

Source of heavy molecular ions based on Taylor cones of ionic liquids operating in the pure ion evaporation regime

I. Romero-Sanz, R. Bocanegra, and J. Fernandez de la Mora^{a)}
Mechanical Engineering, Yale University, New Haven, Connecticut 06520-8286

M. Gamero-Castaño
Busek Co. Inc., 11 Tech Circle, Natick, Massachusetts 01760-1023

(Received 12 August 2002; accepted 12 June 2003)

The full spray emitted by Taylor cones of the ionic liquid 1-ethyl-3-methyl imidazolium tetrafluoroborate ($\text{EMI}^+\text{BF}_4^-$) held in a vacuum is investigated at room temperature by time of flight mass spectrometry. The current is composed mainly of ions under most conditions studied, but contains a small component of nanometer drops that tends to dominate the emitted mass flow. Exceptionally, drop ejection vanishes close to the smallest flow rate at which the Taylor cone is steady. The present discovery of a stable strictly ionic regime in Taylor cones of substances other than liquid metals owes much to earlier observations with sulfuric acid, where most but not all the current was ionic. Most striking is the fact that this purely ionic regime is obtained at an electrical conductivity K of only 1.3 S/m, much smaller than that of sulfuric acid, and smaller than that at which formamide electrolytes with $K > 2$ S/m do still emit substantial drop currents. The ion emission includes primarily the dimer $(\text{EMI}-\text{BF}_4)\text{EMI}^+$, accompanied by fair currents of the monomer EMI^+ and the trimer ions. The modest spread of ion energies observed and considerable currents attained ($0.6 \mu\text{A}$) suggests the use of this and other ionic liquids as ion beam sources with a much wider range of mass/charge and chemical compositions than previously available. The present data provide a direct proof of the reality of the often doubted mechanism of ion evaporation from liquid surfaces. © 2003 American Institute of Physics. [DOI: 10.1063/1.1598281]

I. INTRODUCTION

Ion beams may be generated in a variety of ways: from gas or plasma sources; from positively charged liquid metal surfaces by field evaporation from the tip of a Taylor cone; from solid surfaces, for instance by laser ablation ionization; etc. Unfortunately, these methods are able to yield only relatively restricted classes of ionic species. For instance, *gas sources* may form ion beams only of gaseous or volatile substances. Liquid metal ion sources rely on charging the surface of a molten metal held in a vacuum to a high voltage with respect to a neighboring *extractor* electrode. Within a suitable range of voltage differences, the charged liquid meniscus forms a so-called Taylor cone, whose sharp apex region emits predominantly metal ions. Such sources have high brilliance and can be focused into submicron spots.¹ But they can deliver only ions of metals, with exclusion of all negative species. Existing ion beam sources are therefore limited to mass/charge (m/q) values smaller than 200 Dalton, such as Cs^+ (133 Dalton), or Au^+ (197 Dalton) in liquid metal ion sources, or Xe^+ (131 Dalton) in plasma sources. They are also restricted in chemical composition, limiting the possibilities to combine chemical attack with purely physical erosion in applications such as etching. Hence, no chemically assisted focused ion beam analog exists to the etching processes commonly performed with the assistance of masks. Because chemical composition and mass/charge are

key parameters determining the properties and breadth of applications of ion beams, there is a need to introduce new ion sources able to cover a much wider range of ionic chemical composition and m/q than presently available. One of the advantages to be expected from ion beams of increased m/q are decreased space charge limitations per unit mass flux (hence, the ability to focus more sharply a more intense flux of ions for localized deposition or erosion). Increased ionic mass is also of much interest in electrical propulsion, because it could reduce drastically the energy consumed per unit thrust while still yielding high specific impulse.

Electrostatic atomization via Taylor cones of organic electrolytes (rather than liquid metals) has provided a related but different scheme to produce charged beams in a vacuum environment.² These beams are generally composed primarily of liquid drops, but sometimes contain also solute ions. In these systems, a liquid of low volatility and electrical conductivity K is supplied at a mass flow rate m' (kg/s) to the tip of a capillary tube. A voltage difference V is established between this tip and a neighboring electrode, generally called the *extractor*. Within a suitable range of values of m' and V (where $m'_{\min} \sim 1/K$), the liquid meniscus takes the form of a cone, whose tip ejects a steady microjet, which in turn breaks into drops. This structure is often referred to as a *cone jet*, following the classification of Cloupeau and Prunet-Foch.³ The spray of drops streaming from the end of the jet is generally referred to as an *electrospray*, a term that has had a large impact in mass spectrometry.⁴ When the cone jet forms in a vacuum environment, the charged drops pro-

^{a)}Electronic mail: juan.delamora@yale.edu

duced are accelerated by the voltage difference V towards the extractor, and pass through an orifice in it, forming a beam. These beams of charged drops have proven useful in applications such as electrical propulsion² and surface cleaning.⁵ This approach has been successful mainly with glycerol electrolytes, having high dielectric constant and a relatively small volatility. Furthermore, Taylor cones of glycerol held in vacuum in a multicone highly stressed regime under high voltage are capable also of producing ions of dissolved substances, and this feature has found applications in mass spectrometry.⁶ However, the electrospraying technique to produce beams of small drops and ions in vacuo has been limited by the relatively large size and associated large m/q of the drops, and by the relatively small concomitant ion currents; also by the wide range of energies and solvation states in which the ions are produced. In other words, Taylor cones of glycerol are ineffective as ion sources, with low ion intensities, and wide energy and m/q distributions.

The poor performance of glycerol Taylor cones as ion sources has long been known to be due to its high viscosity, which greatly hinders ion mobility and limits its room temperature electrical conductivity K to values below 0.02 S/m. As soon as K is increased to values in the range of one or a few tens of S/m, one encounters a behavior akin to that of liquid metals, where ion currents dominate over drop currents. Such an interesting situation has been described for sulfuric acid,⁷ though only once, and with scanty detail. It has never been pursued further, either with this acid or any other comparatively conducting liquid. The most conducting organic electrolytes so far electrosprayed in vacuum have been based on formamide solutions, with K values of about 2 S/m.^{8–10} They lead to ion currents up to several times larger than the corresponding drop currents, but most of the liquid mass is still ejected in the form of drops. These studies have found applications in electrical propulsion,¹¹ and offer also some promising new possibilities for ion beam generation. However, it would be more desirable for ion source development to identify liquids operating much closer to the pure ion evaporation regime, if it really exists. This regime can probably be approached and even reached with a handful of organic solvents such as formamide and propylene carbonate. However, these solvents are somewhat volatile at room temperature, and their evaporative loss makes the unambiguous interpretation of their emissions difficult. A natural alternative to reach this purely ionic regime of Taylor cones over the conductivity range from 2 to a few tens of S/m is to seek substances similar to sulfuric acid, namely, purely ionic materials in the liquid state. Many molten salts do indeed reach conductivities in the desired range at temperatures at which they still have negligible vapor pressure. They also offer a wide range of m/q ratios and chemical compositions. Furthermore, their study can now be undertaken under simplified experimental conditions thanks to the discovery and commercial availability of room temperature molten salts, often referred to also as *ionic liquids*. A number of water and air stable ionic liquids are known with room temperature conductivities in the range of 1 S/m.¹² Even more interestingly, their volatilities remain negligible at temperatures well above 100 C, where K values in excess of 10 S/m are

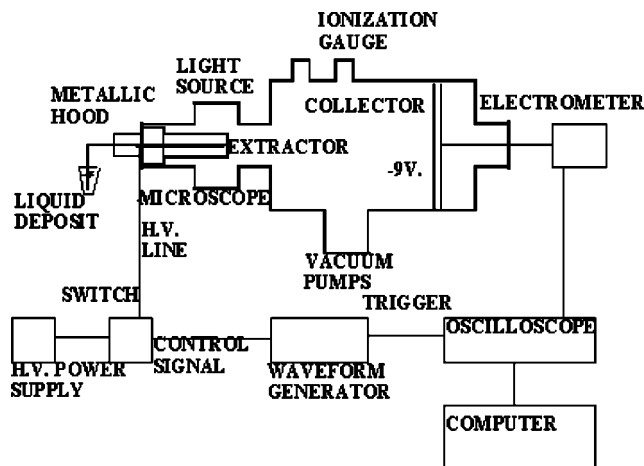


FIG. 1. Sketch of the experimental system.

expected.¹³ The vast range of possible combinations of anions and cations potentially leading to room temperature ionic liquids and the rapid rate at which new ones are actually synthesized every year assures that many will soon become available for ion beam generation.

Given our long-term goal of developing Taylor-cone-based heavy ion beam sources for electrical propulsion, we have examined various heated ionic liquids. Our starting material was the most conducting of those commercially available (Fluka), 1-ethyl-3-methyl imidazolium tetrafluoroborate (EMI-BF₄). The striking finding that the purely ionic regime can be reached with this fluid, even at room temperature, has warranted the present report.

II. EXPERIMENT

An experimental system has been built based on a previous time of flight (TOF) setup,¹⁴ as sketched in Fig. 1. The liquid is introduced from a propylene vial (1 cm³) into the sharpened tip of a silica needle [20 or 40 μ m inner diameter (i.d.)] raised to high voltage V and facing an extractor electrode whose potential was kept at -8 V. The liquid flow rate is controlled through the pressure P in the vial, but is not directly metered. The chamber is evacuated by a small turbopump (Leybold, 50 l/s) backed by a mechanical pump. The stable Taylor cone forming at the needle tip is grounded at time $t=0$, and the arrival time to the collector of the previously emitted full spray current $I(t)$ is monitored in a digitizing oscilloscope (Tektronic TDS220). Most relevant changes from the previous design are the following. The length of the 1.9 in. i.d. tube joining the ion source and the TOF chamber (5.75 in. i.d.) has been reduced to 2.5 cm in order to eliminate ion losses to the walls. This now enables an ion flight length $L=12.3$ cm with interception of the full beam in the collector (13.76 cm diameter). Slightly better vacuum standards have been followed, reducing the pressure in the flight chamber down to some 5×10^{-6} Torr. The response time of the electrometer has also been reduced by a factor of 5 by use of an amplifier resistor of 20 k Ω for high-resolution ion detection (100 k Ω for drop detection). The delay time in the earlier switch has been almost eliminated

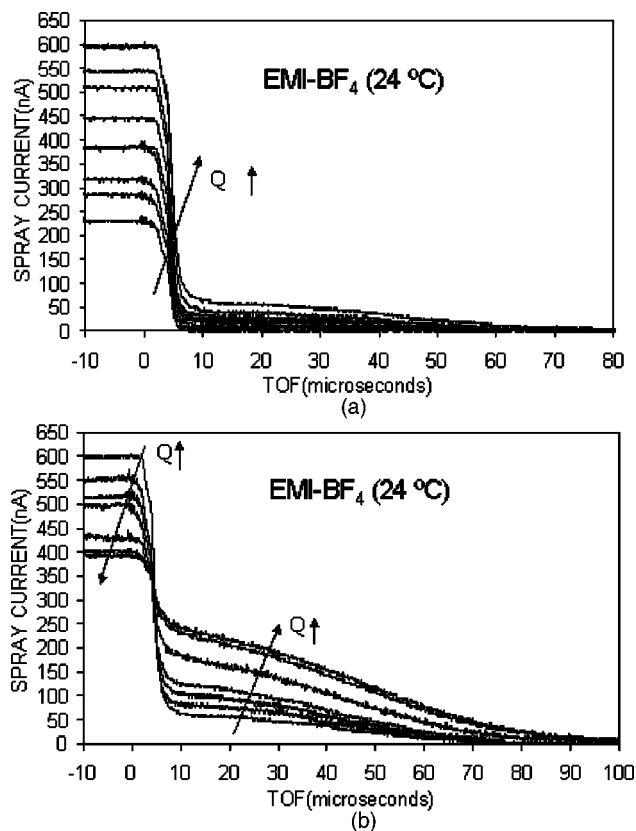


FIG. 2. TOF curves for the ionic liquid 1-ethyl-3-methyl imidazolium tetrafluoroborate at several flow rates, controlled by the pressure difference P between reservoir and meniscus (Table I). The high steps to the left are due to ions (monomer, dimer, trimer, etc.). The wide and short step to the right is associated with drops, and disappears on the lowest curve ($T=24\text{ }^\circ\text{C}$). Figures 2(a) and 2(b) correspond to conditions where the total current either decreases or increases with increasing mass flow rate (see arrows).

by introducing a resistor of $55\ \Omega$ between the wave form generator controlling the switch and the switch control input.

III. RESULTS

Figure 2 shows various TOF traces for electrosprays of room temperature EMI-BF₄, at different flow rate of liquid

injected into the Taylor cone. The wide and short steps to the right are associated with drops, while the sharp and tall steps to the left are due to ions. Most notable is the fact that the purely ionic regime is attained even at room temperature, as seen in the lowest curve ($P=28$ Torr). Surprisingly, this happens at the modest conductivity of EMI-BF₄ ($K=1.3$ S/m at $26\text{ }^\circ\text{C}$),¹³ considerably lower than expected based on the experience previously available (formamide-NaI at K in excess of 2.2 S/m does emit most of its mass in the form of drops).⁹

Table I collects the main characteristics associated with these curves, where P is the pressure pushing the liquid through a $20\ \mu\text{m}$ i.d. capillary line some 30 cm long. The mass flow rate m' of liquid going to the Taylor cone is not measured, but inferred through the integral (2) of the distribution of $I(m/q)$, given from the TOF curves through the relation (1) between m/q and the flight time t [limits of integration in Eq. (2) are from 0 to infinity; L is the flight length].

$$m/q = 2t^2 V_a / L^2, \tag{1}$$

$$m' = 4V_a L^{-2} \int I(t)t\ dt. \tag{2}$$

The acceleration voltage V_a differs from the needle voltage V due to irreversibilities in the tip region of the Taylor cone. V_a has been inferred previously from stopping potential curves,¹⁵ and found to be one or a few hundred volts below the needle potential, both for the ions and the drops.^{14,9,16} It is therefore safe to take V_a to be within 80% – 90% of the needle voltage. There is an associated $\sim 10\%$ error in the mass flow rate determination, but this is of little relevance to our observations here. We have hence computed m' based on Eq. (2) with the assumption that the drop energy V_a is 275 V lower than the needle voltage.

The energies of the ions follow from their known m/q and the sharp ionic steps seen in the TOF curves. These steps are clearly distinguishable for the monomer and dimer ions in Fig. 2 (barely so for the trimer), even though this figure is based on a slow electrometer ($100\ \text{k}\Omega$ resistor in the ampli-

TABLE I. Characteristics of the TOF curves shown in Fig. 2.

P (Torr)	m' (10^{-12} kg/s)	EMI ⁺ current (nA)	EMIBF ₄ EMI current (nA)	[EMIBF ₄] ₂ EMI ⁺ current (nA)	Drop current (nA)	V (V)	V_a (V)
28	0.561 926	88	124	20	0	1375	1100
40	1.811 04	108	152	20	4	1375	1100
68	2.365 62	112	176	20	8	1375	1100
104	4.083 54	112	228	28	12	1375	1100
172	8.220 49	100	296	28	20	1375	1100
206	9.430 07	104	352	28	24	1375	1100
236	10.9038	116	376	28	28	1375	1100
606	13.9912	112	412	32	40	1375	1100
760	23.3442	100	404	40	56	1375	1100
941	26.0863	132	264	80	80	1375	1100
1070	33.2497	120	196	100	100	1375	1100
1225	41.1585	128	156	96	120	1375	1100
1587	70.3312	64	124	60	184	1375	1100
2155	100.063	48	68	52	232	1375	1100
2310	111.770	40	68	44	240	1375	1100

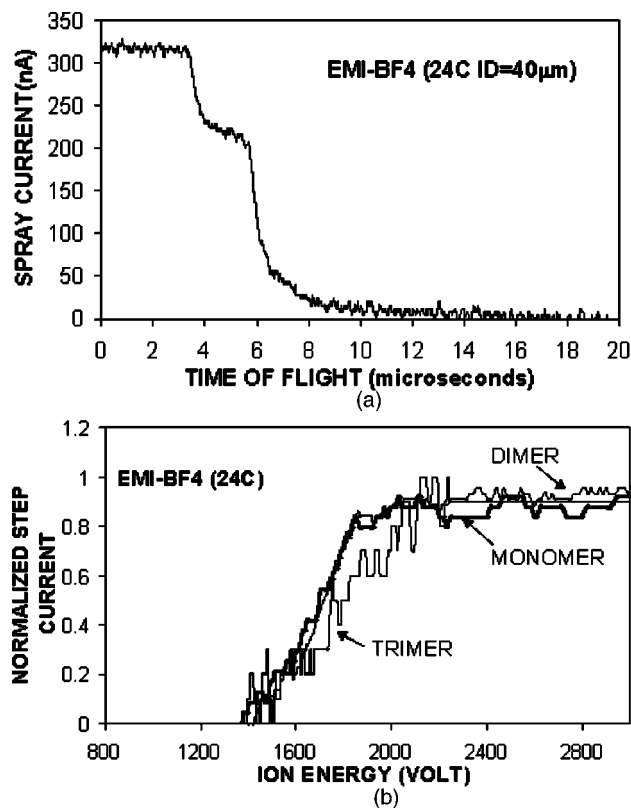


FIG. 3. TOF curves for 1-ethyl-3-methyl imidazolium tetrafluoroborate at higher resolution than in Fig. 2, obtained by using a faster electrometer (amplifier resistor of 20 k Ω), increasing the flight length, reducing beam broadening by operating at higher needle voltages (emitter i.d. of 4 rather than 20 μm) and skimming the edge of the beam ($T=25^\circ\text{C}$). (a) shows the raw TOF curves, (b) transforms the time into an energy variable according to Eq. (1) using the nominal masses of the monomer, dimer, and trimer ions.

fier). We have found that a much better definition of the steps can be obtained by using a faster electrometer (based on an amplifier resistor of 20 k Ω), increasing the flight length, operating at a larger needle voltage, and skimming the extreme edge of the beam to the walls of the vacuum system [Fig. 3(a)]. Unexpectedly, among these variables, the one with the largest influence is the needle voltage V . Its control at fixed geometry is limited by the relatively narrow domain of voltages over which a Taylor cone is stable. However, V scales approximately with the square root of the needle tip diameter, so that theoretically a 41% increase in V results from shifting from a needle tip of 20 μm to another of 40 μm (1375 V vs 2000 V in our actual experiments). At the higher resolution obtained in Fig. 3, we can confirm that the ionic steps correspond indeed to the monomer (EMI^+), dimer ($\text{EMI-BF}_4\text{EMI}^+$), and trimer [$(\text{EMI-BF}_4)_2\text{EMI}^+$] of the salt, because the energies V_a obtained for the three steps [based on Eq. (1) and the nominal masses of these ions: 111.078, 308.96, and 506.84 amu] coincide among themselves within the precision with which the step position can be defined [Fig. 3(b)]. Given the purity of the sample (97.0%), the presence of other ions in the abundances seen is unlikely. Some particularly volatile ion impurities could conceivably have dominated the ion spectrum had the ratio of ion over drop current been small. But this option is precluded in the experiments with essentially no drops. The alternative sce-

nario where positive ions would be formed by electrolysis in the needle tip must also be discounted because the silica needle was made conductive by deposition of a thin semi-conducting film of tin oxide, whose dissolution would have made the tip nonconducting. This problem has never been encountered, even with needles drawing currents of hundreds of nanoamperes many hours a day over several weeks.

The reasons why the ionic steps of Fig. 3(a) are much narrower than those in Fig. 2 deserve some discussion. Since the various steps correspond each to pure species, their finite width must be due to either slow electronic response (switch and electrometer) or to genuine spread in the axial velocity of the ions. The high voltage is grounded within about 0.2 μs , but the spray is interrupted as soon as the voltage drops by just a few hundred volts. Hence, the switching time is surely smaller than 100 ns. $RC=40$ and 200 ns for the fast (20 k Ω) and slow (100 k Ω) electrometers, respectively. Consequently, it is highly unlikely that the poor resolution seen in Fig. 2 for the ionic steps is due to the electronics. This point is confirmed by the fact that the steps of Fig. 2 remain similarly wide when we use the fast electrometer. The most significant difference between the two figures is the higher voltage made possible in Fig. 3 by the larger emitter tip diameter (20 μm in Fig. 2, 40 μm in Fig. 3). This does not affect the emissions from the Taylor cone tip, but must influence the evolution of the ion beam, either directly (different ion velocities and directions) or indirectly, through changes in space charge beam broadening (a function of $V^{3/2}/I$). The spray structure is evidently important because ions of a fixed mass will have different flight times t if they travel at different angles θ off axis ($t \sim 1/\cos \theta$). Lozano and Martinez-Sanchez¹⁷ have in fact compared the arrival time distributions of unfocused, focused, and collimated beams from a Taylor cone of a highly conducting formamide electrolyte, and shown that much of the spread (but not all) is due to the wide radial dispersion of unfocused beams. The spread we see in arrival times could alternatively be due to the fact that ions are originally ejected at different energies. However, this hypothesis is unlikely, as ions would tend to evaporate from the region of the meniscus subject to the highest normal electric field.⁸ Since the rate of ion evaporation is exponential with the field (with a very large exponent), this region must be rather narrow, whereby the voltage at the point of emission should be very well defined. The beam should therefore be closely monoenergetic, an expectation that has in fact been confirmed by several parallel studies.^{18–20} Taylor cones of ionic liquids, hence, share with liquid metal ion emitters the exceptional features of having an emitting tip of nanometer dimensions and a narrow energy range. They offer in addition the advantage of being able to form positive and negative molecular ions, with a much wider range of compositions masses, and charge states. We note, however, that the feature of a narrow ion energy distribution can be expected only from ions originating at the meniscus, and not from those coming from the jet breakup point or from the drops in the case where both drops and ions are issued.^{8,15} Fortunately, this downstream contribution is negligible (current-wise) in the data of Fig. 3.

The evidence available indicating that the ion beam is ap-

proximately monoenergetic implies that the steps of Fig. 3 are narrower than those of Fig. 2 because the ion beam angle is narrower at the higher voltages. We originally thought that space charge effects were primarily responsible for these differences. However, Professor Martinez-Sanchez has noted that the space charge group $V^{3/2}/I$ takes comparable values in both cases. It follows that an increase in needle diameter and voltage creates more focused ion beams due to purely electrostatic reasons.

Note finally that neither the currents shown in Figs. 2 and 3, nor the mass flow rate m' reported in Table I are corrected for the 31% beam loss in the metallic screen preceding the collector. Both should be augmented through division by 0.69. This screen is kept at -9.5 V with respect to the virtually grounded collector in order to repel secondary electrons.

IV. DISCUSSION

Two basic questions deserve further consideration.

A. Why is the purely ionic regime attainable at $K = 1.3$ S/m in pure EMI-BF₄, and not in formamide-Nal solutions at $K = 2.2$ S/m?⁸

Our provisional answer is that the observed facile ionization of EMI⁺ is not due to any peculiarity of the ionic liquid EMI-BF₄, but simply to the greater volatility of EMI⁺ over Na⁺. A similar behavior has been recently reported, where Na⁺ evaporates abundantly from formamide, but NH₄⁺ does not from comparably conducting formamide solutions.¹⁴ Since ion volatility is controlled by its solvation energy ΔG (rate $\sim e^{-\Delta G/kT}$), it is clear that this energy is larger for ammonium than for Na⁺ (both in formamide). Recent work of Guerrero *et al.*²¹ has established similarly that Na⁺ is substantially less volatile than EMI⁺, both in propylene carbonate. A facile ionization of the EMI⁺ ion from its own molten salt is therefore to be expected.

That the relatively small differences in the solvation energies of NH₄⁺, Na⁺, and EMI⁺ should have such drastic consequences on the critical electrical conductivities required for their evaporation follows also qualitatively from existing theory. In the limit of high solvent dielectric constant and small surface curvature effect, the reduction in the activation energy for ionization associated with the electric field on the liquid-gas interface is²²

$$G_E(E) = (e^3 E / 4\pi\epsilon_0)^{1/2}. \quad (3)$$

In turn, the electric field attainable in the liquid meniscus scales with the quantity⁸

$$E_k = \gamma^{1/2} \epsilon_0^{-3/2} (\rho K / m')^{1/6}. \quad (4)$$

We have computed E_k based on the measured m' , literature values $\rho = 1.294$ g/cm³ and $K = 1.3$ S/m (26 C).¹³ The surface tension was determined by a home-made system (based on the capillary rise method) to be $\gamma = 51.8$ dyn/cm (24 C), with an estimated error of about 5%. Since the smallest liquid mass flow rate m' at which a Taylor cone is stable varies as $1/K$,²³ it follows that E_k increases as $K^{1/3}$, and G_E as $K^{1/6}$. Halving K therefore implies only an 11% reduction in G_E . A typical value for E at the onset of ion evaporation is 1

V/nm.^{22,8} This corresponds in Eq. (3) to $G_E = 1.2$ eV, 11% of which is only 0.13 eV. As a reference, this difference is smaller than that in the published ΔG values for Li⁺ and Cs⁺, both in water (2.65 and 2.34 eV, respectively).²⁴ Literature values for ammonium and sodium ions in water (2.41 and 2.45 eV)²⁴ indicate that ΔG is only 0.04 eV larger for Na⁺ than NH₄⁺. The sign of this difference is in fact opposite to what is seen in the far more direct study of Bocanegra *et al.*¹⁴ (in formamide rather than water), possibly because the datum for ammonium is estimated.²⁴ But the order of magnitude of this difference in solvation energy is probably correct, confirming that such slight variations suffice to either activate or suppress the evaporation of ions.

B. What does it take to reach the pure ionic regime?

We have so far considered the reasons why intense ion currents arise at electrical conductivities K as small as 1.3 S/m, perhaps smaller. Even more important is the notable observation that drop emission can be entirely suppressed. There is at present no theoretical framework from which one could have predicted this outcome. However, now that its reality has been confirmed experimentally, it pays to place it in perspective.

The only regime of operation of electrostatic atomization that has been studied systematically and is reasonably well understood, is the so-called cone-jet mode. In this regime, the electrified meniscus takes the shape of a cone whose tip emits a steady jet. The scaling laws for this jet are known approximately,²³ and its diameter is typically of 10 nm at $K \sim 1$ S/m. One fundamental observation for this regime is that it takes a certain minimal flow rate and a minimum current to establish it. The minimum flow rate is approximately linear with $1/K$, while the minimum current is almost independent of K , with typical values between several tens to a few hundred nanoamperes. Note therefore that is not possible to form a stable Taylor cone jet without ejecting a certain minimal mass flow and current of drops. These drops may be made smaller at higher electrical conductivities and smaller flow rates. However, even at the highest conductivities and the smallest flow rates attainable (prior to ion emission), these drops are still some 20 nm in diameter, vastly larger than ionic dimensions. Hence, if the onset of ion evaporation were to preserve the scaling laws relating the current associated with the drops, their size and the electrical conductivity of the liquid, it would not be possible to reach a regime where ions would be formed without a dominant mass flow of accompanying drops.

Since this regime is in fact attained, it follows that the onset of ion evaporation must modify fundamentally the known scaling laws for cone jets in the pure drop regime. This is evident in Fig. 2(a) by simply looking at the height of the steps associated with the drops, also shown more directly in Fig. 4. The drop currents for the four lowest curves shown are of approximately 12, 8, 4 nA, and almost zero (less than 1 nA), respectively. These values are all well below the range of drop currents at which a cone-jet in the pure drop mode has ever been stabilized for any polar liquid.

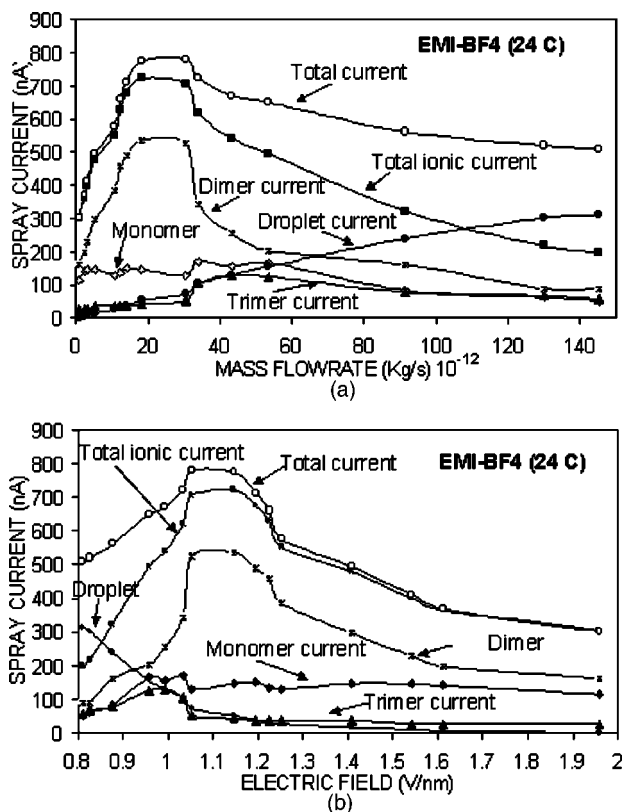


FIG. 4. Collected current for the full spray, the drops, and the monomer, dimer and trimer ions represented as a function of (a) the mass flow rate, and (b) the electric field variable defined in Eq. (4).

The TOF distributions of the drops are not readily discernible in the lowest traces of Fig. 2, and are shown normalized to unity in Fig. 5. This representation shows clearly that the drops do not disappear by increasing their q/m , eventually turning into ions, since their times of flight vary little from trace to trace. The drop component vanishes at decreasing flow rates because its current decreases continuously down to zero at approximately fixed (or weakly vary-

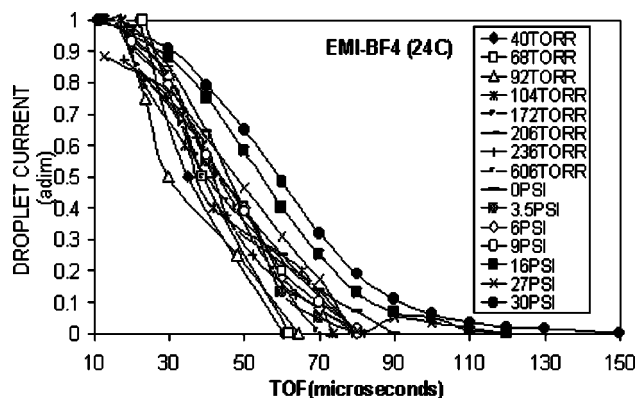


FIG. 5. Drop component of the TOF curves of Fig. 2 normalized to unity, to provide a comparative view of the corresponding m/q distributions. One sees that the increased mass flow is obtained primarily by increasing the magnitude of the current, with modest variation in the m/q distribution. This behavior is in sharp contrast with that observed in the pure drop regime, where the drop current varies as the $1/2$ power of the mass flow rate, so that the mean value of m/q increases as the square root of the mass flow rate: $\langle m/q \rangle \sim m^{1/2}$.

ing) q/m . This is only possible if the frequency of drop ejection decreases with flow rate, down to a critical point where it vanishes. Prior to that point the meniscus must have a characteristic jet-like protrusion some 10 nm in diameter. As the critical flow rate is approached, this drop-shedding protrusion must become shorter and more stable, until it finally becomes stationary, leading to the purely ionic regime. At this point, the meniscus must have a convex surface, whose shape is essentially steady (except for the intermittent departure of individual solvated ions). These ions have dimensions typically one order of magnitude smaller than the drops.

An important question that remains to be settled is over how wide a range of liquid flow rates does the purely ionic regime exist. Our experiments indicate that, for EMI-BF₄ at room temperature, this range is fairly narrow. It reduces to almost one point, since the Taylor cone could not be stabilized much below the smallest flow rate shown in Fig. 2. However, the meniscus associated with this trace was completely stable. This particular TOF curve was averaged for about 10 min, and its stability would have allowed observing it for hours. This feature was in fact essential to increase the signal to noise ratio, and hence be able to assure that the level of drop current for that particular condition is less than 1 nA.

Some final remarks are worth making in relation to Fig. 4. The behavior is unusual due to the relatively high ion currents present even at the highest flow rate achieved, and particularly so because of the complete disappearance of drops at the lowest flow rate. But the trend of a decreasing ion current and an increasing drop current with increasing m' is in many ways similar to that previously seen with highly conducting formamide solutions.^{8,9} At still higher flow rates we would expect a minimum in the total current, followed by the typical pure drop emission behavior where the current increases as the square root of m' .²³ This high flow rate regime was not experimentally accessible here due to the relatively high flow resistance of the 20 μm needle used. At a critical value of the characteristic surface electric field E_k [Eq. (4)] of about 1.08 V/nm [Fig. 4(b)], one notes an abrupt increase of the dimer ion current (by far the dominant ionic component), and a stepwise decrease of the monomer and trimer ions, as well as the drop current. At still higher m' , the total ion current goes through a maximum and begins to decrease at increasing E_k values (decreasing m'). We are not aware of any prior observation of this maximum, but its presence is inevitable if a transition to the pure ion evaporation regime is to take effect. The reason is that, if only ions of a fixed m/q are ejected, then the current must rise linearly with m' as $I = (q/m)m'$, in a behavior typical of liquid metal ion sources. The total current curve of Fig. 4(a) does not show this linear behavior through the origin of coordinates because there is only one datum with no drop mass, and the next point already contains about twice as much mass flow in the form of drops than in the form of ions.

Summing up, the current versus m' curve should start somewhere in the pure ion evaporation line $I = (q/m)m'$; perhaps continue through it through a finite m' range; then

curve downwards until eventually going through a maximum; then moving rapidly downwards to connect with the pure drop regime, and proceeding upward through it as $I \sim m'^{1/2}$. The transition from pure drop emission to the onset of ion evaporation is in reality not as abrupt as indicated, because ions originate also from drops (or from sharp points at the jet breakup region) at rates which are weakly dependent on m' .⁸ The distinction between ions from these two different origins can be better characterized by means of energy-resolved time of flight.²⁵ Low energy ions from this downstream region are more prominent in the case of viscous substances such as EMIBF₄, whose jets tend to break into large highly charged drops with anomalously large surface electric fields. As a result, only a slight sign of an abrupt transition is seen in our data at $E_k = 1.08$ V/nm. Room temperature EMIBF₄ is able to cover in part essentially all these various regions. All prior results with formamide solutions have lied to the right of the maximum. The following laconic description of Perel *et al.*⁷ surely locates their pioneering data well to the left of this maximum, but not quite in the purely ionic regime:

“Concentrated H₂SO₄ exhibited a very high specific charge with (propulsion) efficiencies larger than 90%. The TOF data indicate that a large portion of the spray consisted of negative ions corresponding to single and multiple groupings of H₂SO₄ molecules and a specific impulse of about 4000 s”

V. CONCLUSIONS

A TOF mass spectrometric study of the full plume from Taylor cones of EMIBF₄ at room temperature has revealed the following.

(1) Ion currents dominate over drop currents, except at very large flow rates, even though the electrical conductivity is only of 1.3 S/m.

(2) A regime of pure ion evaporation with no company of drops is attained, though only very near the minimum flow rate at which the Taylor cone is stable. There are no prior observations of a purely ionic regime of emission from Taylor cones of nonmetals.

(3) The m/q distribution of the drops is relatively invariant at flow rates near the minimum. The pure ionic regime is therefore approached by reduction of the current of drops at approximately fixed drop m/q .

(4) The energy of the ions evaporated is sufficiently well defined to suggest that most originate at a fixed position in the meniscus. This speculation has been confirmed by recent work by Lozano¹⁹ and our own²⁰ implying that ionic liquids can form the basis for high quality ion sources.

(5) Observations (1) and (2) seem to indicate that the EMI⁺ ion is considerably more volatile than Na⁺.

(6) The observation of ions with no drops shows unambiguously that ion evaporation is taking place directly from

the liquid surface, as originally hypothesized by Iribarne and Thomson.²⁶ This puts definitively to rest an extensive literature expressing doubts or even flatly denying the leading role played in electrospray ionization by the Iribarne–Thomson mechanism.

ACKNOWLEDGMENTS

This study has been supported by AFOSR Contract No. F-49620-01-1-1416. The authors are also much indebted to their colleagues at Sciex for their gift of a turbopump. The insights from M. Martinez-Sanchez and P. Lozano (MIT), I. Aguirre (Madrid), B. Thomson (Sciex), I. Guerrero (Yale), and V. Hruby (Busek) are gratefully acknowledged.

- ¹P. D. Prewett and G. L. R. Mair, *Focused Ion Beams from LMIS* (Wiley, New York, 1991).
- ²V. E. Krohn, *Liquid Metal Droplets for Heavy Particle Propulsion* (Progr. In Astronautics and Rocketry, A. C. N. Y. 1961, Vol. 5); V. E. Krohn, *Glycerol Droplets for Electrostatic Propulsion* (ARS Electric Propulsion Conference, Berkeley, CA, 1962); M. N. Huberman and S. G. Rosen, *J. Spacecraft* **11**, 475 (1974); P. W. Kidd and H. Shelton, *AIAA 10th Electric Propulsion Conference, Lake Tahoe, NV, 1973*, paper AIAA 73-1077.
- ³M. Cloupeau and B. Prunet-Foch, *J. Electrostat.* **25**, 165 (1990); M. Cloupeau, *J. Aerosol Sci.* **25**, 1143 (1994).
- ⁴J. B. Fenn, M. Mann, C. K. Meng, S. K. Wong, and C. Whitehouse, *Science* **246**, 64 (1989).
- ⁵J. F. Mahoney, J. Perel, C. Sujo, and J. C. Andersen, *Solid State Technol.* **41**, 149 (1998); J. F. Mahoney, *Int. J. Mass. Spectrom.* **174**, 253 (1998).
- ⁶K. D. Cook, *Mass Spectrom. Rev.* **5**, 467 (1986).
- ⁷J. Perel, J. F. Mahoney, R. D. Moore, and A. Y. Yahiku, *AIAA J.* **7**, 507 (1969).
- ⁸M. Gamero-Castaño and J. Fernández de la Mora, *J. Chem. Phys.* **113**, 815 (2000).
- ⁹M. Gamero-Castaño and V. Hruby, *J. Propul. Power* **17**, 977 (2001).
- ¹⁰M. Gamero-Castaño and V. Hruby, *J. Fluid Mech.* **459**, 245 (2002).
- ¹¹M. Martinez-Sánchez, J. Fernández de la Mora, V. Hruby, M. Gamero-Castaño, and V. Khayms, *26th International Electric Propulsion Conference, Kitakyushu, Japan, 1999*.
- ¹²J. S. Wilkes and M. J. Zawarotko, *J. Chem. Soc., Chem. Commun.* **13**, 965 (1992); J. Fuller, R. T. Carlin, R. A. , H. C. De Long, and D. Haworth, *J. Electrochem. Soc.* **3**, 299 (1994); H. L. Ngo, K. LeCompte, L. Hargens, and A. B. McEwen, *Thermochim. Acta* **357**, 97 (2000); J. Fuller, R. T. Carlin, and R. A. Osteryoung, *J. Electrochem. Soc.* **144**, 3881 (1997).
- ¹³A. B. McEwen, H. L. Ngo, K. LeCompte, and J. L. Goldman, *J. Electrochem. Soc.* **146**, 1687 (1999); A. B. McEwen, S. F. McDevitt, and V. K. Koch, *ibid.* **144**, L84 (1997); P. Bonhote, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram, and M. Graetzel, *Inorg. Chem.* **35**, 1168 (1997).
- ¹⁴R. Bocanegra, J. Fernandez de la Mora, and M. Gamero, *J. Propul. Power* (accepted for publication).
- ¹⁵M. N. Huberman, *J. Appl. Phys.* **41**, 578 (1970).
- ¹⁶M. Gamero-Castaño, Ph.D. thesis, Yale University, 1999.
- ¹⁷P. Lozano and M. Martinez-Sanchez, *AIAA J.* (submitted).
- ¹⁸Y.-H. Chiu, *presented at the first Colloid Thruster/Nano Electrojet Workshop, MIT, Cambridge, MA, 3–4 October 2002*.
- ¹⁹P. Lozano, Ph.D. thesis, MIT, December 2002.
- ²⁰I. Romero-Sanz and J. Fernandez de la Mora, *J. Appl. Phys.* (submitted).
- ²¹I. Guerrero, R. Bocanegra, and J. Fernandez de la Mora (unpublished).
- ²²I. G. Loscertales and J. Fernández de la Mora, *J. Chem. Phys.* **103**, 5041 (1995).
- ²³J. Fernández de la Mora and I. G. Loscertales, *J. Fluid Mech.* **260**, 155 (1994).
- ²⁴L. Tang and P. Kebarle, *Anal. Chem.* **65**, 3654 (1993).
- ²⁵M. Gamero-Castaño, *Phys. Rev. Lett.* **89**, 147602 (2002).
- ²⁶J. V. Iribarne and B. A. Thomson, *J. Chem. Phys.* **64**, 2287 (1976); B. A. Thomson and J. V. Iribarne, *ibid.* **71**, 4451 (1979).