

Operational Modes of Dual-capillary Electrospraying and the Formation of the Stable Compound Cone-jet Mod

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Abstract

Experiments were performed to investigate the operational modes in a dual-capillary electrospraying (ES) system in the point-to-plate configuration. For a fixed distance from the capillary tip to the plate, four possible primary modes were observed with increasing of applied voltage. They are the dripping mode, silver-bullet-like mode, stable compound cone-jet mode (if attainable), and unstable cone-jet mode (or called multi-jet mode). The characteristics (i.e., the transformation of liquid meniscus shapes and spray current) of these modes and the transitions between the modes were described. Special attention was paid to identifying the sufficient conditions to establish the stable compound cone-jet mode in the dual-capillary ES system. With the designed experimental matrix for test liquid pairs (i.e., for inner and outer liquids) it was found that a stable compound cone-jet mode can be formed for miscible and partially miscible liquid pairs. For immiscible liquid pairs, two sufficient conditions were identified for the formation of stable compound cone-jet mode: (1) the liquid of low dielectric constant in the liquid pair should be used as outer liquid, and (2) the surface tensions of the liquid pair should satisfy the total or particle engulfing conditions for a three-phase interaction system at static condition. The reasoning for the two observed sufficient conditions is also given.

Keywords: Dual-capillary electrospraying; Cone-jet mode; Stable mode formation.

INTRODUCTION

Electrospraying (ES) technology has been proposed and investigated for many practical

applications. Examples of these applications include macromolecular detection, nanomaterial synthesis, monodisperse nanoparticle production, fuel injection for internal combustion engines, micro-thrusters for space propulsion, and drug delivery by inhalation (Tang, 1994; Chen and Pui, 1995; Siuzdak, 1996; Cole, 1997; Gamero-Castano

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and Hruby, 2001; Gomez, 2002; Kaiser *et al.*, 2003). The typical configuration of ES systems is the point-to-plate arrangement. For simplicity, spray liquid is fed through a single capillary from one end and the other end of the capillary serves as the spray tip (or point). The operational modes in a single-capillary electrospray system have been extensively investigated and summarized in the literature (Cloupeau M., Prunet-Foch, 1989, 1990; Rosell-Llompart and Fernandez de la Mora, 1994; Loscertales and Fernandez de la Mora, 1994; Saville, 1997; Higuera, 2004; Ganan-Calvo *et al.*, 1994, 1997, 2004; Fernandez de la Mora, 2007). Great attention has been paid to the cone-jet mode in which ES systems produce highly charged, monodisperse particles with diameters varying from a few nanometers to the supermicrometer range (Rosell-Llompart and Fernandez de la Mora 1994; Chen and Pui, 1995; Lohmann and Schmidt-Ott, 1995). Such highly-charged, monodisperse particles, especially with diameters in nanometer range, are much desired for nanotechnology applications. Limitations of the single-capillary technique, however, emerge when applying it in more complex applications.

First of all, the stable operation of a single-capillary ES system in the cone-jet mode requires ionized solutions with electrical conductivity in a suitable range. The requirement of ionized solutions is often achieved by dissolving additives in spray solutions. Suitable additives are, however, difficult to identify for solutions with low dielectric constants. For example, organic

solvents of low polarity are widely used in biomaterial processing. Identification of ion additives to vary the electrical conductivity of such low-polarity solvents is a great challenge for ES users. The additive must be bio-compatible and have an appropriate pH. In the few cases even where an ion additive is available, the changeable range of the electrical conductivity of the solvents is often very limited. Consequently, it limits the capability of varying the particle sizes generated by the single capillary ES technique. Secondly, if the solute (i.e., particle material) is dissolved and ionized in solvents, single-capillary ES cannot independently control the droplet size and electrical charge level of produced particles. The lack of droplet size control makes it impossible to directly produce monodisperse particles of a fixed size and at different electrical charge levels. Lastly, the encapsulation of colloidal suspensions by single-capillary ES is possible only when the coating material can be dissolved in the same solvent and the dissolution will not destabilize the suspension. Tight control of the coating thickness of capsules also presents a challenge, even when the above-mentioned conditions are met. To overcome the limitation of single-capillary ES, the dual-capillary electrospraying (ES) technique has thus been proposed.

Instead of a single capillary, the spray head of a dual-capillary ES system consists of two capillaries co-axially assembled. The dual-capillary configuration of ES systems was first proposed and demonstrated to introduce biomaterial into cells for gene transfection

(Chen and Pui, 2000). Making use of the space charge effect to propel biomaterial particles at high speed prior to reaching target cells, the dual-capillary ES system was proposed to “coat” more electrical charges on the particles by sheathing the biomaterial suspension (in the inner capillary) with highly conductive and volatile liquid (in the outer capillary) during the spray process. Using the coaxial electrospray, Loscertales *et al.* (2002) demonstrated the production and control of monodisperse capsules in submicron sizes, varying from 0.15-10 microns. They also found that the diameter of capsules produced in coaxial electrospray is influenced not only by the operational parameters, such as liquid feed flowrates, but also by the physical properties of spray liquids as well as the interaction between inner and outer liquids during the spray process. Lopez-Herrera *et al.* (2003) further investigated electrified coaxial jets of two immiscible liquids issuing from a structured Taylor cone. To interpret the experimental observation, they introduced the concept of a driving liquid and presented the linear scaling law for the compound jet diameters. However, the work did not identify the requirements to form the stable cone-jet mode in a dual-capillary ES system. Chen *et al.* (2005) studied compound jet electrospray modes using an ethanol/glycerol/tween mixture and cooking oil, two immiscible liquids. They found that the spray phenomena were mainly controlled by the property of outer liquid, which was very viscous and electrically conductive. However,

generalization of the finding in the work of Chen *et al.* (2005) is limited and may be questionable, because only one liquid pair, with a very viscous one as the outer liquid, was investigated.

The dependence of liquid meniscus phenomenology in dual-capillary ES is rather complex and only a few publications on the subject have been presented. At the same time, the ability to operate a dual-capillary ES system in different modes is in high demand. This is especially true for the cone-jet mode, due to its capability of producing highly charged and monodisperse particles. The basic knowledge to establish the cone-jet mode in a dual-capillary ES system is, however, unclear in the literature. The objective of this study is thus to investigate the condition(s) required to establish a stable cone-jet mode in a dual-capillary ES system through data collected from the electrospraying of a broad collection of solvent pairs using a well-defined dual-capillary ES system.

REVIEW OF FINAL CONFIGURATION FOR THREE-PHASE FLUID SYSTEM

Because of the involvement of three fluid phases (i.e., two liquid menisci/filaments suspended in a gas) in a dual-capillary ES system, it is necessary to review existing theories on three-phase interaction when fluids are placed in a system. Torza and Mason (1970) were the first to theoretically investigate the final configuration when two

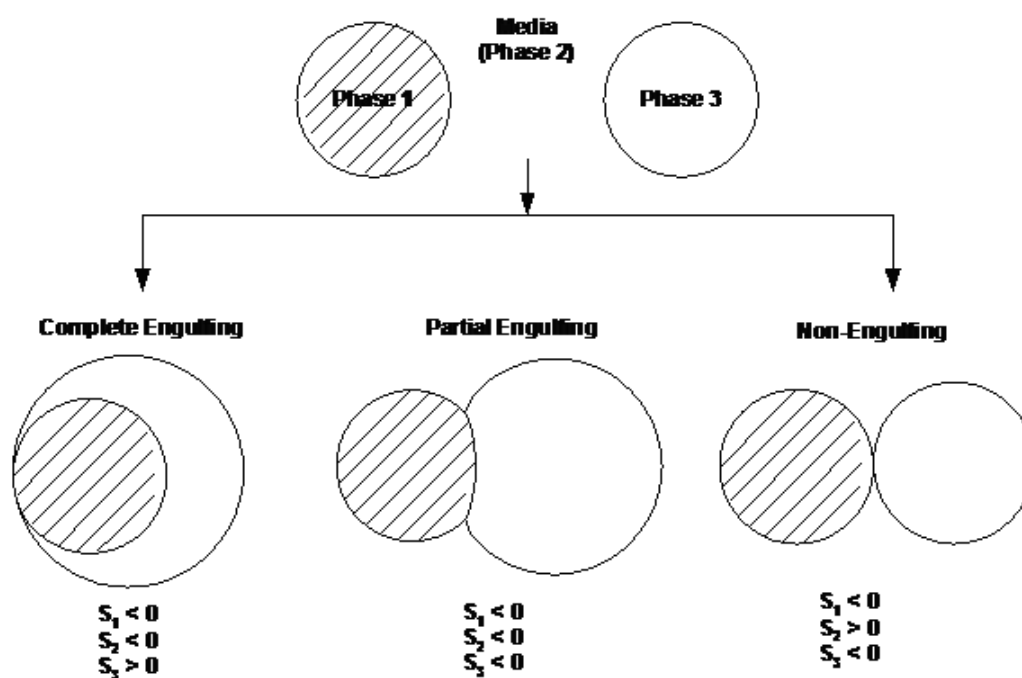


Fig. 1. Possible equilibrium configurations corresponding to the three sets of relations for S_i .

liquid droplets in suspension media are in contact and exposed to shear and electrical fields. The study also included substantial experimental data on two-fluid droplets in shear and electric fields, and it examined the dynamics of coalescence, i.e., engulfing. They considered two immiscible liquid droplets, designated as the phase-1 and phase-3, with phase-1 having the highest surface tension, suspended in a third immiscible fluid, designated as phase-3. They proposed that the equilibrium configuration of the suspended two immiscible liquid droplets, when brought into contact, could be predicted from the interfacial tensions σ_{ij} (between phase- i and phase- j) and spreading coefficients, defined as $S_i = \sigma_{jk} - (\sigma_{ij} + \sigma_{ik})$, as shown in Fig. 1.

Three equilibrium configurations were identified in the study: one (labelled as 2s) is

the complete engulfing of phase-1 by phase-3 when $S_1 < 0$, $S_2 < 0$ and $S_3 > 0$; in another (labelled as 1s), there is no engulfing when $S_1 < 0$, $S_2 > 0$ and $S_3 < 0$; and in the third (labelled as 3s), there is partial engulfing when $S_1 < 0$, $S_2 < 0$ with $S_3 < 0$. Mori (1978) investigated a gas-liquid system using a rather crude order-of-magnitude analysis and obtained the same conclusion as that reported by Torza and Mason (1970). Johnson and Sadhal (1985) analyzed a three-phase system based on $G = \sum \sigma_{ij} A_{ij}$, where G is the Gibbs free energy of the studied system. It was found that each particular morphological configuration described in Torza and Mason (1970) has a different value of G , and the arrangement with the minimal free energy will be the thermodynamically favored one. Note that the above theoretical analyses were

restricted to the static condition, without any fluid motion, gravity, buoyancy, inter-phase forces, or extra force. To the knowledge of the authors, besides these reviewed works, no other research has further advanced the subject.

EXPERIMENTAL SETUP AND TEST LIQUIDS

Fig. 2 shows the dual-capillary ES system and details of the capillary tubes used in the system. The point-to-orifice-plate arrangement is used in the spray chamber, with the dual-capillary tube facing the orifice plate. The dual-capillary tube consists of two stainless steel capillaries, with the I.D. of the outer capillary larger than the O.D. of the inner capillary. Two liquid flow channels are thus

formed. Two immiscible or slightly miscible liquids, the inner and the outer liquids, were separately introduced into the flow channels by two different syringe pumps (Harvard Model PHD, 2000). The ES capillary tube was electrified by a high voltage DC power supply (Bertan, Model 250B-10R). Both capillaries were connected to the same electrical potential, which was at a few kilovolts relative to the ground electrode (i.e., the spray chamber wall and orifice plate). In this experimental setup, we used an inner capillary tube with an I.D. of 0.005" (127 μm) and O.D. of 0.02" (508 μm), and an outer capillary tube with an I.D. of 0.03" (762 μm) and OD of 0.05" (1270 μm). Air was filtered and introduced to the spray chamber as the particle carry gas.

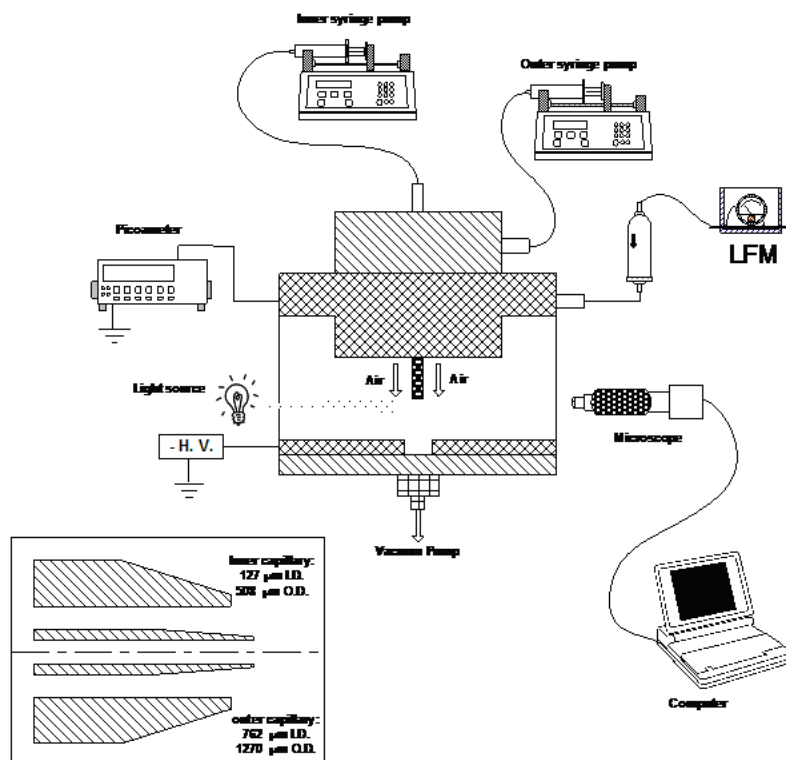


Fig. 2. Schematic diagram of the coaxial jet electrospraying system.

Table 1. Physical properties of test solvents (Riddick *et al.*, 1986)

Samples	Viscosity (cP = mPa·s)	Dielectric Constant	Surface Tension (dyn/cm = mN/m)*	Density (g/cm ³)*	Conductivity (μS/cm)*
Glycerol	1490	42.5 (25°C)	63.3	1.1261	0.06 (25°C)
Olive oil	84	3.1	32.92	0.8865	1.76×10^{-4}
Mineral oil	58.4*	2.1 (25°C)	30.47	0.8496	$\sim 1.0 \times 10^{-8}$
Soybean oil	40	3.1	36	0.8-0.92	$\sim 1.0 \times 10^{-6}$
Ethylene glycol (EG)	21.0	37.7 (25°C)	47.74	1.1135	1.16
Tri-ethylene glycol (TEG)	49.0	23.69	45.59 42.56 (doped)	1.1255	0.0020
Tri-butyl phosphate (TBP)	3.39 (25°C)	7.959 (30°C)	27.55	0.9760	0.024
Ethanol	1.074	24.3	22.40	0.7851	0.044 (I) 1.8 (II)
Water	1.0019 0.3371 (15°C)	80.20	72.58	0.9982	15
Acetone	0.3040 (25°C)	20.7 (25°C)	23.32	0.78998	4.9×10^{-3}
Toluene	0.5866	2.38 (25°C)	28.53	0.8670	8.0×10^{-10} (25°C)
Benzyl ether (BE)	5.333	3.8	38.2 (35°C)	1.0428	4.2×10^{-3}

* The values are measured at 20°C in the lab.

The air flowrate was kept at 6 lpm, controlled by a needle valve and monitored by a laminar flow meter.

To observe the spray modes, two viewing ports on the opposite sides of the spray chamber were designed. One is for the illumination light and the other for observation of the liquid meniscus shape using the microscope system. The system consists of a microscope lens (Infini-Van Video Microscope), digital camera (Model KR 222, Panasonic), high resolution monitor (Sony Trinitron, 1028 x 768 Pixels) and computer. A pico-ammeter (Keithley, Model 6485) was

connected to the ground electrode for measurement of the spray current.

Table 1 summarizes the physical properties of the test solvents in this experiment. The unmarked values of the physical properties, given in the table, were obtained from Riddick *et al.*, (1986). Those marked with star symbol (*) were measured by the apparatus available in the lab. The viscosity of test solvents was measured by a viscometer (Model SV-100 vibro viscometer, A&D Company). The electrical conductivity of the spray solvents was characterized by two different methods. One was to use the conductivity meter

Table 2. Measured interfacial tensions of test solvents at 20 °C

Samples (mN/m)	Olive oil	Mineral oil	Soybean oil	Equilibrium configurations		
				Olive oil	Mineral oil	Soybean oil
EG	11.95	18.85	9.71	2s	3s	2s
TEG	7.96	12.67	6.13	2s	2s	2s
TBP	0.09	0.18	0.18	2s	2s	2s
Ethanol	0.05	0.02	0.40	2s	2s	2s
D. I. water	6.42	53.45	8.53	2s	3s	2s
Tri-butyl phosphate						
EG	Mineral oil		D. I. water		2s	
Acetone	0.03		0.21		2s	

(Orinon 162A, Thermo Electron Corporation), and the other was to measure the electrical resistance with a lab-made liquid cell. The surface tensions of all tested solvents were measured by a tensiometer (Sigma 703D, KSV instruments). The Sigma 703D tensiometer was also used to measure the interfacial tension of the tested liquid pairs, as given in Table 2.

EXPERIMENTAL OBSERVATION

Operational modes for dual-capillary ES system

With olive oil and mineral oil as the outer liquid, four functional modes were observed in most cases. As shown in Figs. 3 and 4, they were the dripping mode, silver-bullet mode, stable compound cone-jet mode, and unstable cone-jet mode (or multi-jet mode).

For a fixed distance from the capillary tip to the orifice plate, the dripping mode was formed in weak electric fields (when the applied voltage is low). The feed liquid departs drop by drop from the liquid exit of

the dual-capillary ES tube. Increasing the applied voltage between the ES tube and orifice plate resulted in an increase in the drop emitting frequency and a reduction of drop size. When the applied voltage was increased beyond a certain critical value (around 3.0 kV in most test cases), the liquid meniscus changed suddenly to the silver-bullet mode. As the applied voltage was continuously increased further, the ES mode smoothly switched to the cone-jet mode and then the cone-jet mode became unstable. In this mode, the liquid jet emitted from liquid meniscus was dynamically altered and pointed in various directions. The cone shapes were also skewed.

At a sufficiently high voltage (typically higher than 4.5 kV) or in cases with a high inner liquid feed flowrate, the unstable cone-jet (multi-jet) mode may be reached directly from the dripping mode in the dual-capillary ES system. Note that, among all the modes, the dripping and unstable cone-jet modes were observed in all the immiscible liquid pairs we tested.

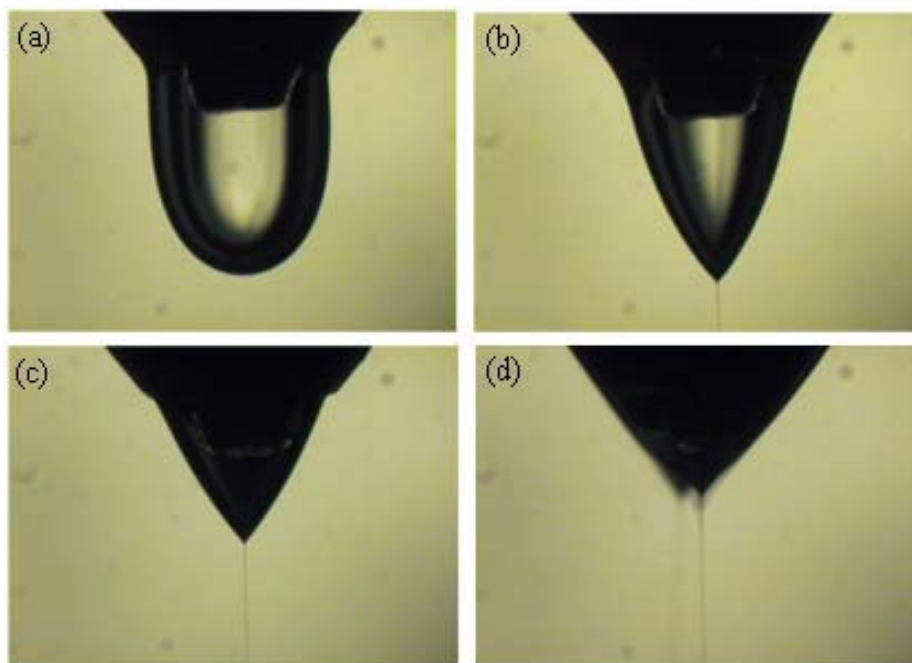


Fig. 3. Shapes of EG (1 $\mu\text{L}/\text{min}$) - olive oil (1 $\mu\text{L}/\text{min}$) liquid pairs' meniscus at the (a) dripping mode; (b) silver-bullet mode; (c) stable compound cone-jet mode; (d) unstable cone-jet mode.

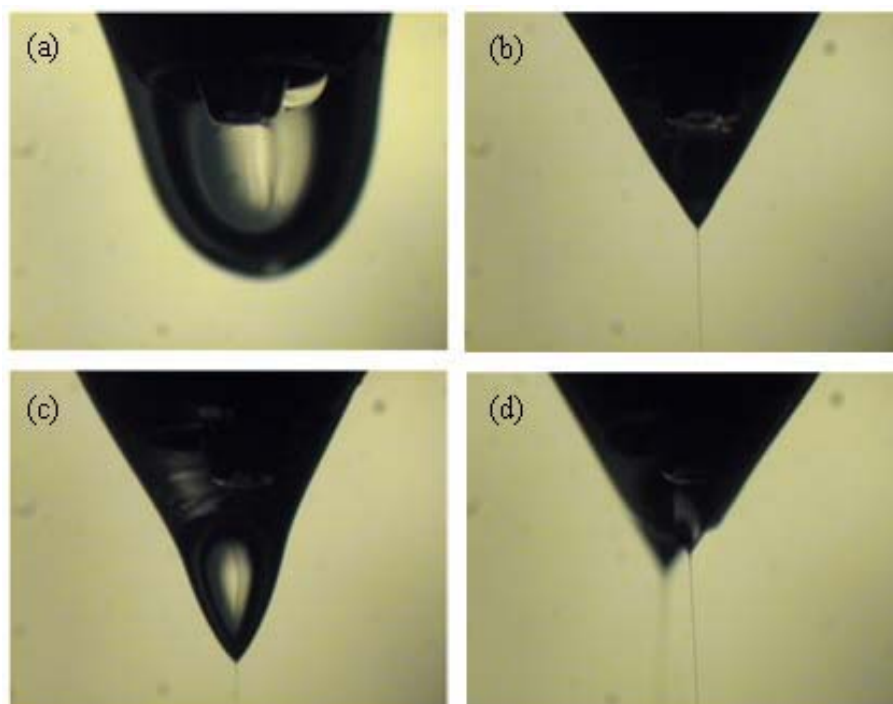


Fig. 4. Shapes of EG (1 $\mu\text{L}/\text{min}$) - mineral oil (1 $\mu\text{L}/\text{min}$) liquid pairs' meniscus at the: (a) dripping mode; (b) silver-bullet mode; (c) compound cone-jet mode; (d) unstable cone-jet mode.

Unique liquid meniscus behaviors were observed at the silver-bullet and stable

compound cone-jet modes. As shown in Figs. 3b and 4b using different outer liquids (for

example, olive oil and mineral oil) at the same feed flowrate (for example, 1 $\mu\text{L}/\text{min}$) resulted in different liquid meniscus shapes in the silver-bullet mode. Moreover, the use of different outer liquids also led to various meniscus shapes in the stable compound cone-jet modes. Images of stable compound cone-jet shapes when different outer liquids were used are shown in Figs. 3c and 4c.

The variation in cone-jet shapes with different outer liquids can be explained as follows: in principle the establishment of a stable cone-jet shape in any ES system requires the balance of the normal electrical force with the surface tension along the liquid surface. The formation of the inner liquid cone is at least partially attributed to the same force balance mechanism mentioned above. In other words, the normal electric field, directed outwards along the inner-outer liquid interface, must be present to balance the interfacial tension, pointed inwards. The balance between the interfacial tension and the electric force will then determine the cone shapes of the inner and outer liquids.

Characteristics of spray current vs. applied voltage

Figs. 5a and b plot the spray current as a function of applied voltage. In general, the characteristics of the spray current curve are similar to those obtained for a single-capillary ES. The level of spray current is negligible when the applied voltage is slowly increased from zero to a certain value (i.e., the 1st plateau). During this stage, the liquid meniscus suspended at the ES tube exit

remained in round and eventually departed from the capillary tip (i.e., dripping mode). As the applied voltage exceeds a certain value, the spray current leaps to a different level and remains constant (the 2nd plateau). The stable compound cone-jet mode was observed in this stage. Further increase of applied voltage will result in the unstable cone-jet (or multi-jet) spray mode. At last, the breakdown of the surrounding gas ceased the spray process as the applied voltage was further raised. Different from that observed in a single-capillary ES system, the dripping mode for dual-capillary ES was not very obvious when either olive oil or mineral oil was used as the outer liquid. More, changing the outer liquid flowrate did not vary the initial voltage and voltage range of the stable compound cone-jet mode. As the inner liquid flowrate was increased, the initiation point and range of voltage for the compound cone-jet mode were reduced and increased, respectively.

As the applied voltage was reduced from the corona breakdown voltage of the surrounding, a hysteresis loop was observed in the dual-capillary ES system. A similar loop was observed in a single-capillary ES system. In our experiment, the size of the hysteresis loop was affected by the outer liquid feed rate. In this study the loop for the mineral oil case is wider than that for the olive oil case.

With the identified characteristics of spray current as a function of applied voltage, one can then identify the spray modes in a dual-capillary ES system by simply monitoring the spray current.

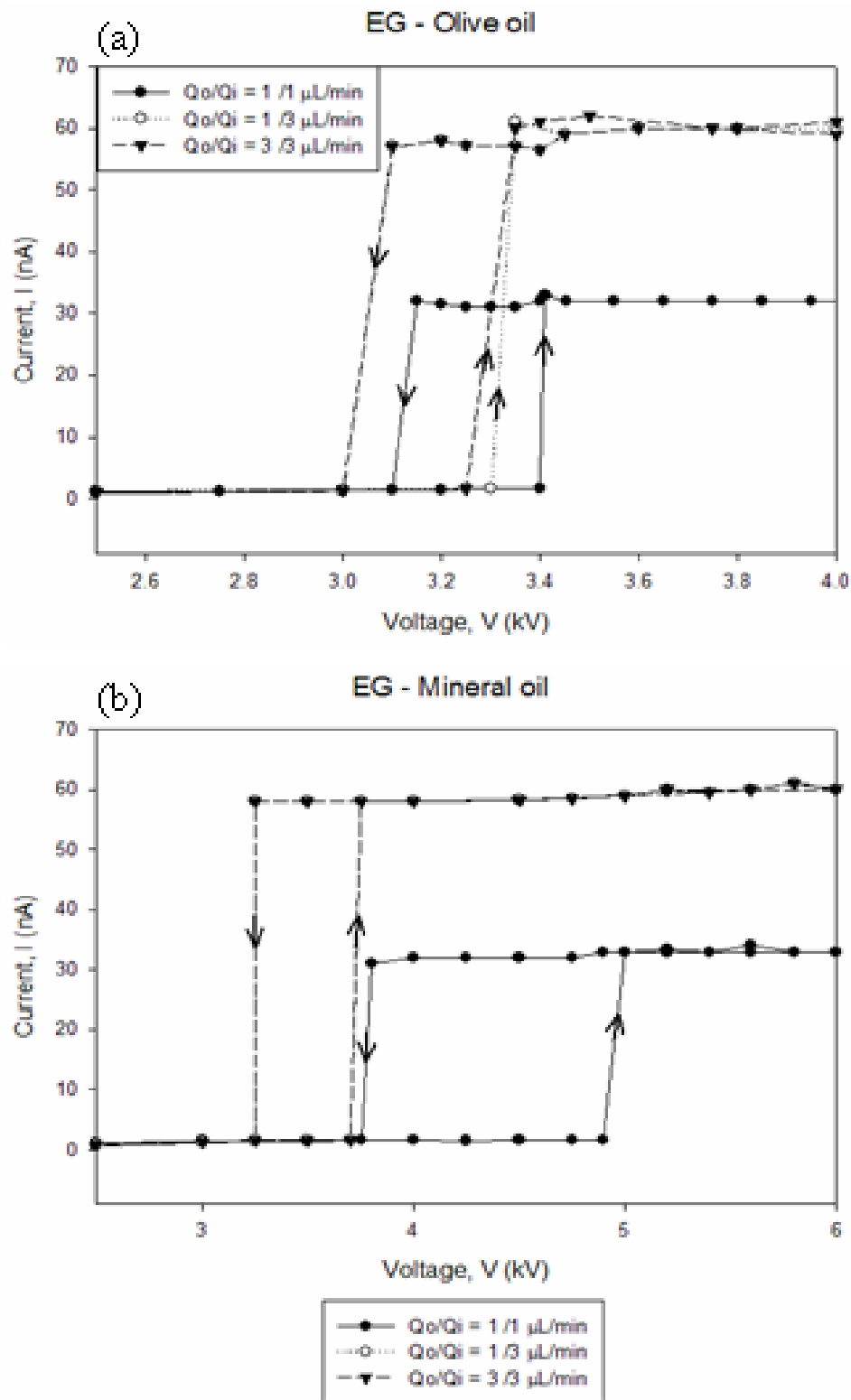


Fig. 5. Spray current vs. applied voltage curve showing the current plateau and hysteresis loop (a) for the EG/olive oil pairs (b) for the EG/mineral oil pairs. The curves at different flowrates of inner and outer liquids are also given.

Sufficient conditions for the formation of stable compound cone-jet mode

Table 3 shows the matrix of liquid pairs that have been tested in this study. In this part of the discussion we mainly focus on the immiscible liquid pairs for cone-jet mode establishment. For the miscible or slightly miscible liquid pairs, the compound cone-jet meniscus can be easily formed under operational conditions similar to those for a single-capillary ES system, because the interface tension for miscible or slight miscible liquid pairs is negligible. Our attention was consequently focused on the immiscible liquid pairs in which we observed the appearance of a distinct liquid interface in compound cone (if successfully formed) in a dual-capillary ES. The results of the test were summarized in Table 3.

To identify the conditions for the formation of the compound cone-jet mode, we analyzed the liquid pairs for which the stable compound cone-jet mode can be practically established using the spreading-coefficient criterion for three-phase interaction (reviewed in the Section 2). The theory of three-phase interaction is for static and equilibrium cases. Rigorously, one should not apply the theory to the dynamic situation experienced by the liquid pairs used in a dual-capillary system. However, due to the slow liquid movement in the liquid cones (i.e., the inner and outer liquid ones), it was hypothesized that the dynamic condition of the liquids in dual-capillary ES system should not depart much from the equilibrium condition. The results of the analysis are given in Table 2. It was found that

all the analyzed liquid pairs for which the stable compound cone-jet mode can be formed are either totally engulfing (i.e., $S_1 < 0$, $S_2 < 0$, and $S_3 > 0$) or partially engulfing (i.e., $S_1 < 0$, $S_2 < 0$, and $S_3 < 0$). Under the total and partial engulfing conditions the liquid interface tension is always less than the surface tensions of the liquid pair used. It is thus concluded that a stable compound cone-jet mode can be established if the surface tensions of the liquid pair can satisfy the criteria of three-phase's total and partial engulfing at the static condition.

Further examination of the results presented in Table 3 also reveals that, to form the stable compound cone-jet mode, it is more desirable to have the liquid of low dielectric constant serving as the outer liquid (i.e., ϵ_I (dielectric constant of inner liquid) $>$ ϵ_O (dielectric constant of outer liquid) $>$ ϵ_0 (dielectric constant of surrounding gas)). The value of the dielectric constant measures the permeability of the electrical flux passing through a medium. The greater the dielectric constant value, the denser the electrical flux in a material exposed to an external electric field. As described in the last paragraph of the section 4.1, the formation of the inner cone is primarily due to the balance of the interfacial tension with the normal electrical force at the interface. Since the direction of the interfacial tension is inward to keep the liquid medium intact, a divergent electrical field is needed to balance the force. For the cone-jet mode in the single-capillary system the electrical flux was uniformly emitted from the cone base (if the positive HV was applied at the capillary),

penetrated through the liquid surface (i.e., the presence of normal electric stress along the liquid surface) to the surrounding gas medium, and finally terminated at the ground electrode (i.e., orifice plate).

When liquids with higher dielectric constants than that of the inner liquid are the outer liquids in a dual-capillary ES system, the electric flux emitted from the cone base of outer liquid should be denser than that emitted from the inner liquid base. As a result, the electrical flux should be more concentrated in the outer liquid medium, penetrate across the

liquid surface to the surrounding medium, and end up at the ground electrode. In other words, the normal electric force along the interface will be either very weak or negligible because of reduced electrical flux crossing the interface. Thus, liquid pairs following the simple dielectric constant rule ($\epsilon_1 > \epsilon_0 > \epsilon_2$) are more likely to form a stable compound cone-jet meniscus at the tip of a dual-capillary ES assembly.

Note that the formation of stable compound cone-jet mode in the dual-capillary electrospray system does not indicate the

Table 3. Test matrix for forming a stable cone-jet mode.

I/O	Mineral oil	Soybean oil	Olive oil	Toluene	BE	TBP	Acetone	TEG	Ethanol	EG
Mineral oil	----	MS	MS	MS	MS	×	×	×	×	×
Soybean oil	MS	----	MS	MS	MS	×	×	×	×	×
Olive oil	MS	MS	----	MS	MS	×	×	×	×	×
Toluene	MS	MS	MS	----	×	×	×	MS	MS	×
BE	MS	MS	MS	MS	----	×	×	MS	MS	MS
TBP	Δ	Δ	Δ	MS	MS	----	MS	×	×	×
Acetone	Δ	MS	MS	MS	MS	MS	----	×	MS	×
TEG	Δ	Δ	Δ	MS	MS	MS	Δ	----	×	MS
Ethanol	Δ	Δ	Δ	MS	MS	MS	MS	MS	----	MS
EG	Δ	Δ	Δ	MS	MS	Δ	MS	MS	MS	----
D. I. water	Δ	Δ	Δ	Δ	Δ	MS	Δ	MS	MS	MS

× can not form stable cone-jet mode.

Δ can form stable cone-jet mode under suitable operation conditions.

MS inner and outer liquids are totally miscible and are not considered as a test pair.

formation of coated particles. As published in our previous experimental work (Mei and Chen, 2007), other condition is required to form coated particles when the dual-capillary ES system is operated in a stable compound cone-jet mode. A dual-capillary ES process is different from that in single-capillary ES system. When a single-capillary ES system operated in a stable cone-jet mode, one can expect the formation of monodisperse particles. For a dual-capillary ES system the formation of highly monodisperse, encapsulated particles is determined by both the establishment of a stable compound cone-jet mode, and the break-ups of the inner and outer jets in the spraying process.

CONCLUSIONS

Different operation modes were observed in a dual-capillary ES system. With the increase of applied voltage, four typical operation modes were observed: dripping mode, silver-bullet mode, compound cone-jet mode (if possible), and pulsated cone-jet mode (or multi-jet mode). The formation of stable and unstable cone-jet modes was mainly determined by the properties of the inner and outer liquids, i.e., their surface tension and dielectric constant. The characteristics of the spray current as a function of applied voltage in the dual-capillary ES system were also recorded. In general, the spray current characteristics are similar to those in a single-capillary ES system. The current characteristics at observed spray modes offer

an alternative to monitor or identify the mode of operation in a dual-capillary ES system.

To further identify the sufficient conditions to form the stable compound cone-jet mode in a dual-capillary ES system, a matrix of solvent pairs covering broad ranges of liquid viscosity and dielectric constant were studied. We found that the stable compound cone-jet mode can be easily established for miscible and partially miscible liquid pairs. For an immiscible liquid pair, the liquids should satisfy two sufficient conditions to form a stable compound cone-jet mode: (1) the liquid of high dielectric constant should be used as the inner one; and (2) the surface tensions of liquid pair should satisfy the spreading-coefficient criterion for the engulfing and partial engulfing cases in three-phase interaction. For the first condition, the density of electric flux emitted from the outer liquid cone base will be more than that from the inner liquid cone base, if the dielectric constant of the outer liquid is higher than that of the inner liquid. As a result, the normal electric force along the interface will be greatly reduced or negligible. The formation of the inner cone, based on the balance of normal electric stress and interfacial tension, thus becomes impossible. For the second condition, the dynamic condition of the liquid pair used in a dual-capillary ES system should not depart much from the static condition of three-phase interaction, because of the slow fluid motion in the liquid cones in the stable compound cone-jet mode.

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