Single event AC – DC electrospraying

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Abstract. Electrospraying is an innovative method to deposit very small amounts of, for example, biofluids (far less than 1 pl) that include DNA or protein molecules. An electric potential is applied between a nozzle filled with liquid and a counter electrode placed at 1–2 millimeter distance from the nozzle. In our set-up we use an AC field superposed on a DC field to control the droplet generation process. Our approach is to create single events of electrospraying triggered by one single AC pulse. During this pulse, the equilibrium meniscus (determined by surface tension, static pressure and the DC field) of the liquid changes rapidly into a cone and subsequently into a jet formed at the cone apex. Next, the jet breaks-up into fine droplets and the spraying stops. The meniscus returns to its equilibrium shape again. So far we obtained a stable and reproducible single event process for ethanol and ethylene glycol with water using glass pipettes. The results will be used to generate droplets on demand in a controlled way and deposit them on a pre-defined place on the substrate.

1. Introduction

Electrospraying has been used as a deposition method of biofluids that contain, for example, proteins or DNA. The aim is to apply this technique to make a bio-fluidic device for biological and biomedical assays. In this device femto- to attoliters of a bioactive compound have to be deposited with sub-micron placement accuracy. There are ink jet deposition techniques, which are usually limited due to the inner capillary diameter. Electrospraying, often referred to as electrohydrodynamic atomization (EHDA), is a technique to generate fine aerosol droplets through electrical forces. It seems to be the only method to generate jets and/or droplets much smaller then the inner diameter of the nozzle [1]. Therefore, we have designed and built an experimental set-up to investigate the possibilities and limitations of the electrospray technology.

In this technique, the potential is applied between the capillary and a ground plate placed at a certain distance from the tip of the capillary. The high field strength in the capillary tip region causes surface charge to build up on the exposed meniscus of the liquid. The meniscus assumes a conical shape from the apex of which a jet emerges, which breaks up into droplets [2]. Based on Balachandran and Machowski’s work, the application of AC pulses onto a bias voltage with well adjusted frequency gives a possibility to control droplet size [3]. The electrospraying deposition is used in the work of Moerman et. al. They used electrospraying to form spots of 130-350 µm diameter. The depositing was stopped by increasing the distance between the capillary and the substrate (counter electrode) [4]. Yogi et. al presented a method to make smaller dots. This group developed a technique to produce microarrays of dye molecules on a surface [5;6]. The recent work of Chen et. al showed the
possibility of jetting in a similar way. In this pulsed electrohydrodynamic jetting the liquid is collected as a series of droplets during a single electrical pulse [7;8].

2. Experimental set-up
In our electrospraying set-up an electric potential is applied between a nozzle of a glass pipette filled with liquid and a counter electrode placed at 1-2 millimeter distance. We use an AC field superposed on a DC field to control the droplet generation process. The apparatus used in all experiments is shown schematically in figure 1. A high voltage power source (AC/DC) is connected to a glass capillary with a copper wire in it, as in figure 2. We apply rectangular voltage pulses with very low frequency (1.6-2.5 Hz) for generating droplets. The equipment is mounted on a heavy plate, supported by soft rubber springs in order to suppress mechanical vibrations. The liquid is deposited on a metal substrate, which is grounded. The distance between the nozzle and the ground electrode can be adjusted to obtain the desired spacing for optimal operation. The static meniscus is controlled through hydrostatic pressure. This hydrostatic pressure during the experiments is very low (a few centimeters water column). The power source, XY stage and camera are software controlled. An optical system, consisting of a microscope with progressive scan CCD camera and a stroboscope with adjustable flash delay, is used to record the experiments. The imaging system is triggered by the first ramp of the rectangular pulse.

![Diagram of experimental set-up](image1)

**Figure 1.** Schematic diagram of experimental set-up.

![Diagram of glass capillary with wire](image2)

**Figure 2.** Schematic drawing of glass capillary with wire connected to high voltage source.

![Diagram of ethanol electrospraying](image3)

**Figure 3.** Single event electrospraying of ethanol.

![Diagram of ethylene glycol and water electrospraying](image4)

**Figure 4.** Single event electrospraying of ethylene glycol and water (70/30).

3. Results
We were able to create single events of electrospraying triggered by one single AC pulse. During this pulse, the equilibrium meniscus (determined by surface tension, static pressure and the DC field) of the liquid changed rapidly into a cone and subsequently into a jet formed at the cone apex. Then, the
jet broke-up into fine droplets and after a while the spraying stopped. The meniscus returned to its equilibrium shape again. The first presented experiment was carried out with ethanol. We used a glass capillary (i.d. = 50 \, \mu m, o.d. = 600 \, \mu m), which was placed at a distance of 1.4 mm from the metal plate (counter electrode). The measurements were taken at 1.5 kV (DC field) with a 5 ms rectangular pulse of 0.4 kV (AC field) every 400 ms. Figure 3 shows the droplet formation process during the application of the pulse. Figure 4 shows similar results for ethylene glycol/water (70/30) where the DC voltage was set to 2.3 kV with a 4 ms block pulse of 0.7 kV every 600 ms. The distance between the nozzle and the metal collector was 1.5 mm. For both fluids stable and recurrent processes were achieved. We noticed that single events did not depend on the time between the rectangular pulses as long as it was between the range of 100 - 700 ms. Our set-up allowed us to see and study each step (during the single event caused by one pulse) in great detail. We could observe that the wetting properties of the two fluids studied were different and this affected the meniscus shape and size.

4. Discussion
Experiments were performed with very low hydrostatic pressure. When a sufficiently high voltage was applied, the electric forces overcame surface tension and we could observe the deformation of the meniscus. Single event electrospraying is a combined action of electrical and hydrodynamic phenomena such as:

- charge relaxation,
- charging the capacitance between the tip of the nozzle and the grounded plate over the resistance of the fluid between the tip of the electrode in the capillary and the meniscus
- natural vibrations of the pending drop volume
- damping effects

Table 1. Characteristic parameters for ethanol and ethylene glycol/water (70/30) solution with calculated electrical and hydrodynamic relaxation times.

| Fluid                  | \( \gamma \) [mN/m] | \( \eta \) [mPa·s] | \( \rho \) [kg/m\(^3\)] | \( \sigma \) [S/m] | \( \tau_C \) [ms] | \( \tau_H \) [ms] | \( \frac{1}{f} \) [ms] | \( \tau_{RC} \) [ms] |
|-----------------------|----------------------|---------------------|---------------------------|-------------------|----------------|----------------|-----------------|----------------|
| Ethanol               | 22.10                | 1.2                 | 789                       | 1·10\(^{-5}\)     | 1.71·10\(^{-3}\)| 1.63          | 2.181           | 0.255           |
| Ethylene glycol/water (70/30) | 55.4                | 10.5                | 1079.24                   | 8.7·10\(^{-6}\)  | 3.24·10\(^{-3}\)| 5.69          | 1.611           | 0.293           |

The charge relaxation time is given by [9]:

\[
\tau_C = \frac{\varepsilon_{\text{fluid}}}{4\pi\sigma}
\]

where \( \sigma \) is electrical conductivity and \( \varepsilon_{\text{fluid}} \) is the electric permittivity of the fluid. To calculate the RC time of the electrical circuit consisting of the capacitance between the tip of the nozzle and the grounded plate over the resistance of the fluid between the tip of the electrode in the capillary and the meniscus we proceed as follows. The resistance between the tip of the electrode in the pipette and the meniscus is given by [10]:

\[
R = \frac{l}{\sigma A}
\]

with \( l \) is the distance between tip of electrode and meniscus and \( A \) is the cross section of the fluid volume between the tip of the electrode and the meniscus. To estimate the capacitance of the meniscus and the ground plate we take the formula of the capacitance of two parallel plates with air in between \( (S_M \text{ -- the surface area of the meniscus, } \varepsilon_{\text{air}} \text{ -- the permittivity of air and } d \text{ -- the distance between tip of the nozzle and grounded plate}) [10]:

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\[ C = \frac{e_{air} S_M}{d} \quad (3) \]

In our set-up we have \( l = 3 \text{ mm}, \ d = 1.5 \text{ mm}, \ A = \pi (\text{i.d.})^2 /4 = 1.963 \times 10^{-9} \text{ m}^2, \ S_M = \pi (\text{o.d.})^2 /4 = 2.83 \times 10^{-7} \text{ m}^2, \ C = 0.0017 \text{ pF} \) and \( R = 150-180 \text{ G}\Omega \), leading to a RC time \( \tau_{RC} \) in the range of 0.3-0.5 ms. To calculate the natural frequency of a pending droplet we use Rayleigh’s formula \([11]\):

\[ f_{Rayleigh} = \frac{1}{2\pi} \left( \frac{8\gamma}{\rho r^3} \right)^{1/2} \quad (4) \]

With \( r \) – the radius of the pending droplet (approximately equal to \( \text{o.d.}/2 \)), \( \gamma \) – surface tension of liquid and \( \rho \) – the density of the fluid of the pending drop. The damping can be estimated by the hydrodynamic relaxation time \([9]\):

\[ \tau_H = \frac{\eta r}{\gamma} \quad (5) \]

where \( r \) is radius of the capillary (\(\text{o.d.}/2\)) and \( \eta \) is viscosity of liquid. When we compare all characteristic times constants (see table 1), we clearly see that the hydrodynamic relaxation time and Rayleigh time are the most determining factors.

5. Conclusion

Although the behavior of AC-DC electrospraying has been studied in detail, this paper has provided another approach to look at the problem of single event electrospraying. In our single event experiment the frequency of the rectangular pulse does not play a role as long as it is below a certain value. It is the first time that single event electrospraying has been performed and reproduced with high accuracy. The measurement system using stroboscopic illumination with adjustable flash delay allows us to see and study all different modes (single events as well) during electrospraying in great detail. Single event electrospraying provides a reproducible method for the generation of micro and nanometer sized jets and streams of droplets. Most probably, the natural vibrations of the pending droplet determine the pulse time.

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