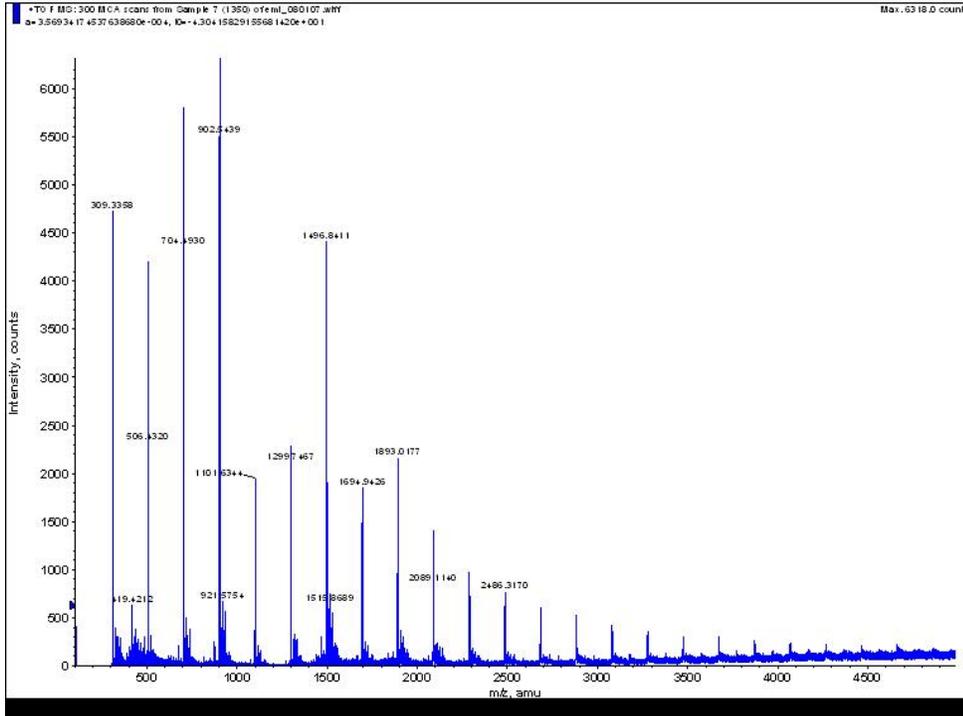


Figure 5 The detailed  $m/z$  spectrum of EMI  $\text{BF}_4$  obtained at 1350 volts showing presence of large singly charged ion clusters

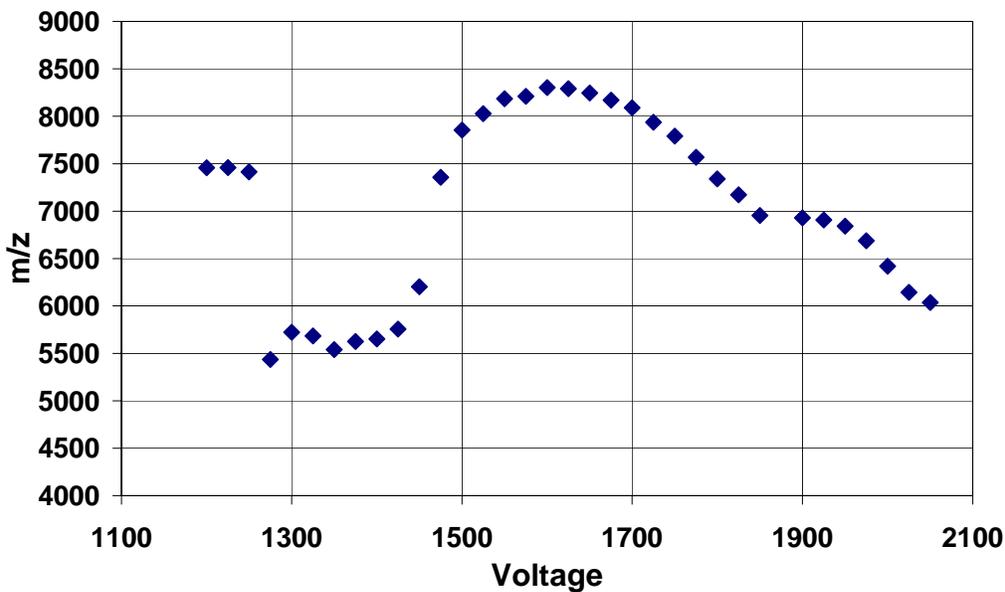


Figure 6 Mean value observed for droplet distribution as a function of voltage

## References

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1 Smith, K.L., Alexander, M.S., Stark, J.P.W., *Voltage Effects on the Volumetric Flow Rate in Cone-Jet Mode Electro spraying*, J. Applied Physics, 99,064909-1 (2006)