Anomalous conical menisci under an ac field-departure from the dc Taylor cone

Siddharth Maheshwari and Hsueh-Chia Chang[a)]
Chemical and Biomolecular Engineering Department, University of Notre Dame, Notre Dame, Indiana 46556 and Center for Microfluidics and Medical Diagnostics, University of Notre Dame, Notre Dame, Indiana 46556

(Received 16 August 2006; accepted 25 October 2006; published online 7 December 2006)

Observation of steady conical menisci with longitudinal growth is reported for electrospraying under high frequency alternating current (ac) electric fields. The authors report conical shapes that are analogous to the well-known direct-current (dc) cone-jet mode in the occurrence of conical menisci, but have some very distinctively ac features. The ac cones show a unique longitudinal growth that result in very high aspect ratio cones. The cone half angle for ethanol is approximately 9° for the ac case as compared to 47° for the dc case. These dissimilarities point to different mechanisms for dc and ac sprayings. © *2006 American Institute of Physics*.
[DOI: 10.1063/1.2402883]

The manipulation of liquids by an electric field is important for different applications and can be divided into electrokinetics or electrohydrodynamics,[1] depending upon the magnitude of the applied field. Electrohydrodynamic atomization under a dc electric field, i.e., dc electrospraying, has been studied extensively because of its manifold applications.[2] When a thin metal capillary, 10–100 μm in diameter, is filled with a liquid and charged to a high dc potential of several kilovolts, the liquid meniscus that protrudes from the end of the capillary deforms into a conical shape, known as the Taylor cone.[3] A steady thin liquid jet emanates from the conical meniscus tip, subsequently breaking up to form charged drops in the submicron range. The mechanism behind this process is well known. In response to the applied electric potential, charge separation inside the liquid takes place;[4,5] coion accumulation at the meniscus tip can then occur by interfacial tangential conduction. Such charge accumulation eventually produces a theoretically singular field at the tip, whose singular Maxwell pressure exactly cancels the singular capillary pressure of the observed Taylor cone. Evidently for this steady cone-jet mode, the charge relaxation time $\beta\varepsilon_0/K$ needs to be much smaller as compared to the hydrodynamic time LR^2/Q such that the free charges are confined to a thin layer near the cone surface and the bulk is quasineutral.[6] Here L and R are the axial and radial length scales in the jet, Q is the liquid flow rate, β and K are the dielectric constant and conductivity of the liquid, respectively, and ε_0 is the permittivity of free space. There have been some reports of a jetting phenomenon at extremely low conductivities,[7] such that the above inequality is not satisfied; however, the voltage-spray characteristics are quite different than the classic cone-jet mode.

In contrast to the well understood field of dc spraying, there have been relatively few studies on spraying trends under an ac electric field. At low frequencies behavior analogous to a changing dc field has been reported. The cones are formed and terminated every half cycle.[8] In addition, at frequencies coincident with the natural vibrating frequencies of free drops, resonant spraying behavior is observed as well.[9] At higher frequencies jetting behavior has been reported, with the absence of conical shapes.[10]

Here, we report the observation of steady conical shapes at a very wide range of operating frequencies until 200 kHz. The experiments reported here are for ethanol as the spraying liquid, although similar behavior is observed for acetonitrile, methanol, propanol, and butanol. We use denatured high performance liquid chromatography grade reagent alcohol (90.6% ethanol, 4.9% 2-propanol, and 4.5% methanol, Fisher) with liquid viscosity $\mu \sim 1.2\times10^{-3}$ Pa s, conductivity $K\sim0.7\times10^{-6}$ S/m, and dielectric constant $\beta\sim24.5$. The experiments were performed by applying a high frequency ac voltage across a metal needle (Mcmaster-Carr 6710A38, inside diameter=0.152 mm, outside diameter=0.305 mm, length=5 cm) and a ground electrode. The needle was inclined at an angle of approximately 45° with the horizontal and placed at a distance of 5 mm from a flat metal ground electrode. The inclination of the needle did not cause a variation in the results and the angle of 45° was chosen for convenient imaging. The needle inlet was connected to a syringe pump for supplying ethanol at a predetermined rate. The high voltage generation and measurement along with the optical imaging technique have been described elsewhere.[9]

Figure 1 shows the phase diagram for the spraying of ethanol depicting the three observed spraying modes as a function of the applied voltage and frequency. We note that the voltage demarcation between the various modes is practically independent of the applied frequency. At voltages lower than $\sim$4 $\mathrm{kV_{p\text{-}p}}$ (kilovolt, for peak to peak) dripping takes place, which is accelerated by the applied field. At voltages higher than $\sim$6 $\mathrm{kV_{p\text{-}p}}$ corona discharge becomes visible at the needle tip with the appearance of a bluish glow. This assists the ejection of drops periodically from the needle. For the imposed flow rate of 5 μl/min, drops are ejected at a rate of approximately 5/s, which remains constant throughout the frequency range. This discharge assisted ejection sequence is shown in Fig. 2. Bounded by these two spraying regimes, a stable conical meniscus is observed which does not alternate with the applied frequency but shows temporal growth. At frequencies between 15 and

[a)]Author to whom correspondence should be addressed; electronic mail: hchang@nd.edu

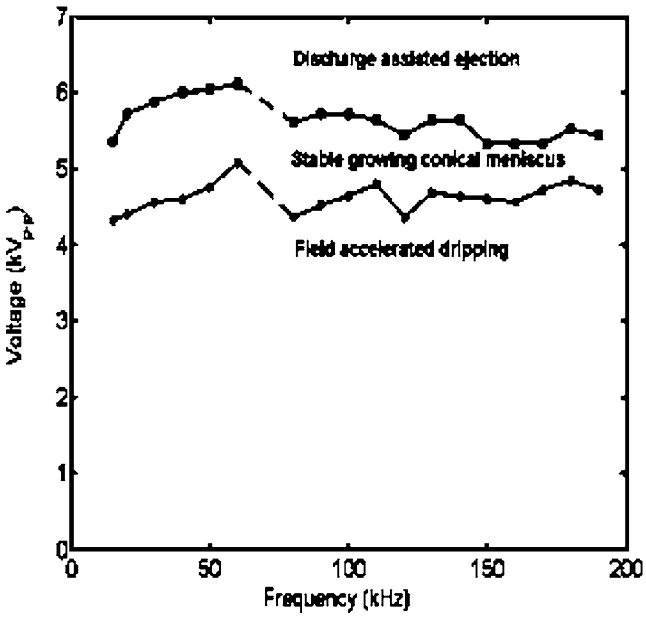

FIG. 1. Voltage-frequency phase diagram for three spraying modes observed with pure ethanol pumped at 5 μl/min.

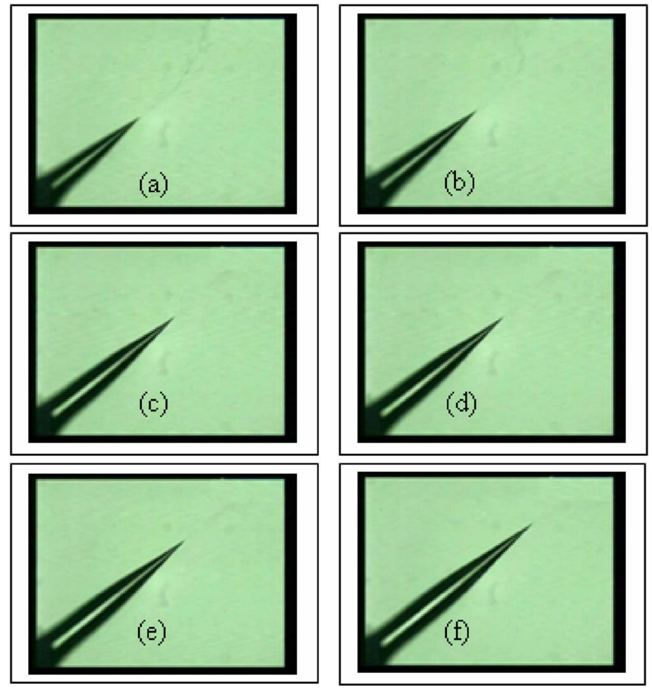

FIG. 3. (Color online) ac stable growing cone at 5 kV$_{p-p}$ and 95 kHz: successive images at 0, 2, 4, 6, 8, and 12 s.

30 kHz the meniscus is not perfectly stable and localized waves originate at the meniscus tip, with frequencies around 500 Hz, which is much lower than the applied frequency. However, with increasing applied frequency the conical meniscus becomes perfectly stable. At lower voltages, near the boundary of the conical spraying regime with the dripping regime, cone formation competes with the dripping phenomena. Once a conical protrusion appears, its growth at such voltages is smaller than the growth of the spherical meniscus due to dripping. Consequently, it is overtaken by the large drop and the conical shape is lost. After the drop has dripped away, the conical meniscus reappears and the entire cycle is repeated. As the voltage is increased, charge separation in the liquid phase is strengthened and, consequently, the growth of the conical meniscus becomes faster than the rate of dripping. Near the boundary between the conical spraying mode and the discharge assisted ejection mode, the growth of the conical shape continues unabated until an aspect ratio of around 15:1 (L/R), after which the meniscus become unstable and pinches off and again this process continues. In contrast, the aspect ratio for dc cones is around 1:1. A thin jet, which breaks to form drops, is always ejected from the cone tip, analogous to dc spraying. An important experimental feature is the very sensitive dependence of the spraying behavior on the sample conductivity. The presence of impurities that increase the sample conductivity can totally change the behavior at the meniscus, and the appearance of cones is delayed to higher frequencies. In contrast, conductivity changes the jet dimension for dc spraying.[8]

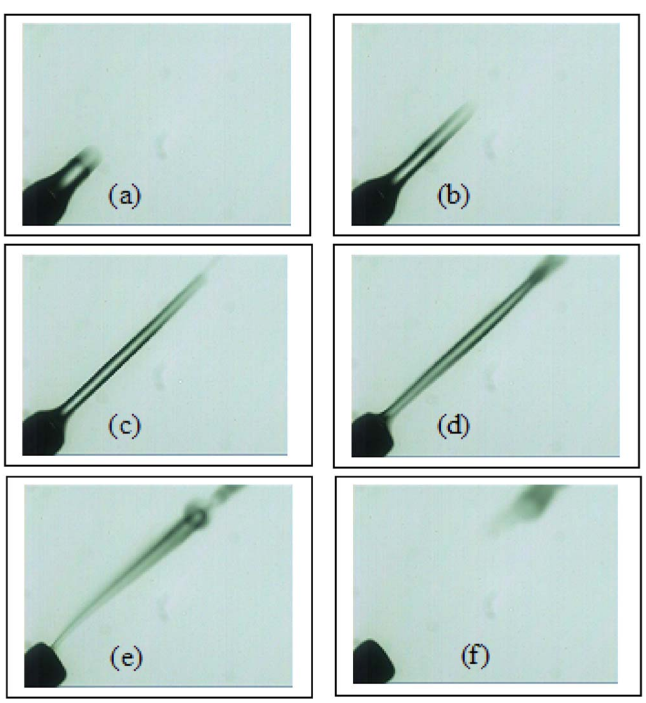

FIG. 2. (Color online) Discharge assisted ejection at 6.5 kV$_{p-p}$ and 150 kHz: successive images at 0, 0.5, 1, 1.5, 2, and 2.5 ms.

The most obvious discrepancy observed here is the steadiness and growth of this conical shape. Extension of classical dc spraying theory suggests the formation and annihilation of cones every half cycle, since the polarity of liquid phase charge is changing every half cycle. This is consistent with the behavior observed at low frequencies. However, as our experiments show, the behavior at high frequencies is quite different. Instead of forming and deforming every half cycle, the cone remains steady, as shown in Fig. 3. The successive images in Fig. 3 also illustrate the longitudinal temporal growth of the meniscus. To verify that this growth process is an intrinsic feature of the ac spraying mechanism and not due to a flow-rate mismatch between the flows coming out of the cone tip and being supplied by the pump, similar experiments were performed without any imposed flow rate from the pump. But even then, the cone growth continued until the meniscus became very slender and unstable. After pinch off, if there was some residual liquid at the needle tip, the conical meniscus was reformed and the same process continued until there was no more liq-

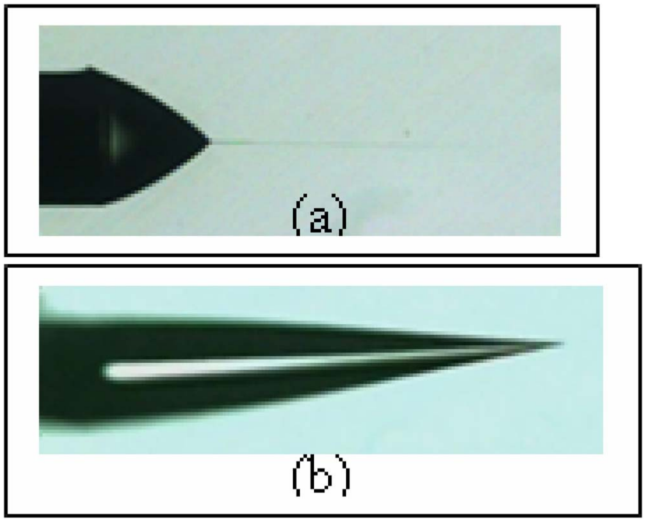

FIG. 4. (Color online) Comparison of (a) dc cone-jet mode at 3 kV and (b) ac conical mode at 100 kHz and 5 $kV_{p\text{-}p}$.

uid remaining. Similar experiments with a dc field did not produce any such growth effect. Due to zero flow from the pump, the dc cone became unsteady and continued to form and break until all the liquid at the needle tip was exhausted. This unsteadiness was a result of the flow-rate mismatch, because there was a definite amount of liquid being ejected from the cone tip but there was no liquid supply from the pump. Even in this unsteady cone, the aspect ratio remained constant at approximately 1:1 throughout. This demonstrates that the growing meniscus is the effect of the applied ac potential and is limited to high frequency ac spraying. Another important distinction between the dc cone jet mode and the ac conical regime is the half angle of the cones. As seen from Fig. 4, the half angle of the dc cone is ~47° which is very close to the Taylor angle of 49.3°. However, for the ac case the angle is ~9° which is significantly less than the dc case, although the same liquid has been used. The cone angle remains approximately constant throughout the applied frequency window.

Thus we report the observation of an ac cone-jet mode which is similar to dc cone jets in the appearance of a steady conical meniscus with a thin jet emerging from the cone tip, but exhibits a growing and much slender meniscus. Additionally, as per the behavior observed at low frequencies (<1 kHz), the cones should appear and disappear every half cycle. Instead, the observed conical shape at high frequency (>10 kHz) is stable and does not alternate with the frequency. These distinctions suggest some mechanistic differences between high frequency ac spraying and dc/low frequency ac spraying. The origin of these differences might be explained by the additional dominant time scale for these experiments, the half period of the applied field where the frequency ranges from 15 to 190 kHz, as reported in Fig. 1. The half period then corresponds from 33 to 2.6 μs. For the sprayed ethanol the charge relaxation time is ~310 μs. Consequently, the relevant frequency time scale is at least an order of magnitude smaller than the relaxation time, indicating that the liquid bulk is not discharged fully, which is different from the dc cone-jet mode. The insufficient time available for charge relaxation and the continuous growth of the conical meniscus suggest some preferential charge entrainment taking place every period leading to a progressive accumulation of charge in the liquid bulk resulting in a growing meniscus. Further work is being carried out in order to understand this mechanism.

This research is supported by a NASA grant NAG3-2701 and a NSF grant CTS04-54956. One of the authors (S.M.) acknowledges partial support from the Center for Applied Mathematics at the University of Notre Dame.

[1] D. A. Saville, Annu. Rev. Fluid Mech. **29**, 27 (1997).
[2] O. V. Salata, Current Nanoscience **1**, 25 (2005).
[3] G. I. Taylor, Proc. R. Soc. London, Ser. A **280**, 383 (1964).
[4] P. Kebarle, J. Mass Spectrom. **35**, 804 (2000).
[5] R. B. Cole, J. Mass Spectrom. **35**, 763 (2000).
[6] A. M. Ganan-Calvo, J. Davilla, and A. Barrero, J. Aerosol Sci. **28**, 249 (1997).
[7] S. N. Jayasinghe and M. J. Edirisinghe, Appl. Phys. Lett. **85**, 4243 (2004).
[8] J. P. Borra, Y. Tombette, and P. Ehouarn, J. Aerosol Sci. **30**, 913 (1999).
[9] P. Wang, S. Maheshwari, and H-C. Chang, Phys. Rev. Lett. **96**, 254502 (2006).
[10] L. Y. Yeo, D. Lastochkin, S.-C. Wang, and H-C. Chang, Phys. Rev. Lett. **92**, 133902 (2004).