Available online at www.sciencedirect.com

ScienceDirect

International Journal of Mass Spectrometry 272 (2008) 199–203

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

Short communication

Electrospraying of water in the cone-jet mode in air at atmospheric pressure

J.L. Li[a,*], A. Tok[b]

[a] *School of Materials Science and Engineering, Shanghai University, Shanghai 201800, China*
[b] *School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore*

Received 8 December 2007; received in revised form 15 January 2008; accepted 15 January 2008

Abstract

The electrospraying of water, with high surface tension, in the cone-jet mode in air was generally impeded by an electrical breakdown. In this work, a novel nozzle with a non-conductive fiber was used to electrospray deionized water in the cone-jet mode in air at atmospheric pressure. Results show that the fiber introduced a kinetic energy gain to the liquid before it was electrosprayed, which then successfully overcame the traditional impediment that only a tiny capillary could be used in electrospraying water in air. Our work paves an important way for the electrospraying of water in air.

Keywords: Electrospray; Water; Cone-jet

1. Introduction

Electrospraying, mainly in the cone-jet mode, has been applied in many fields, such as materials synthesis and coating preparation [1–6]. Among these applications, the electrospraying of water in the cone-jet mode is of special interest in chemical surface treatments and generation of new biomaterials. Especially, the use of pure water solutions is highly desirable in mass analysis of biomolecules because water is the natural surrounding of most biomolecules [7–9]. Also water droplets produced by electrospraying can be used for targeted drug delivery by inhalation [10].

The generation of electrospraying of pure water in the cone-jet mode, however, is still rather difficult. Researchers argue that the threshold value of the electric field required for pure water to form a Taylor cone-jet is larger than the electrical breakdown threshold of air; as a result, corona discharges would appear before the formation of the cone-jet for pure water. As a solution to this problem, a gas sheath of CO_2 or SF_6 was used to obtain a steady cone-jet of water without electrical discharge [9,10].

However, a recent paper by Lopez-Herrera et al. reported that by using a tiny silica nozzle (20 μm and 50 μm inner and outer diameters, respectively) the authors performed electrospraying of water in cone-jet mode in air [11]. They suggested that an operation window for the cone-jet of water exists. But, the tiny needle used in their experiment seems likely to experience some difficulties, especially in materials preparation, because of the evaporation of solvent in the spray process, which sometimes gives rise to the blockages in the nozzle.

On the other hand, from the energy point of view, a jet forms if a critical rate is reached, that is, the kinetic energy of the liquid is greater than the surface energy required for creating the surface of the jet [12,13]. In our previous work on sunflower oil, we found that using a non-conductive fiber inserted in a conventional needle nozzle greatly reduced the onset voltage for the cone-jet mode [14]. The liquid in above work receives additional kinetic energy before it reaches the fiber end, which does not take place in a conventional nozzle. We thus realized that this method could be used to electrospray water in the cone-jet mode without an electrical breakdown in air, because the reduced onset voltage for a cone-jet means that to some extent less intense electrical field is needed. In this communication, we report the effort to electrospray deionized water in the cone-jet mode in air using our novel nozzle.

2. Materials and methods

A typical ring-nozzle configuration was used. The nozzle was positively electrified while the ring was earthed. The noz-

---

[*] Corresponding author. Tel.: +86 21 56331429; fax: +86 21 56331704.
E-mail address: jlli@shu.edu.cn (J.L. Li).

1387-3806/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2008.01.005

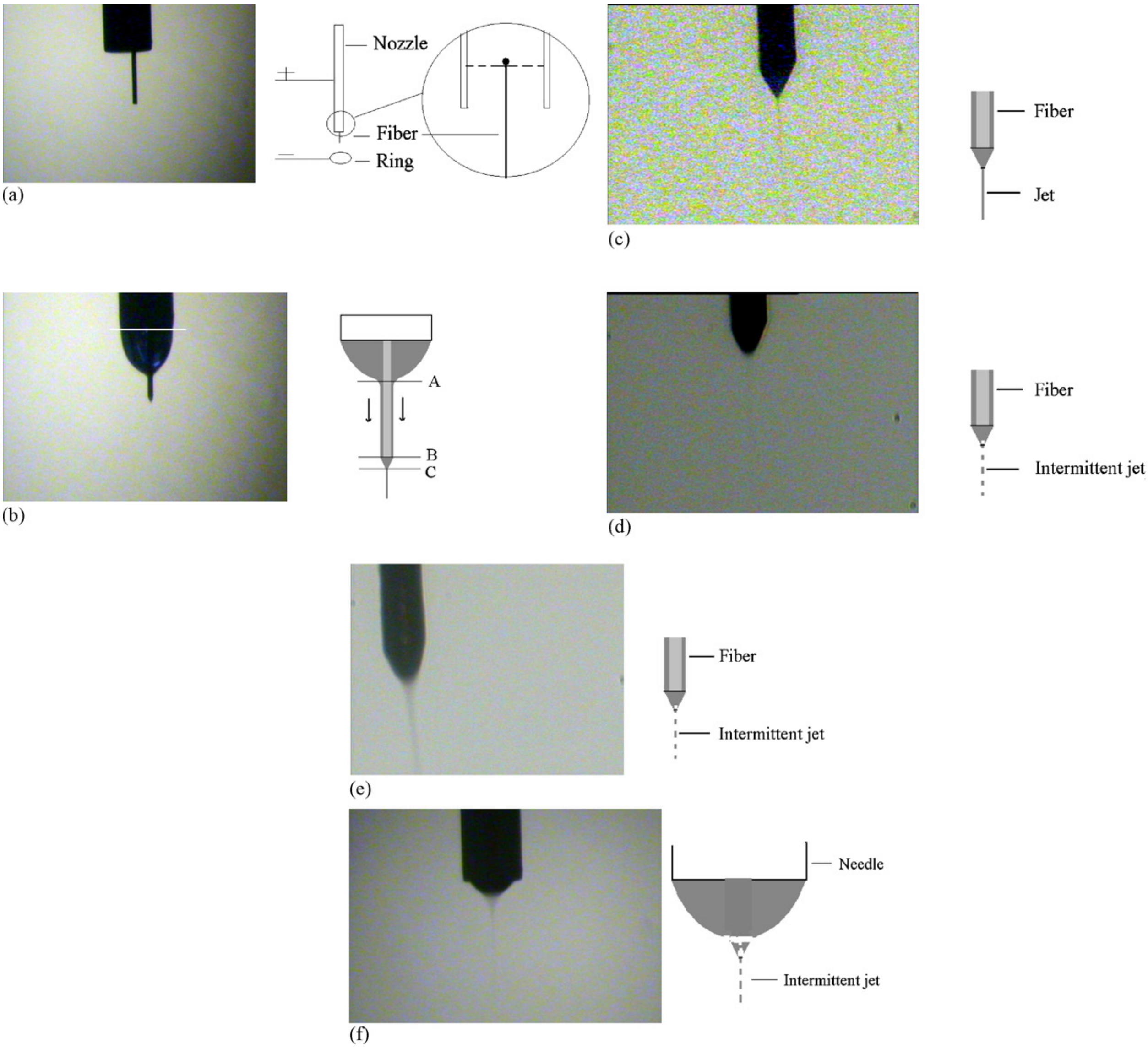

Fig. 1. Profiles (a) showing our novel nozzle and its schematic, (b) electroapraying of water in the cone-jet mode in air, its schematic showing the flow of water along the fiber surface during the electrospraying process. In this work, the meniscus (A site) refers to the meniscus attached to the needle while the meniscus at the end of the fiber (B site) is called the Taylor cone (C site) from which the cone-jet is emitted. (c) A close view of picture (b) and its schematic showing the spraying of water from the end of the non-conductive fiber, (d) and (e) intermittent jets from the end of a copper wire and a bamboo fiber, and their schematics, respectively, and (f) an intermittent jet from the needle without a fiber and its schematic. The applied voltage was 5.7 kV when the images were recorded.

zle consisted of a stainless steel needle (with the inner and outer diameters of 600 μm and 900 μm, respectively) and a non-conductive glass fiber with a diameter of 90 μm inserted in the needle. The fiber was also water-proof. One end of the fiber was fixed to a metal frame with a flexible central, similar to that used in our previous work [14] (Fig. 1a). When water flowed through the needle, the fiber was aligned automatically to the axis of the needle. A copper ring with a diameter of 20 mm was used as an extractor electrode, and placed 18 mm away from the needle tip. Deionized water with a surface tension of 71 mN/m and a conductivity of 8.1×10^{-4} S/m was contained in a glass syringe and continuously fed into the nozzle through a silicone rubber tube with a perfusor syringe pump. The flow rate of the water was kept at 5×10^{-11} m^3/s throughout the experiment.

3. Results and discussion

As shown in Fig. 1b, a meniscus was formed between the fiber and the end of the needle when the water flowed down along the fiber. At the end of the fiber, the Taylor cone was formed, from which a steady cone-jet emitted (Fig. 1c). Here, the tangential electric stress acting on the meniscus surface forced the liquid to move down and flow along the fiber surface to the tip of the fiber. Just as in a common electrospraying, before the applied voltage reached the onset voltage for the cone-jet, the water exhibited an intermittent spray. In order to further investigate the effect of the fiber on the spray, a copper wire with the same thickness and length of the non-conductive fiber was employed to perform the spray. The copper wire was electrically

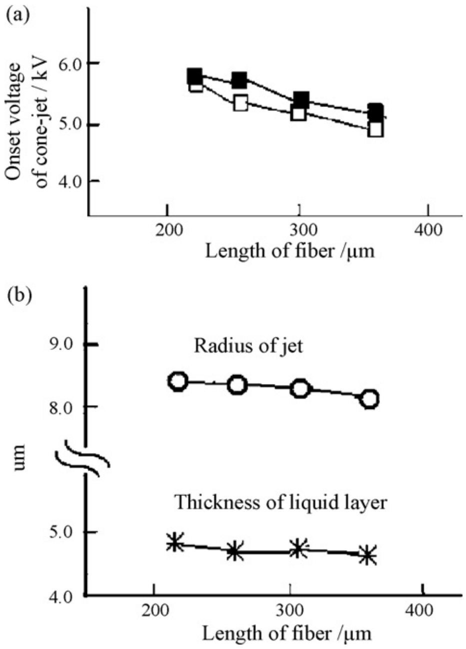

Fig. 2. (a) The dependence of operation voltage for cone-jet mode on fiber length. The fiber length refers to the length of the fiber below the meniscus close to the needle, and (b) thickness of the liquid layer on the fiber surface near the end of the fiber. The applied voltage corresponds to that shown in Fig. 2a (lower line). To make a comparison, the thickness of the jet is also included. This measurement was made where the jet was just extracted from the meniscus and exhibits the greatest curvature. It is estimated that the data here has an error of about 10%.

connected with the steel needle by the metal frame; as a result, no potential difference along the wire existed, leading to the disappearance of the tangential electric stress along the copper wire. As expected, no operation window was found for the cone-jet mode in this case; only an intermittent jet was produced (Fig. 1d). This experimental study thus rooted out the possibility that the local electric field around the fiber tip was strong enough for the water to spray in the cone-jet mode. When we replaced the non-conductive fiber with a bamboo fiber of the same thickness and length, only intermittent jets were formed (Fig. 1e).

As a comparison, the electrospraying of water directly from the needle was recorded (Fig. 1f). After a dripping mode, a typical intermittent jet emitted from the meniscus and no cone-jet was produced by changing the applied voltage.

When the cone-jet was formed at the fiber end, with the increase in fiber length, the onset voltage for the cone-jet mode decreased (lower line in Fig. 2a). If the applied voltage exceeded the upper limits (upper line in Fig. 2a), the meniscus became unstable and the cone-jet at the fiber end was thus deconstructed. From this figure one can see that the length of the non-conductive fiber affected the onset voltage for a cone-jet. It seems that a longer fiber extruding to the counter electrode means a more intensive local electric field around the fiber end, indicating that the increase in fiber length led to the decrease of onset voltage for the cone-jet formation (Fig. 2a).

Shown in Fig. 2b is the thickness of the liquid layer on the fiber surface near the fiber end. To make a comparison, the thickness of the newly born jet is also included in this figure. With the increase in fiber length, the thickness of the jet and of the water layer along the fiber was slightly decreased. Previous researches have demonstrated that the diameter of a cone-jet is significantly affected by flow rate, but not affected by applied voltages [15,16]. Therefore, the slight decrease in the jet thickness might be caused by the evaporation of water. As shown in Fig. 2b, a longer fiber was associated with slightly more evaporation of water.

As shown in Fig. 1b, while the water flows from the meniscus onto the fiber surface driven by the electrical stress (A site in Fig. 1b), the cross-sectional area reduces dramatically by 170 times (Fig. 2b), indicating a 30,000 times increase in kinetic energy of the flowing water. This is not surprising; the average speed of liquid in the meniscus is extremely low, around 10^{-4} m/s, with a given flow rate of 5×10^{-11} m^3/s in this work.

The electrical stress seems to stabilize the water layer along the fiber. Especially, the tangential electric stress along the fiber meets the energy demand from the internal friction of the water running along the fiber, avoiding losses to its kinetic energy obtained from the upstream.

In previous works, using the Navier–Stokes equations for Newtonian liquids, some researchers completed numerical modeling of electrospraying in the cone-jet mode [17,18]. In the current work, as shown in Fig. 1b, if a modeling is made, for the Taylor cones (at B site) with and without a fiber inside, the results will have a constant difference, because only the boundary condition was slightly changed. That is, around the Taylor cone impending on the fiber end, the boundary condition for the axial velocity is not 0, but the speed acquired before the liquid arriving at the fiber end. In the case without a fiber, the boundary condition for the axial velocity is assumed to be 0.

Shown in Fig. 3 are two figures cited from Yan et al.'s work [18], which are re-plotted. Other investigators reported the similar results. As shown in Fig. 3a, near the apex of the meniscus (F point), the dramatic jump in velocity from V_0 to V_F is associated with the formation of the cone-jet. In our work, when the velocity of the liquid obtained from upstream is taken into account, the baseline of the velocity should be shifted upwards, from V_0 to V_M. This means that the velocity jump needed to produce a cone-jet is reduced. Especially, the required jump in velocity is changed to $V_F - V_M$.

As discussed above, at A site in Fig. 1b, the huge velocity increase, 170 times, which survives the traveling along the fiber, is caused by the tangential electric stress acting on the lateral surface of the meniscus. Therefore, when the velocity jump (Fig. 3a) needed for the cone-jet formation is decreased (at C site in Fig. 1b), the applied electric stress and thus the electric field strength could be lowered, as shown in Fig. 3b. But the final velocity of the liquid at the apex of the Taylor cone was still large enough for the cone-jet formation. This suggests that the necessary voltage for the operation of the cone-jet could be reduced. Especially, the electrospraying of water in the cone-jet mode in air can be realized without an electrical breakdown, as demonstrated in our work. The set-up used here is absolutely different from that of Lopez-Herrera et al. [11], a much huge needle nozzle, about 20 times bigger their needle, being used in the present work.

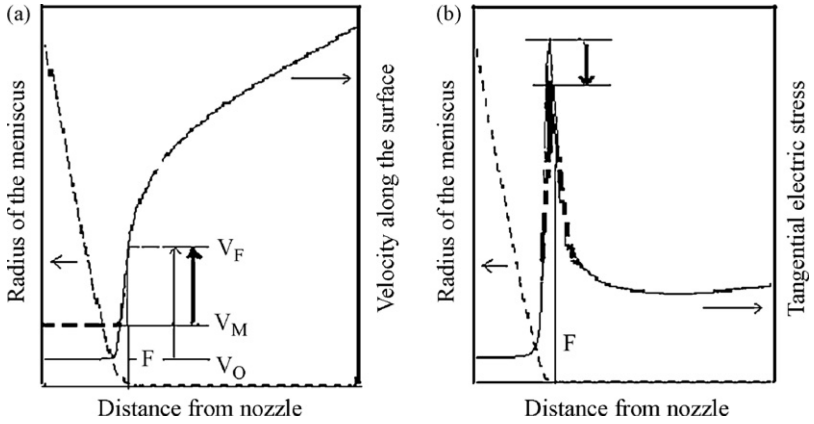

Fig. 3. Curves showing the formation of the cone-jet with the rapid increase in velocity near the apex of the Taylor cone (a), and the change in liquid velocity with the applied electric tangential stress (b). In both figures the thick lines indicate the effect of a non-conductive fiber on the spray.

Now the key point here is whether the liquid obtained considerable kinetic energy when reaching the fiber end. As shown in Figs. 1b and 2b, when the flow rate Q is unchanged, for the liquid layer we have

$$Q = [\pi(d + R)^2 - \pi R^2]V \tag{1}$$

where d is the thickness and V the average velocity of the water layer on the fiber surface, and R is the radius of the fiber.

Here we let the liquid flow out of a needle with a size of $d+R$, thus

$$Q = \pi(d + R)^2 V_{\text{needle}} \tag{2}$$

where V_{needle} is the average velocity of the liquid from such a needle.

Thus

$$\frac{V}{V_{\text{needle}}} = \frac{(d + R)^2}{d(d + 2R)} \approx 6 \tag{3}$$

Therefore, the addition of the non-conductive fiber dramatically speeds up the liquid being provided to the fiber end, which means that the kinetic energy of the liquid increased by 36 times. But it seems that the speed of the liquid layer is still insufficient to produce a hollow meniscus.

Since the liquid running along the fiber is significantly thin, the current along the fiber surface mainly comprises convection current, as in the case of the jet. But, it is difficult to estimate the potential decay at each part of the electric circuit, though the voltage difference over the meniscus attached to the needle can be omitted. According to previous researches, a jet forms if the speed of liquid reaches a critical rate, that is, the kinetic energy of the liquid is greater than the surface energy required for creating the surface of the jet [17,18]. Hence, it is helpful to compare the kinetic energy of the liquid layer E_L and the kinetic energy of the jet, E_J.

The kinetic energy of the moving liquid is proportional to the square of its velocity, which is reversely proportional to the section area. Let r be the radius of the just formed jet, then from Fig. 2b

$$\frac{E_L}{E_J} = \left\{ \frac{r^2}{d(d + 2R)} \right\}^2 \approx 2.5\% \tag{4}$$

This assessment is rough and this contribution seems not so huge, but it really works in some cases. For example, if the onset voltage of the cone-jet is 6 kV, possibly in fact only 5.8 kV is needed if a non-conductive fiber is used in the operation. As a result, the decrease in the onset voltage offers us a window to ensure the happening of the cone-jet without an electrical breakdown.

When a copper wire is used, in the absence of the tangential electric stress along the fiber, the water running over the fiber will lose some of its kinetic energy to overcome its internal friction. As a result, the loss to its kinetic energy leads to the failure in a cone-jet formation at the copper wire end (Fig. 1d). Therefore, during the formation of the cone-jet using a non-conductive fiber, the tangential electric stress along the fiber surface plays an important role.

As shown in Fig. 1e, when a bamboo fiber is used, the water diffuses into the fiber and actually does not have any kinetic energy when it appears at the bamboo fiber end. As a result, without the assistance of the kinetic energy gain, the local electric field near the fiber tip was unable to force the water to spray in the cone-jet mode. Therefore, the change in velocity of the liquid really makes a difference in the cone-jet formation.

In reality, only a very small part, less than 20–30% of the total input energy from the power is used to operate the cone-jet; the rest is spent on further speeding up the jet downstream [19]. In the present work, the physics is that some input energy used to speed up the jet downstream is transferred to the process of the cone-jet formation.

Among the different scaling laws of the jet diameter in electrospray, one is based on the inertia of liquid, that is, the kinetic energy of the jet at the inception point equals to the surface tension, $1/(2\rho V^2) \approx (\gamma/r)$, where ρ is the liquid density, V is the velocity of liquid, γ is the surface tension coefficient of liquid, and r is the radii of jet. Since the ratio of the kinetic energy to the surface tension pressure is 1 at the jet inception point (C site in Fig. 1b), from Fig. 2b, the ratio is about 1/4 at the fiber end (B site in Fig. 1b). That is, the local electrical field contributes 3/4 to the final kinetic energy of the newly born jet, and the rest 1/4 is from the kinetic energy of the water. This is a rough estimate of scaling laws, but clearly tells us in this case the kinetic energy of water obtained upstream plays an important role in the cone-jet formation.

4. Conclusions

By using a novel huge nozzle we have successfully electrosprayed water in the cone-jet mode in air at atmospheric pressure. During the spray, the electric field provides the water additional kinetic energy before it reaches the fiber end. The electric field strength needed for the formation of a cone-jet is thus reduced, indicating that the onset voltage for the cone-jet mode is also decreased. This opens a window for the cone-jet formation of water in air, which is a very important achievement in electrospray study.

References

[1] B. Fenn, M. Mann, C.K. Meng, S.F. Wong, Science 64 (1989) 64.
[2] T. Dulcks, R. Juraschek, J. Aerosol. Sci. 30 (1999) 927.
[3] M. Sato, H. Takahashi, M. Awazu, T. Ohshima, J. Electrostat. 46 (1999) 171.
[4] M.S. Khil, H.Y. Kim, M.S. Kim, Polymer 45 (2004) 295.
[5] Ch.K. Ryu, K. Kim, Appl. Phys. Lett. 67 (1995) 3337.
[6] B.M. Min, G. Lee, S.H. Kim, Y.S. Nam, T.S. Lee, W.H. Park, Biomaterials 25 (2004) 1289.
[7] S.B. Sample, R. Bollini, J. Colloid Interface Sci. 41 (1972) 186.
[8] M. Cloupeau, J. Aerosol. Sci. 25 (1994) 1143.
[9] X.F. Zhu, S. Thiam, B.C. Valle, I.M. Warner, Anal. Chem. 74 (2002) 5405.
[10] K. Tang, A. Gomez, J. Aerosol Sci. 25 (1994) 1236.
[11] J.M. Lopez-Herrera, A. Barrero, A. Boucard, I.G. Loscertales, M. Márquez, J. Am. Soc. Mass Spectrosc. 15 (2004) 253.
[12] N.R. Lindblad, J.M. Schneider, J. Sci. Instrum. 42 (1965) 635.
[13] M. Cloupeau, B. Prunet-Foch, J. Aerosol Sci. 25 (1994) 1021.
[14] J.L. Li, J. Aerosol. Sci. 36 (2005) 125.
[15] B.K. Ku, S.S. Kim, J. Aerosol Sci. 33 (2002) 1361.
[16] P. Noymer, M. Garel, J. Aerosol Sci. 33 (2000) 1165.
[17] R.P.A. Hartman, D.J. Brunner, D.M.A. Camelot, J.C.M. Marijnisse, B. Scarlett, J. Aerosol Sci. 30 (1999) 823.
[18] F. Yan, B. Farouk, F. Ko, J. Aerosol Sci. 34 (2005) 99.
[19] A.M. Ganan-Calvo, Phys. Rev. Lett. 79 (1997) 217.