RECENT ADVANCES IN ELECTROATOMIZATION

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Abstract
Recent advances in electro-atomization are reviewed in this paper. In particular, the generation and control, via electro-hydrodynamics, of steady coaxial jets of immiscible liquids with diameters ranging from tens of nanometers to tens of micrometers. The eventual jet breakup results in an aerosol of monodisperse compound droplets with the outer liquid surrounding or encapsulating the inner one. Following this approach, we have produced monodisperse capsules with diameters which, depending on the running parameters, vary from 10 to 0.15 micrometers. In addition, we report here that conducting liquids can be steadily electrosprayed into a dielectric liquid atmosphere (heptane, silicone oil among others) in the steady cone-jet mode. The technique may be of interest for the production of fine emulsions, coating of particles containing drugs or any other substance, etc. Finally, we report recent experiments that show steady electrosprays of water in air at atmospheric pressure without corona discharge. These experiments contradict the belief that a steady cone-jet of water can never reached in air at atmospheric pressure since the electrical breakdown threshold of the surrounding air medium is lower than the electrical field required to form a water Taylor cone.

Introduction
Production and control of droplets and particles of micrometric or even nanometric size with a narrow size distribution are of interest for many applications in science and technology. Usually, these particles are formed as either an aerosol or a hydrosol phase. Among the several atomization techniques, those which are formed from the break up of a capillary jet are the particular importance. Electrospray is a typical example which finds application to processes such as production of ceramic powders, production of aerosol standards, mass spectrometry, [1], [2], [3]. Other approaches for generating aerosols or hydrosols from the break up of a thin jet are the ones known as selective withdrawal and flow focussing techniques. Usually, the electro-atomization technique consists in the injection of a liquid through a capillary electrified needle. For a range of values of both the applied voltage and the injected flow rate, the electrified meniscus adopts an almost conical shape, see Fig. 1. Charge and mass are emitted from the cone vertex in the form of an extremely thin, charged, steady jet, much thinner than the diameter of the capillary needle, that eventually breaks up into a fine spray of tiny droplets. From the pioneering work

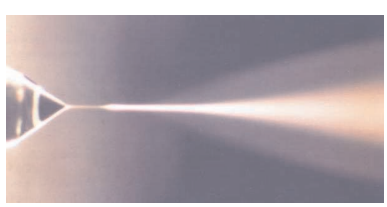

Figure 1: Cone-jet regime.

by Zeleny, [4], much is known on the electrospray physics. For perfectly conducting liquids, Taylor, [5], gave a first explanation of the conical shape of the meniscus as a hydrostatic balance between electrical and surface tension forces. Much more recently, several experimental and theoretical studies have contributed to clarify the phenomenon. Scaling laws showing the dependence of the current and droplet size on the flow rate and the liquid properties (electrical conductivity K, viscosity μ, liquid-gas surface tension γ, density ρ, and permittivity $\beta\epsilon_o$;

ϵ_o being the vacuum permittivity) have been given in [6] and [7]. Finally, theoretical analysis of the cone to jet transition region has been carried out recently by solving an asymptotic, one-dimensional hydrodynamic model of the jet using an appropriate correction of the zero order electrostatic Taylor field [8]. Also, the axisymmetric Navier-Stokes equations together with the Laplace equation governing the electric potential has been numerically solved for the transition region, [9].

In the simplest version of selective withdrawal, [10], [11], the exit of a tube is located at a height S above the interface separating two immiscible liquids (or liquid-gas). For low rates of fluid withdrawal Q, only the upper fluid is sucked through the tube. A sufficient increase in Q, or decrease in S, gives rise to a thin spout of the lower liquid surrounded by the outer fluid. In the flow focusing technique [12] and [13], a liquid is injected through a capillary tube whose exit is located close to a small hole drilled in a thin plate. A stream of another fluid (gas or liquid) surrounding the tube is forced through the hole. The mechanical stresses exerted by this stream deform the meniscus attached to the tube exit. Then, the meniscus develops a cusp like shape from whose vertex a thin jet is issued. As in the electrospray case, the jet diameter is also independent of the much larger diameter of the capillary tube.

Electrified coaxial jets

We report a technique that uses EHD forces to generate coaxial jets of immiscible liquids with diameters in the nanometric range [14]. The spray generated from the varicose break up of the jet consists of monodisperse compound droplets, which can reach sizes well below the micrometer range. The basic experimental set up for the new technique is sketched in Fig. 2. Two immiscible liquids, red and blue, are injected at appropriate flow rates through

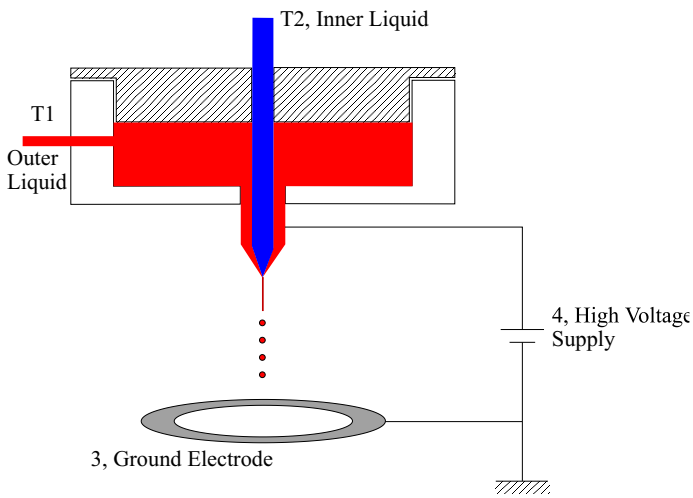

Figure 2: Experimental setup for structured Taylor cones and coaxial jets.

two needles located concentrically. The inner diameter of the inner needle ranges from the order of a millimeter to tens of microns while its outer diameter sets limits to the cross section of the outer needle. The outer needle is connected to an electrical potential of several kilovolts relative to a ground electrode (the extractor). The inner needle is kept to an electrical potential that, depending of the conductivity of the outer liquid, can be varied from that of the outer needle to that of the extractor. For a certain range of values of the electrical potential and flow rates, a structured Taylor cone is formed at the exit of the needles with an outer meniscus surrounding the inner one, see Fig. 3A. A liquid thread is issued from the vertex of each one of the two menisci giving rise to a compound jet of two co-flowing liquids, see Fig. 3B. At the minimum jet section,

the two-layered jet shown in Fig. 3B has an outer diameter of 4 micrometers. In the case of the experiment in Fig. 3A and 3B, the outer liquid was DuPont photopolymer Somos® 6120, and the inner one was died ethylene glycol (EG). To develop this structure we injected Somos, which flowed through the annular gap between the two needles. We then increased the electrical potential of the outer needle V1 until the liquid meniscus jumped into a stable cone-jet mode. In this particular example, the electrical potential of the inner needle was maintained at V2 = V1. The viscosity of the outer liquid is sufficiently high to diffuse the electrical stresses acting on the surface into the bulk. Consequently, the liquid motion inside the Taylor cone is dominated by viscosity, so that the liquid velocity inside the cone is everywhere pointing towards the cone apex. The second liquid flowed through the inner needle to form a new meniscus inside the Somos one. The motion of Somos deformed the EG meniscus to a

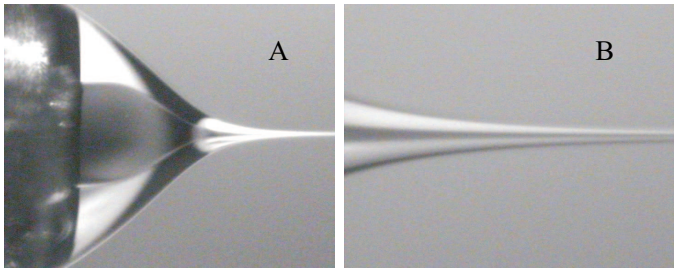

Figure 3: Structured Taylor cone. (A) and downstream detail of the two coaxial jets emitted from the vertex of the two menisci.

conical shape and sucked it from the meniscus' tip to form a thin micro thread. This micro thread of EG merged with that of Somos at the tip of the Taylor cone to finally form a two-concentric layered micro/nano jet. To obtain a structured Taylor cone, the EHD forces must act on at least one liquid, although they may act on both. We shall call the driving liquid the one upon which the EHD forces act to form the Taylor cone. We have introduced a configuration in which the driving liquid flows through the needle's annular gap (see Fig. 2). However, there is an alternative configuration where the driving liquid flows through T2 while the second one flows through the annular gap between T1 and T2. That is the case shown in pictures in Fig. 4A and 4B, where a Taylor cone of water is formed inside a meniscus of a non-conducting liquid such as olive oil.

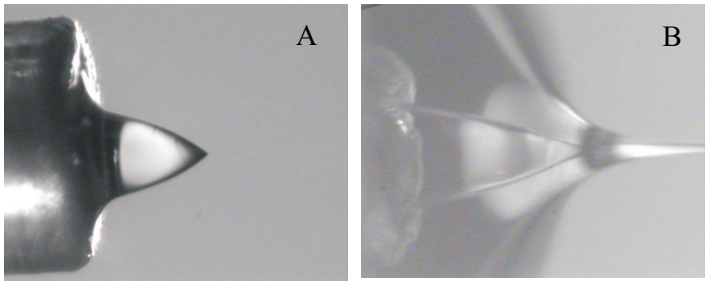

Figure 4: A Taylor cone of water coated by (A) a thin shell of olive oil and (B) a thick shell of olive oil.

The electrical stresses acting on the charged water-olive oil interface, which are efficiently transmitted by viscosity towards the olive oil bulk, set the olive oil into motion, towards the water cone vertex. These two co-flowing streams give eventually rise to a coaxial jet of water coated by oil. Note that, as in regular electrosprays, the motion of the driving liquid in this second configuration does not need to be dominated by viscosity. Also note that olive oil (or any other liquid insulator) cannot be electrosprayed on its own in the cone-jet mode, since the lack of surface charge density prevents the formation of a steady Taylor cone. The stability of the structured Taylor cones and the electrified compound jets strongly depends on the physical properties of the working fluids as well as the liquid flow rates and applied voltages. This complex electro-fluid-mechanical scenario is rather poorly understood, so that the stability domains for most liquid couples remain to be investigated. In the absence of a better knowledge, we should point out that stable structured Taylor cones have been obtained for liquids satisfying the condition $\gamma_i > \gamma_o$, where γ is the surface tension of the liquid-dielectric atmosphere, and subscripts i and o refer to the inner and outer liquid, respectively.

Experiments using ethyleneglycol as outer liquid and olive oil as inner one show that the electrical current transported by the ethyleneglycol-oil coaxial jet scale with the flow rate of the conducting liquid (ethyleneglycol) in the same way that in regular electrosprays. Figure 5, shows the dimensionless current I/I_o as a function of the dimensionless ethyleneglycol flow rate Q/Q_o for different values of the oil flow rate Q_{oil}; $I_o = \gamma\epsilon_o/\rho$ and $Q_o = \epsilon_o\gamma/(\rho K)$. Note the remarkable agreement with the $I \sim Q^{1/2}$ law characteristic of regular electrosprays. Note also that the current is practically independent of the dielectric (oil) flow rate.

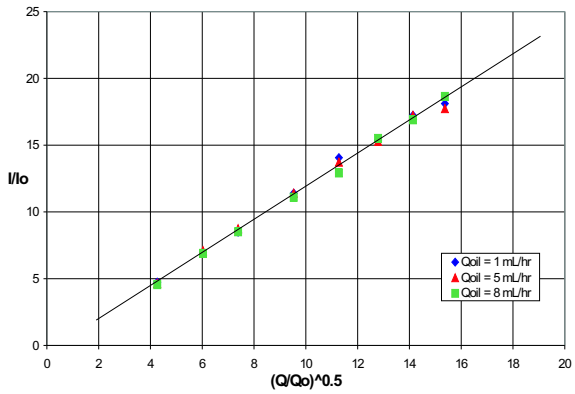

Figure 5: Dimensionless electric current as a function of the ethyleneglycol (the outer liquid) flow rate for different values of the oil flow rate.

Encapsulation via electrified coaxial jets

We have applied this technique to micro encapsulate aqueous solutions. An outer jet of Somos and a co-flowing water inner jet were generated as described before. Compound droplets of water coated by Somos resulted from the jet break up, so that a spray of compound droplets was formed and collected on a plate damped with water. In this case, the outer shell of the droplets was hardened using an ultraviolet light reactor. Prior to the hardening process, the charged aerosol was neutralized by corona discharge, so that losses were minimized. The liquid flow rates in this experiment were selected to obtain capsules in the micrometer range, since capsules in this range can be optically recorded to allow for visual observation, Fig. 6. The hardening process can also be thermally or chemically initiated under the use of appropriate reagents.

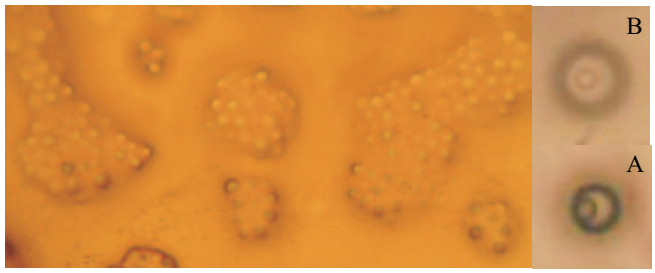

Figure 6: Collection of near monodispersed capsules. Magnified views of two capsules formed under different parametrical conditions are also given in the figure. In (A) the outer diameter is $10\,\mu m$, whereas the diameter of the capsule shown in (B) is $8\,\mu m$.

Encapsulation, tested within the nanometric range, has been carried out via aerosol techniques, since they allow for on-line characterization of the airborne particles. In particular, we resorted to mobility analysis with a differential mobility analyzer (DMA) described elsewhere [15]. Electrospray droplets, when subject to sufficient liquid evaporation, lead to the formation of gas phase ions of substances previously dissolved in the liquid [16], as in the case of aqueous solutions of salts. In Fig. 7A, we show the differential mobility spectra recorded from an electrospray of an aqueous solution of NaCl. The liquid flow rate through the electrospray was $18\,nl/s$.

The scale on the horizontal axis is proportional to I/Z, where Z is the electrical mobility in cm^2/vs. The left-most peak is due to ions of sodium Na^+ at different solvation states. The peak in the middle is mostly due to clusters of salt plus sodium ions at different states of charge and solvation. The third peak is due to the solid residues left after solvent evaporation from the droplets. Since the initially electrosprayed droplets evaporate and undergo Coulombic explosions, the sizes of the solid residues bear little relation to the initial droplet size, if any at all. In Fig. 7B we show the differential mobility spectra gathered from the same aqueous solution, flowing at the same rate, but with 27% (in flow rate) of nonvolatile olive oil co-flowing on the outside. The result is dramatically different. The peaks associated with ions and ionic clusters have completely disappeared. There is only a single dominant peak, associated to the monodisperse electrospray compound droplets. Indeed, the size of such droplets,

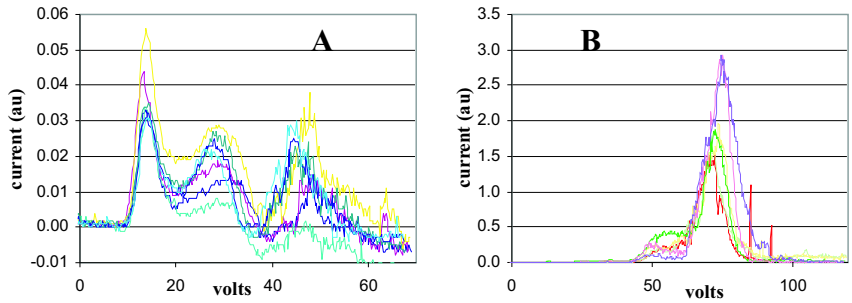

Figure 7: Differential mobility spectra of (A) electrosprays of water solutions and (B) a compound electrospray of the same water solutions (inner) and olive oil (outer).

as inferred from the measured electric current and the liquid flow rate emitted from the electrospray, scales as those predicted by electrospray laws. Thus, the absence of ionic species and Coulomb explosions, together with the matching of predictions in size and charge, strongly support the picture that the water droplets do not evaporate, so a thin shell of nonvolatile olive oil must surround them. Fig. 8 shows the diameter of the capsules generated from structured jets of olive oil (outer fluid) and water solutions (inner fluid) with different electrical conductivities (0.14, 0.05 and $0.01\,S/m$).

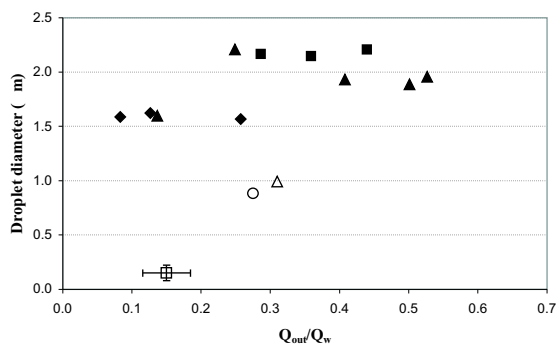

Figure 8: Sizes of capsules of water surrounded by a thin shell of olive oil. ■, $Q_w = 39.8 \times 10^{-12}\,m^3/s$;▲, $Q_w = 26 \times 10^{-12}\,m^3/s$; △, $Q_w = 25.5 \times 10^{-12}\,m^3/s$; ♦, $Q_w = 18.4 \times 10^{-12}\,m^3/s$; ○, $Q_w = 17.8 \times 10^{-12}\,m^3/s$; □, $Q_w = 1.5 \times 10^{-12}\,m^3/s$

The horizontal axis represents the ratio Q_{out}/Q_w, where Q_w is the water flow rate and Q_{out} is the oil flow rate. The diameter is calculated from the measured current, flow rates and electrical mobility. Filled symbols represent situations in which the flow rate of water is kept constant while the flow rate of olive oil is varied. Open symbols represent situations where both flow rates have been varied. The smallest capsule diameter attained during these exploratory experiments is approximately 0.150 microns, corresponding to a sphere of water of about 100 nanometers in diameter covered by a layer of oil whose thickness is about 25 nm. The dispersion of sizes, for each experiment, remains below 7%, except in the case of the smallest capsules (0.150 microns), due to limitations to properly control the flow rate of oil in this extreme case. It should be emphasized that the method described here allows for a precise tailoring of both the outer and the outer-to-inner radius ratio by controlling the flow rates of both liquids. Figure 9A shows the effect of increasing the outer flow rate on the shape of a structured Taylor cone;

the outer flow rate increases from top to bottom while the flow rate of the inner liquid was kept constant. On the contrary, in Fig. 9B, the inner flow rate is increased from top to bottom keeping constant the outer flow rate.

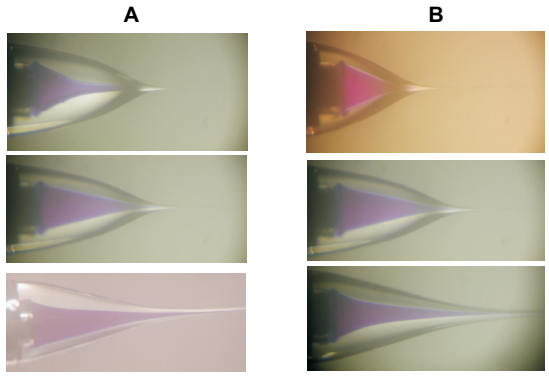

Figure 9: Effect of the outer (inner) flow rate keeping constant the inner (outer) one on a structured Taylor cone of Somos and dyed ethyleneglycol. In column A, the inner flow rate was $Q_i = 83\mu\, l/min$ while the outer one were 100, 200 and $250\,\mu\, l/min$ respectively. In column B, the outer flow rate was $Q_{out} = 200\mu\, l/min$ and the inner flow rate were 33, 83 and $250\mu\, l/min$ respectively.

Dispersion of a conducting liquid into a dielectric liquid atmosphere

Dispersion of liquids in a gas atmosphere or vacuum by applying an intense electric field is a well-known phenomenon since the pioneering work by Zeleny, [4]. We report here that semi-conducting liquids can also be steadily dispersed into a dielectric liquid atmosphere (heptane, silicone oil among others) as shown in Fig. 10 .

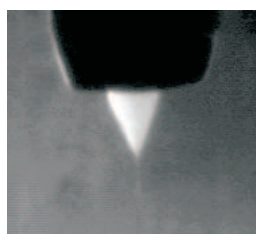

Figure 10: Steady Taylor cone of deionized water into heptane.

In this experiment, deionized water with a conductivity of $1.5 \times 10^{-4}\, S/m$ was electrosprayed at a flow rate of $1.35 \times 10^{-9}\, m3/s$. The technique may be of interest for the production of fine emulsions, coating of particles containing drugs or any other substance, etc. The setup for the spraying does not differ substantially from those used in standard electrosprays in gas atmosphere or vacuum. Measurements of the current emitted from the cone agree well with the scaling laws for electrosprays in air.

The stability limits of the cone-jet mode into a liquid ambient have been also investigated by electrospraying Dupont photopolymer Somos 6120 into heptane. The electrical conductivity of the Somos was $6.25 \times 10^{-5}\, S/m$ and its viscosity $6 \times 10^{-4}\, m^2/s$ (six hundred times larger than that of water).

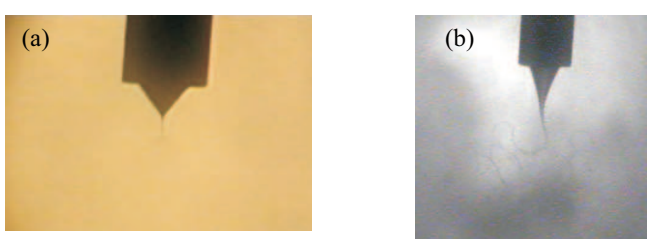

Figure 11: (a) steady cone-jet mode; (b) unsteady whipping mode

Steady cone-jet configurations, Fig. 11a, are obtained for small and moderate values of the flow rate, which correspond to small values of the surface charge density, [17], while the unsteady regimes appear for larger values

of the flow rate, Fig. 11b. The injected flow rate and the applied potential were respectively $1.1 \times 10^{-10}\, m^3 s^{-1}$ and $5000V$ for the experiment shown in Fig. 11a whereas, for the experiment in Fig. 11b, they were $5.9 \times 10^{-10} m^3 s^{-1}$ and $3000V$. The needle to grounded plate distance was $3.5\, cm$ in both cases. Note that the extreme value of the viscosity of the Somos results into remarkable long jets.

Water steady cone-jet in air at atmospheric pressure

Experiments on electrohydrodynamic pulverization of water in air at atmospheric pressure seem to show that a stable cone jet mode is never reached since the electrical breakdown threshold of the surrounding air medium is lower than the electrical field required to form a water Taylor cone; so that corona discharge appears. A sheath of gas with relatively high electrical breakdown threshold has been used to prevent or delay the onset of the corona discharge. Tang and Gomez, [18], used CO_2 as sheath gas to stabilize electrosprays of water in the cone jet mode under conditions relevant to drug delivery applications; SF_6 has been also used as sheath gas in the electrospraying of water.

However, recent experiments have shown that stable cone-jet of water can be formed in air at atmospheric pressure if very narrow tubes are used to anchor the water meniscus.

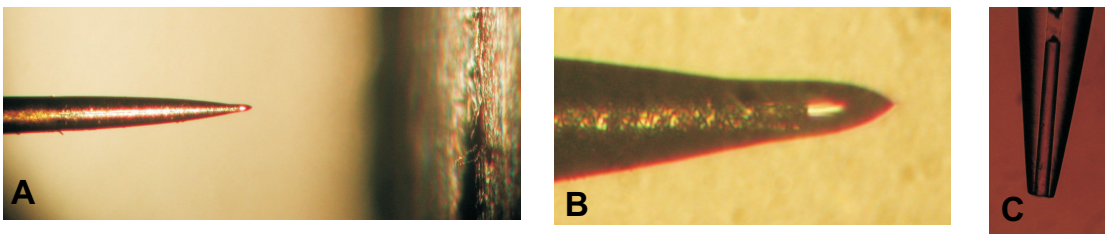

Figure 12: (A) Water cone-jet at the end of a silica tube; (B)magnified view of the water meniscus; (C) magnified view of the sharpened silica tube.

In the experiment shown in Fig. 12, water with a small amount of hydrochloric acid to enhance its electrical conductivity is injected through a silica tube of 360 μm OD and 20 μm ID at a flow rate of $1.6 \times 10^{-12}\, m^3/s$. The water conductivity was 2 S/m. The end of the silica tube has been conveniently sharpened up to an OD of approximately 40 μm, see Figure 12C. Since we have used non-conducting silica tubes in this experiment, the charge process is carried out through the liquid bulk. Figure 13 shows values of the measured emitted current as a function of the flow rate. Experimental results fit well the well-known cone-jet scaling law $I \sim Q^{1/2}$.

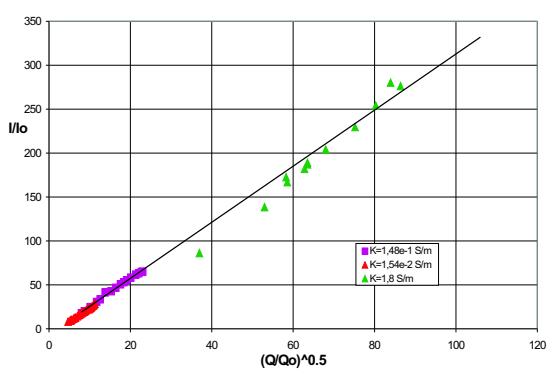

Figure 13: Non dimensional current I/I_o versus flow rate Q/Q_o for several water conductivities.

In spite of the fact that the electric field on the conducting liquid is higher than that of the breakdown threshold, the absence of corona discharge may be explained taking into account the smallness of the volume of the water cone-jet, which is unable to ionize the significant air region needed to trigger the discharge process.

Conclusions

We have presented a technique to generate coaxial electrified liquid jets in the micrometric and sub micrometric ranges by EHD. This method allows for a precise tailoring of both the outer and the outer-to-inner radius ratio by controlling the flow rates of both liquids and the applied voltage. A direct application to the production of monodisperse capsules in the micrometric range has been included. Although in this particular example, the outer fluid consists of a photopolymer, which is solidified under UV light, the use of different polymerization schemes is also applicable with this technique. Also, monodisperse compound droplets of water coated by olive oil, with sizes well in the sub micrometric range, have been obtained. Both the amount of water and thickness of the coating oil layer can be well controlled.

Recent experiments show that steady cone-jet of a conducting liquid can be formed into a dielectric one. Scaling laws for the electrical current and droplet size are the same that those corresponding to the electrospraying of liquids into either a gas atmosphere or a vacuum. This technique can be of interest for the production of fine emulsions, coating of particles containing drugs or any other substance, etc.

Finally, we have found that water with conductivities ranging from that of the deionized water up to values of the order $2\,S/m$ can be electrosprayed in steady cone-jet mode if very small capillary silica tubes are used. Our results show that for a given flow rate there is a voltage range where steady cone jets, without corona discharged, are produced.

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