
An Experimental Study of the Electrospraying of Water in Air at Atmospheric Pressure

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Water solutions with electrical conductivities ranging from that of the deionized water up to 2 S/m have been electrosprayed in air through narrow silica tubes. Results show unambiguously that steady cone jets of water in air without the assistance of glow discharge can be formed for the range of electrical conductivities we have explored. The absence of corona discharge has been proven not only for the good agreement between the experimental results and the scaling laws given in the cone-jet literature but also for the independence of the spray current on the atmosphere (air or CO₂) in which water was being electrosprayed. Other regimes such as the electric dripping and the assisted glow discharge cone-jet mode that appear in the electrospraying of water in air at room temperature have also been investigated. (J Am Soc Mass Spectrom 2004, 15, 253–259) © 2004 American Society for Mass Spectrometry

Electrified conical menisci in the so-called cone-jet mode [1] give rise to sprays of liquid droplets quite monodisperse in size. The droplet diameter ranges from tens of nanometers to hundreds of micrometers. Such a mode can easily be implemented when an electric field, within an appropriate range of values, is applied to a conducting liquid which is forced through a capillary needle. For higher values of the electric field, some other regimes different from the cone-jet mode appear but the dispersion of the droplet size of the resulting sprays is larger than those of the cone-jet electrospray, [2, 3]. For even larger values of the electric field, the air surrounding the conical meniscus may become ionized and a corona discharge appears. It is commonly accompanied by streamers and sparks that are incompatible with steady state conditions.

When solutions with large electrical conductivities, typically larger than 10⁻³ S/m, are electrosprayed in cone-jet mode, the droplets of the resulting spray have

sizes well below the micro-metric range; water solutions are typical examples. Sprays of charged nanodroplets of water could be of great interest in many fields, for example, mass spectrometry incorporating the coupling an electrospray source to a conventional mass analyzer [4]. The use of pure water solutions is highly desirable in mass analysis of biomolecules since water is the natural surrounding of most biomolecules. The high values of the electrical conductivity typically associated to aqueous solutions have another advantage since the resulting highly charged submicrometric droplets yield a larger effectiveness in the production of highly solvated ions [5]. In addition, submicrometric or even nanometric sprays of water can also be of interest in thermal and chemical surface treatments, drug delivery, or generation of new materials.

The electrohydrodynamic pulverization of water in cone-jet mode in air at atmospheric pressure is still a controversial subject. In fact, whereas researchers working on nanoelectrospray ionization mass spectrometry are aware that deionized water could be electrosprayed in cone-jet mode [6–8], others working on electrosprays have reported the impossibility to obtain such steady water cone-jets without corona discharge. The explanation given lies in the fact that the threshold value of the electric field required to form a Taylor cone-jet, which increases with the surface tension of the liquid-gas atmosphere, can become larger than the electrical

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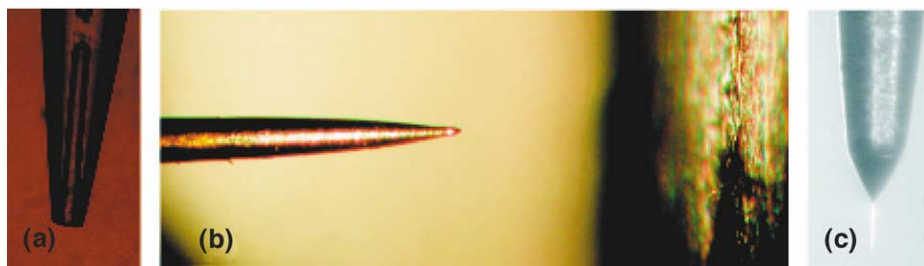


Figure 1. (a) Picture of the sharpened tip of the silica tube (o.d. 360 μm , i.d. 20 μm). The o.d. of the tip was approximately 50 μm . (b) Detail of the silica needle-grounded electrode. Observe the cone-jet of water W1 anchored at the needle exit. (c) Steady cone-jet of deionized water (sample W4) in air.

breakdown threshold of the air, so that corona discharges could appear before the formation of the cone-jet if liquids with sufficiently high surface tension are electro-atomized [1]. Since the electrical breakdown threshold of carbon dioxide is higher than that of the air, some authors have used a sheath of CO_2 (or alternatively, sulphur hexafluoride SF_6) to obtain steady cone-jets of water without electrical discharge [9].

In the above statement, it should be taken into account that the maximum value E_{cj} of the normal electric field acting on the Taylor cone-jet must be attained somewhere at the interface of the cone-to-jet transition region whose characteristic radius is of the order of the jet radius R_j . The order of magnitude of this normal electric field is approximated by a balance between capillary and electrical forces [10],

$$E_{\text{cj}} \approx \left(\frac{\gamma}{\epsilon_0 R_j} \right)^{1/2} \quad (1)$$

The jet radius depends on both the flow rate and the electrical conductivity of the liquid; in fact, it decreases when either the flow rate decreases or the liquid electrical conductivity increases [11, 12]. Therefore, it is plausible that a range of both electrical conductivities and flow rates exist for which water cone-jets without corona discharge can be formed in air at atmospheric pressure.

In this work, we have carried out experimental work to confirm not only the possibility of forming steady cone-jets of water in air at atmospheric pressure without corona discharge but also to find out the ranges of both flow rates and electrical conductivities for which these steady cone-jets of water can be formed.

Experimental

Water contained in a small plastic reservoir is forced through a silica tube line by means of pressurized air. Several water solutions with different electrical conductivities have been investigated. The use of metallic tubes as injection needles for the electrospraying of water is not recommended since any shard or imperfection on the metal surface, especially when moistened, could act as a source of electrical discharges. Therefore, instead of

metallic needles, the silica tube itself with one of its ends conveniently sharpened (as a pencil-like) has been used as injection needle, see Figure 1a. The end of the silica tube was sharpened by using a rotating polishing machine; no chemical deposition was made on the sharpened tip. Two types of silica tubes with different inner diameter (i.d.) have been used. Silica tubes with 20 μm i.d. were used for the dispersion of the most conducting water samples while for the less conducting ones we used 40 μm i.d. tubes. That was just to properly control the liquid flow rate through the silica tube by fixing a certain pressure drop across it; the larger the electrical conductivity of the sample the smaller the flow rate that can be electroatomized in cone-jet mode. The pressure drop through the silica line was measured with a pressure gauge and the flow rate through the silica tube was calculated by the Hagen-Poiseuille formula. The flow rate was also measured from the volume increment of a pendant drop anchored at the end of the silica tube within a given interval of time. The volume increments were computed from pictures of the pendant drop taken at different times. The agreement between both methods was excellent. Of note, in steady state conditions the liquid flow rate emitted from the cone can be assumed to be equal to that imposed through the silica tube since their difference, due to evaporation from the cone surface, hardly exceed a 2% of the imposed flow rate.

The charging process of the liquid was carried out by immersing the high potential stainless steel electrode of a high voltage power supply (model 250B-10R, Bertan, Valhalla, NY, USA) in the liquid contained in the plastic reservoir. A grounded stainless steel plate was located in front of the silica needle, see Figure 1b. In the experiments, the distance between the silica tube tip and the plate ranged from 3 to 5 mm. Note that the electric field at the cone-jet liquid gas interface depends not only on the applied electrical potential V but also on the electrode geometry, the needle to plate distance, and the space charge effect resulting from the charged cloud of the spray, see [13] or [14] for more details. Finally, the silica needle-plate system was enclosed in a grounded metallic cross to isolate it from external perturbations. In addition, the system could be oper-

Table 1. Relevant physical constant of the liquid samples used in the present experiments and their corresponding magnitudes of reference [eq. 2]

Sample	C (mol/l)	ρ (Kg/m ³)	K (S/m)	γ (mN/m)	I_o (nA)	Q_o (nl/s)
Deionized water + HC1 (W1)	6.5×10^{-2}	1000	1.8	67.5	6.4	3.3×10^{-4}
Deionized water + HC1 (W2)	4.4×10^{-3}	1000	1.5×10^{-1}	71.6	6.8	4.3×10^{-3}
Deionized water + HC1 (W3)	5.7×10^{-4}	1000	1.5×10^{-2}	72.0	6.8	4.1×10^{-2}
Deionized water (W4)		1000	3.6×10^{-4}	72.0	6.8	1.6
Deionized water + HC1 (W5)	3.2×10^{-2}	1000	9.0×10^{-1}	68.0	6.4	6.7×10^{-4}
Deionized water + HC1 (W6)	7.7×10^{-3}	1000	2.4×10^{-1}	72.0	6.8	2.6×10^{-3}

ated in an atmosphere of either air at room temperature or CO₂.

The spray current collected at the grounded plate could be led by a commutator either to a picoammeter (model 485, Keithley Instruments, Cleveland, OH, USA), where it was measured, or to a digital oscilloscope (model COR5501U, Kikusui, Yokohama, Japan) to observe the steadiness of the current signal. The electrospray was monitored by using a zoom microscope (model SMZ-2T, Nikon, Tokyo, Japan) and a CCD camera (model SSC-M370CE, Sony, Tokyo, Japan). Images of the cone-jet electrosprayed, as in the example shown in Figure 1, were recorded electronically.

The electrical conductivity of the deionized water was enhanced by adding small amounts of hydrochloric acid, HCl. Its value was determined by measuring the electrical resistivity across the ends of a silica tube filled with the liquid sample. Measured values of the electrical conductivity and those reported in reference [15] are in good agreement. Surface tensions of the samples were measured with a tensiometer (model K10, Krüss,

Hamburg, Germany). The liquid samples used, their concentrations, as well as their measured values of the electrical conductivity and surface tension are summarized in Table 1, which also contains reference values of the current and flow rate, as defined in eq 2 below, for each of the water samples.

Results

We have found four different modes in the electrohydrodynamic atomization of water instead of three as reported in reference [16]; the fourth corresponds to a steady cone-jet mode without corona discharge. Each atomization mode appears for an appropriate range of values of both the liquid flow rate and the applied voltage as described in Figure 2. In this case, liquid sample W2 was injected at a fixed flow rate of 0.98 nl/s and the needle to plate distance was 3 mm in this case. Values of the average current I collected at the plate versus the applied voltage V are plotted in Figure 2 while the inserts in Figure 2 show the time dependence

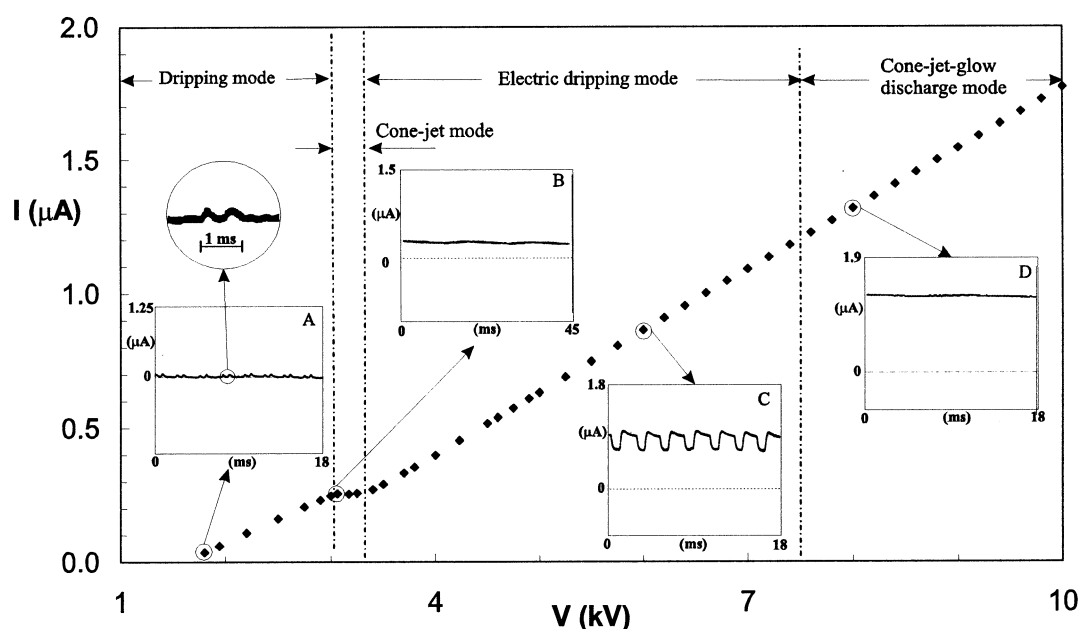


Figure 2. Average current I emitted from the electrified meniscus versus applied voltage V . The typical time dependence of the current in each of the four different modes is also plotted. (a) Dripping mode ($V = 1.8$ kV, $I = 36$ nA); (b) cone-jet mode ($V = 3.0$ kV, $I = 253$ nA); (c) electric dripping regime ($V = 6.0$ kV, $I = 863$ nA); (d) cone-jet glow discharge mode ($V = 8.0$ kV, $I = 1317$ nA). In all experiments, sample W2 was injected at a flow rate $Q = 0.98$ nl/s.

of the current signal recorded on the oscilloscope. For values of V within the interval 0 to 2988 V, the electrified meniscus was in the dripping mode. Although different sub-regimes have been identified within the dripping mode [2, 3], the time dependence of the current shown in Figure 2a seems to indicate that the electrified meniscus alternates from rounded shape to a cone-jet one. A thin liquid ligament is emitted from the cone vertex which eventually breaks up in a train of droplets because of varicose capillary instabilities. Therefore, the peaks of the current observed in Figure 2a correspond to the train of charged droplets falling in a cascade on the grounded electrode. As the applied voltage increases the frequency of the dripping increases too until a certain threshold value is reached for which a steady cone-jet electrospray is formed. We have found that the cone-jet mode exists for voltages in the range of 2988–3312; the near-independence of the current on voltage and its steadiness, as observed in Figure 2b, are characteristic features of the cone-jet mode. For applied voltages in the range of 3312–7920, the existing mode is the so-called electric dripping [16]. As shown in Figure 2c, the current emitted from the electrified meniscus is no longer steady. The process of charge emission follows a cyclic pattern. The meniscus accumulates charge since the charge supplied to the meniscus is larger than that emitted from it until the electric field at some point in the interface reaches the threshold value to ionize the surrounding. At such time, the meniscus is suddenly discharged and the charging process starts again. Experimental results have shown that the width of the electric dripping region narrowed, and even disappeared, for increasing values of the electrical conductivity of the sample. For higher values of the applied voltage, V greater than 7920, a continuous glow discharge from the meniscus was established, giving rise to the so-called cone-jet glow mode [16]. The appearance of the meniscus was similar to that of the Taylor cone-jet without discharge and the current emitted was also steady, see Figure 2d, but larger than in cone-jet without discharge; much of the current was transported through the ionized air.

To rule out any ambiguity about the presence of corona discharge in the cone-jet region, we carried out a new set of experiments by electrospraying water sample W6 with a CO_2 sheath to prevent any possible discharge. Results in Figure 3 showed that neither the cone shape nor the current emitted from the water cone-jet depended on whether the ambient gas was either air or CO_2 . Therefore, one concludes that electrical discharges were absent. On the other hand, the linear dependence of the current on the square root of the flow rate shown in Figure 3 is also a new strong indication that the water sample was being electrosprayed in the cone-jet mode without discharge.

Experimental results have also shown that the range of voltages required to form steady water cone-jets depended strongly on the electrical conductivity of the liquid sample. For example, in the case of sample W1,

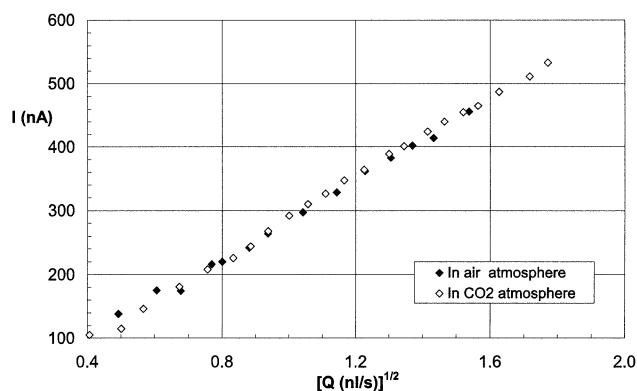


Figure 3. Current I emitted from a water sample W6 cone-jet in either air or CO_2 ambient versus the square root of the injected flow rate $Q^{1/2}$.

the width of the voltage range was as narrow as 20 V while for sample W2 with lower electrical conductivity, that width widened to about 300 V. Therefore, we have investigated the range of electrical conductivities within which cone-jets of water can be formed in air without electrical discharge. Different water samples covering an ample range of electrical conductivities ranging from that of deionized water up to 1.8 S/m have been used. The spray current corresponding to the different water samples has been plotted using appropriate dimensionless variables since they allow for an easy comparison with the scaling laws given in the literature. Therefore, following references [11] and [12], one uses the liquid-gas surface tension γ , electric conductivity of the liquid K , liquid density ρ , and vacuum permittivity ϵ_0 to build reference magnitudes for both flow rate and current:

$$Q_o = \frac{\epsilon_0 \gamma}{\rho K}, \quad I_o = \left(\frac{\epsilon_0 \gamma^2}{\rho} \right)^{1/2}. \quad (2)$$

Note in Figure 4 that the dimensionless results obtained for different samples, when plotted in appropriate dimensionless form, collapse close to a straight line. Moreover, the good agreement between our exper-

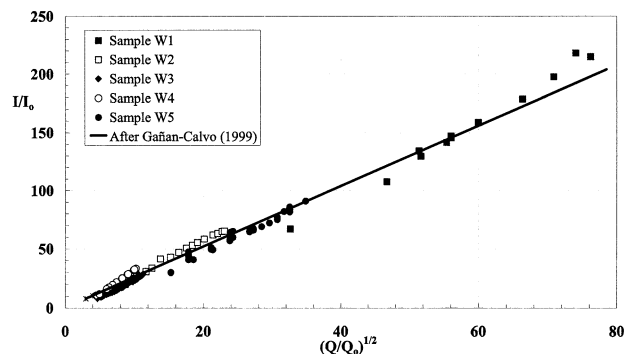


Figure 4. Dimensionless current I/I_o versus the dimensionless square root of the injected flow rate $(Q/Q_o)^{1/2}$ for different liquid samples.

imental data and the well known scaling current law for steady cone-jets $I/I_0 \sim (Q/Q_0)^{1/2}$ [12, 17], yields another unambiguous proof of the absence of corona discharge in the cone-jets obtained in the experiment. The influence of the electrical conductivity of the liquid on the onset of corona discharge in water cone-jets in air can be semi-empirically investigated by comparing the characteristic maximum value of the electric field on the cone-jet E_{cj} with the typical field required for air breakdown E_c . The field E_c for cylindrical liquid jets was firstly given in [18]; for fine cylindrical wires of radius r , Rouse gave the following experimental formula [19]:

$$E_c = 6.27(1 + 8.8 \times 10^{-4} r^{-3/2}) \text{ MV/m for } 15 \times 10^{-6} \text{ m} \leq r \leq 10^{-4} \text{ m.} \quad (3)$$

In the absence of better experimental results, for the calculations we have extrapolated eq 3 beyond its limit of validity. For sufficiently small values of r , the liquid discharge could be induced by ion evaporation field since the onset for the ion evaporation mechanism could be reached before corona discharge takes place. The ion evaporation threshold E_i is a function of the couple solvent-ion but this dependence seems to be quite narrow for most of the sets [20, 21]. Roughly speaking, a representative value of the electric field for the onset of the ion evaporation phenomenon could be 10^3 MV/m.

On the other hand, E_{cj} can be estimated from the empirical jet radius scaling law valid for small flow rates [12],

$$R_j \approx \beta^{1/6} R_0 \left(\frac{Q}{Q_0} \right)^{1/3}, \quad R_0 = \left(\frac{\gamma \epsilon_0^2}{\rho K^2} \right)^{1/3} \quad (4)$$

R_0 is a characteristic jet radius and β is the liquid to vacuum permittivity ratio. Introducing eq 4 in eq 1, one arrives at

$$E_{cj} \approx \frac{\rho^{1/6} (\gamma K)^{1/3}}{\epsilon_0^{5/6} \beta^{1/12} [Q/Q_0]^{1/6}}; \quad (5)$$

which reaches its maximum values for the smaller flow rates. Our experimental results seem to indicate that flow rates very close to the minimum one which can be electrospayed in the cone-jet mode have been experimentally reached in the electrospaying of samples W3 and W4. Note that the minimum flow rates obtained for the sets W3 and W4 agree well to condition $Q_{\min} \sim \beta^{1/2} Q_0$ given in reference [12]. It is worthy of noting that the liquid samples with higher conductivities, and therefore smaller minimum flow rates, have been operated at flow rates much larger than their minimum ones since for these latter flow rates, the pressure drop across the feeding line, which we used to measure the flow rate, could not be accurately fixed.

Figure 5 shows values of E_c , (eq 3), and E_{cj} , (eq 5), as

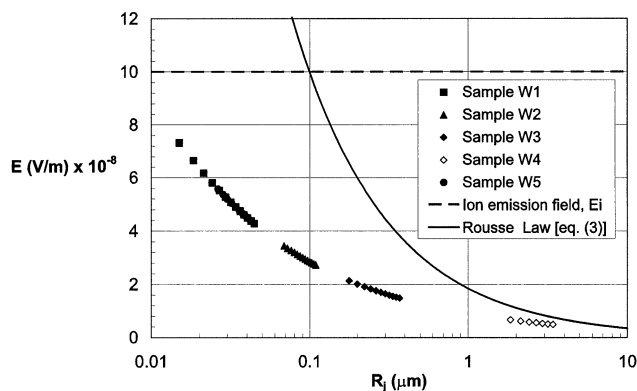


Figure 5. Estimated values of the maximum electric field E_{cj} at the surface of the cone-jet, corona discharge threshold field E_c (continuous line), and ion emission threshold field (dashed line) versus the jet radius R_j .

a function of the jet radius; the ion evaporation field E_i is also plotted. As expected, for the experiments considered in Figure 5, the estimated normal electric field at the water jet surface E_{cj} is smaller than both E_c (corona threshold) and E_i (ion evaporation field). E_{cj} becomes larger than E_c for jet radii larger than 16 microns. Therefore, corona discharge would always be present in the electrospaying of water solutions with electrical conductivities lower than 10^{-5} S/m since the resulting jet radius would be larger than 16 microns ($E_{cj} > E_c$). Note, however, that values of the electrical conductivity of the water of 10^{-5} S/m or smaller are quite unrealistic under normal experimental conditions. On the other hand, corona discharge is never present in the electrospaying of high conducting solutions since E_{cj} is much smaller than E_c and their difference increases when the conductivity increases (small jet radius).

On the contrary, ion evaporation is the discharging mechanism in the electrospaying of liquids with very large values of the electrical conductivity (small jet radius) since E_{cj} can easily reach the limit E_i ; this is the case found in references [20] and [21]. Note that in the case of water with electrical conductivity of 1 S/m electrospayed at flow rates near the minimum one, $Q_{\min}/Q_0 \sim \beta^{1/2}$, expression (5) yields an estimated value $E_{cj} = 10^9$ V/m, which equals the ion evaporation limit E_i . It is worthy of noting that in our experiments no water cone-jet could be formed without discharge for electrical conductivities larger than 2 S/m although the maximum limit of the electrical conductivity for which water cone-jets without discharge can be obtained was found to be sensitive to the room conditions. In fact, cone-jets of water sample W1, with a value of the electrical conductivity slightly lower than 2 S/m, were obtained during the summer period but not in winter when the ambient atmosphere of the laboratory was more humid.

We have investigated the transition from the cone-jet regime to the electrically dripping regime in air. In

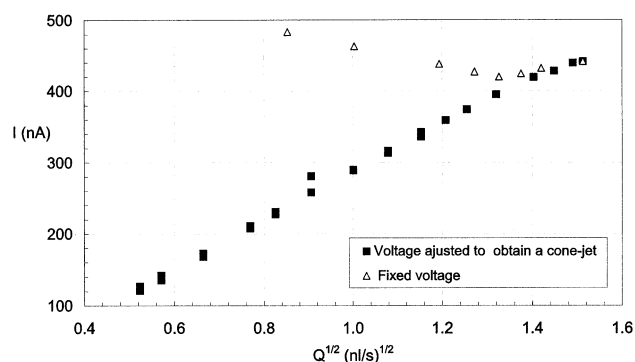


Figure 6. Average current I versus the square root of the injected flow rate $Q^{1/2}$. Filled squares correspond to cone-jets without discharge; open triangles correspond to both regimes: Cone-jet (the largest flow rates) and electrical dripping (the remainder). All the experiments were carried out in air.

Figure 6, black squares represent the current emitted from a steady cone-jet of water sample W2; for each flow rate, the applied voltage was properly adjusted to have a steady cone-jet. Consider now that the liquid is being electrosprayed from one of these steady cone-jets, particularly, one of those corresponding to the largest flow rates in Figure 6. If the flow rate is then decreased keeping the applied voltage fixed, the obtained values of the emitted current is followed by a new branch in Figure 6 represented by open triangles. This branch corresponded to the electric dripping regime characterized by an emitted average current significantly larger than that of the cone-jet. We found that the electric dripping branch disappeared when the same set of experiments was carried out with a CO_2 sheath.

The regime called cone-jet glow has been also investigated for water sample W1 ($K = 1.8 \text{ S/m}$) electrosprayed at a flow rate of 0.28 nl/s for the whole experimental set. The range of the applied electrical potentials was appropriate for corona discharge in the presence of air. However, no discharge occurred when the water sample was electrosprayed with a CO_2 sheath; black square symbols in Figure 7 yield the values of the current in this case. Note the indepen-

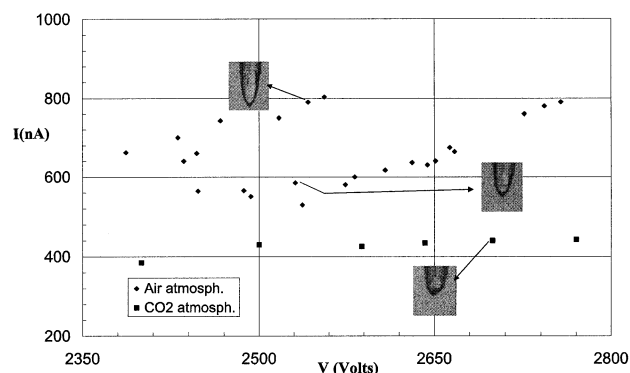


Figure 7. Current emitted from water sample W1 cone-jets with and without discharge. The flow rate was $Q = 0.28 \text{ nl/s}$.

dence of the current on the applied voltage that characterizes the cone-jet mode. For the experiments carried out in air at atmospheric pressure, black rhombus symbols, we have found that the current presents a bifurcation (two branches with different values of the current, for the same values of the flow rate and voltage). The two branches correspond to different steady cone-jet glow discharge configurations (different cone elongation). The lower branch is obtained by setting the voltage at a very large value and then decreasing it slowly until a steady cone is obtained while the upper one is reached acting in the opposite way (from sufficiently low voltages to higher ones). Note that the larger the emitted current from the cone the larger the cone elongation. The space charge of the charged cloud (spray), which reduces the value of the electric field at the cone interface increases with the emitted current; therefore, the smaller the current emitted from the cone the larger the resulting field and the smaller the cone elongation. Note also that for applied voltages sufficiently large only short cones (lower branch) are found. This is because the more elongated cones (upper branch) become unstable due to the increase of the space charge (decrease of the electric field at the cone surface and increase of the cone elongation) which takes place when the applied voltage increases. It is worthy to note that the existence of two branches in the cone-jet glow discharge mode has not been observed in the electrospraying of water samples with conductivities of 0.9 S/m and lower.

Acknowledgments

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