Analysis of Droplet Formation Near Onset Voltage of Aqueous Electrosprays

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***Abstract*— There is a lot of research on liquid atomization by means of electrospray, particularly because of its many practical applications. Nevertheless, the full understanding and control of the electrospray mechanisms are still incomplete. An experimental setup was developed in order to investigate the frequency characteristics of droplet formation and ejection at the tip of Taylor's cone of aqueous electrosprays. Droplet formation and oscillations are monitored using a Kodak Ektapro high-speed camera. The frequency of droplet formation at the tip of the capillary needle is analyzed. Droplet frequency formation appears to exhibit three distinct regimes with an abrupt transition from one regime to another. Droplet formation is recorded at different needle-plate electrode distances. Based on the analysis of experimental data a scaling law for droplet formation was found.**

Keywords: aqueous electrosprays, droplet formation, scaling laws, Taylor's cone, onset voltage, charged droplets.

I. Introduction

Interesting phenomena take place when high voltage is applied to a conductive capillary/needle containing a polar fluid. As voltage is increased the liquid air interface becomes polarized with an excess ionic charge producing Taylor's cones [1, 2]. Droplets are emitted from the capillary tip with a frequency increasing with voltage. At a certain voltage (onset voltage), which depends on the diameter of the capillary, the distance to the counter electrode, as well as on other parameters, the frequency of droplet emission increases exponentially and an elecrospray is generated. The charged droplets emitted at the tip of Taylor's cone undergo coulombic fissions around Rayleigh limit [3, 4, 5]. The droplets evaporate and may pass through a succession of coulombic fissions as they reach the Rayleigh limit on their way towards the counter electrode.

There are various regimes in which the electrospray can operate [6, 7, 8], such as dripping, pulsating, cone-jet, burst, and astable [8]. Transitions from one regime to another are not very well understood and are not easily amenable to control given the many variables involved [9]. The stable cone-jet regime is widely employed for generation of molecular ions for mass spectroscopy analysis. The regime can be obtained for submillimeter needle diameters and needle – counter electrode distances lower than one centimeter. The onset voltage in such cases is rather distinct voltage. However, there are other applications of electrosprays, such as electrostatic painting, drug delivery, or powder production [10] which may involve larger capillary – counter electrode distances. In such cases, droplets are emitted with a frequency increasing with voltage, but it may often be difficult to determine precisely what the onset voltage is.

The purpose of the present work is to investigate the emission frequency of capillary droplets of aqueous electrospray, particularly near the onset voltage. We aim at a better understanding of the electrospray onset and possibly at finding a systematic way of analyzing it.

II. Data Acquisition

A. Experimental Setup

The generation of electrospray was studied in a horizontal needle-plate configuration as shown in Fig.1. The capillary used in our experiments was a modified BD PrecisionGlide hypodermic syringe needle, regular wall type and regular bevel 25G x 1.5 in (ID 0.241 mm, OD 0.508 mm). The needle was modified in our electro-mechanical shop: it was cut, microscopically examined and polished, until a blunt tip metal capillary was obtained. The needle was attached to a 3 mL BD Luer-Lok™ syringe with positive plunger rod stop and tapered plunger rod design. The syringe was also modified so that it could be connected by means of clear vinyl tubing to a large plastic cylindrical water container (18 cm diameter) in order to ensure a flow rate driven by quasi-constant differential hydrostatic pressure of water (9.3 cm column of water).

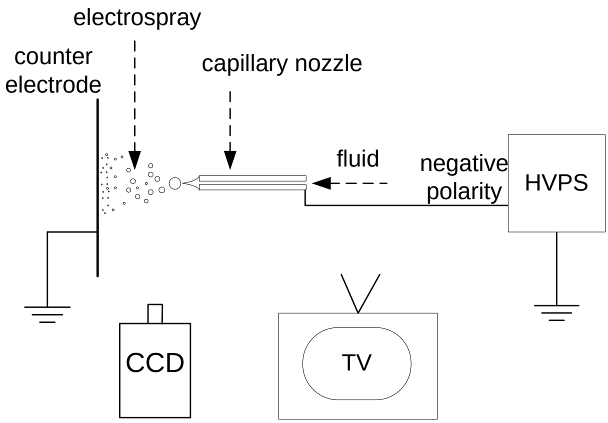

Fig. 1. Schematic of the experimental setup.

A 14.5 cm long adaptor was manufactured out of Polytetrafluoroethylene (Teflon) and it holds the syringe.

The counter electrode consists of a circular metal plate axially sustained in a vertical position, coaxial with the needle. A 6 mm thick metal plate (12.6 cm in diameter) was employed as grounded counter electrode. The plate has a 6.5 mm diameter central hole used by the plate holder. The needle-plate axis was maintained 78.3 cm above the floor. The needle was connected to the negative polarity of the high voltage during all the reported measurements. The needle position was fixed and the needle-plate distance was varied by changing the plate position.

The high voltage is supplied by a Glassman ($\pm$ 50kV DC) high voltage power supply (HVPS). A precision high voltage divider EMCO V1G was used in order to measure more precisely the high voltage at the needle. The high voltage divider is internally compensated for by the 10 MΩ input impedance of the digital Fluke 73 III multimeter we used, ensuring a 1000:1 voltage ratio.

A Kodak high-speed camera (Kodak EktaPro 1012) was used to monitor the generation of the electrospray. The CCD output was observed on a 32 in screen Sanyo TV. All experiments were performed at atmospheric pressure (air humidity varied between 40% and 50%) and temperature of 45-47^{o}C in the needle-plate region.

B. Procedure

The distance between needle and counter electrode was set successively to 0.5 cm, 1cm, 5 cm, 10 cm, and 15 cm. The natural aqueous flow determines the droplet frequency generation with no voltage applied. For each needle-plate distance high voltage was applied initially in increments of 1 kV and with smaller increments in the voltage region more sensitive to droplet generation. In order to avoid hysteresis-like phenomena associated with electrosprays, we observed the droplet rate at constant voltage (changing to another voltage always higher than the previously applied one). Droplet generation was observed using a Kodak EktaPro high-speed camera. At each voltage droplet emission was recorded for 1-5 minutes. The frequency count was performed based on the recorded optical observations.

III. Experimental Results

Experimental data collected for the studied aqueous electrosprays are plotted in Fig. 2. The frequency of the emitted drops as a function of the applied voltage is shown for the previously mentioned needle-plate distances. As the frequency of droplets increases with applied voltage, droplet size decreases. The relationship between droplet size and droplet rate could provide the flow rate and will be the subject of future investigations.

The frequency-voltage curves show that three regions can be associated with electrospray formation:

1. at relatively low voltages there is a slow increase in the droplet formation rate;
2. at intermediary to relatively high voltage there is a sharper increase in the frequency of droplet emission;
3. at high voltage there is a very abrupt increase of the droplet formation rate with voltage; this appears to be the region of actual electrospray generation.

Close observation of droplet formation at the tip of the needle shows that within the second region occasionally there are oscillations of the droplet attached to the needle not noticed within the first region. As the distance between needle and counter electrode is reduced, the intermediary second region of the frequency - voltage curves appears to shrink. Both the curves in Fig. 2 and our many direct observations of the electrospray formation suggest that there is a unitary mechanism of droplet formation reflected on the variation of the droplet formation with applied voltage.

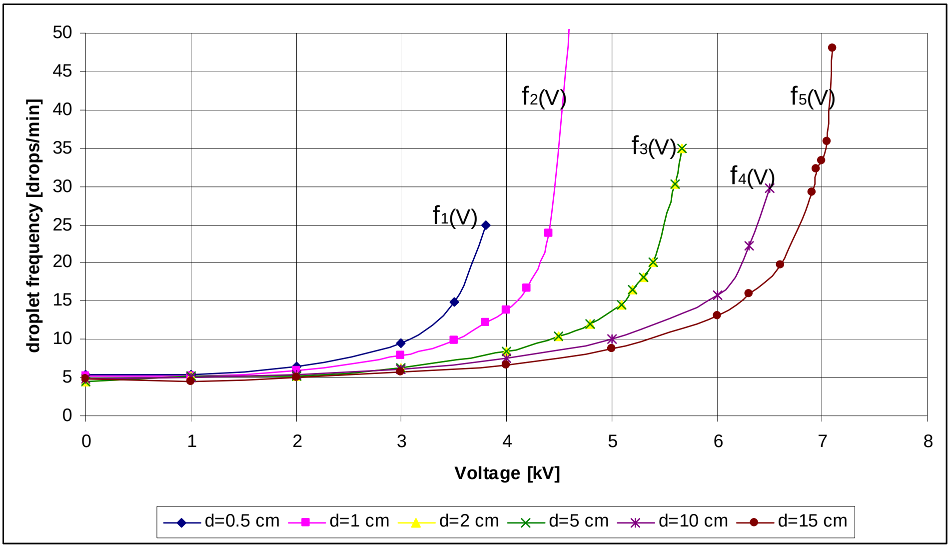

Fig. 2. Frequency of droplet formation as a function of applied voltage and distance between electrodes (25 G needle).

IV. Data Analysis and Discussion

A. Data Analysis

In our search for the common pattern of droplet formation, translations and scaling of the experimental data were proposed and performed.

The five frequency-voltage curves $f_1(V)$, …, $f_5(V)$ from Fig. 2 were translated and scaled in an attempt to overlap them as much as possible. The following operation was used for each of the curves:

$$f_i(V) \rightarrow f_i(V+K_{1i})/K_{2i} \quad (i=1,2,\ldots,5) \tag{1}$$

where K_{1i} is a voltage constant and K_{2i} is a scaling constant corresponding to frequency curve f_i.

Figure 3 shows the result of operation (1) purposely trying to overlap the resultant five curves. The attempt appears to be reasonably successful in demonstrating a general pattern for the droplet formation rate as a function of voltage. The coefficients used in transformation (1) are plotted as a function of needle-plate distance in Fig. 4. An increasing tendency (although not linear but rather logarithmic) of coefficients K_{1i} and K_{2i} can be noticed.

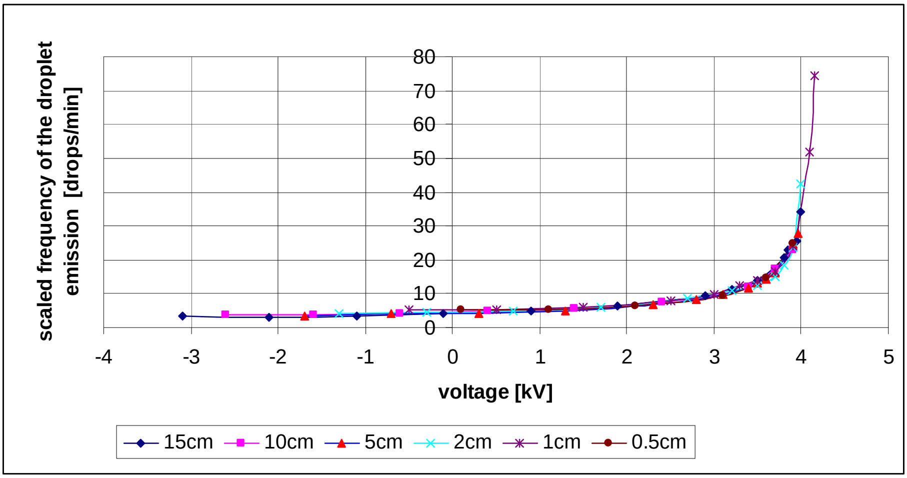

Fig. 3 Superposition of droplet frequency data shown in Fig. 2. All recorded data appear to fit the same type of curve.

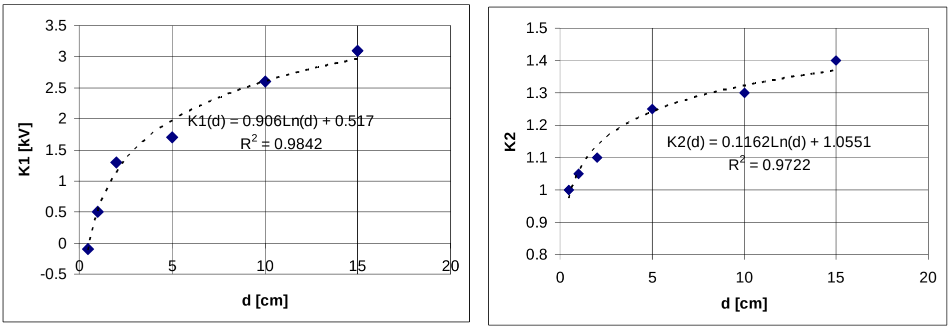

Fig. 4 Variation of coefficients K1 and K2 with needle-plate distance.

B. Discussion

All the experimental frequency-voltage data could be transformed according to

$$\frac{f_i(V + K_{1i})}{K_{2i}} = f_0(V), \qquad (2)$$

where (i=1, 2,…,5) and $f_o(V)$ is the reference curve. In our case we have transformed all the curves to overlap $f_1(V)$. Coefficient K_{1i} will be positive if curve $f_i(V)$ is on the right of $f_o(V)$ and negative otherwise. From relation (2) it follows that any arbitrary curves $f_i(V)$ and $f_j(V)$ are related to each other by coefficients K_{1i} and K_{2i}:

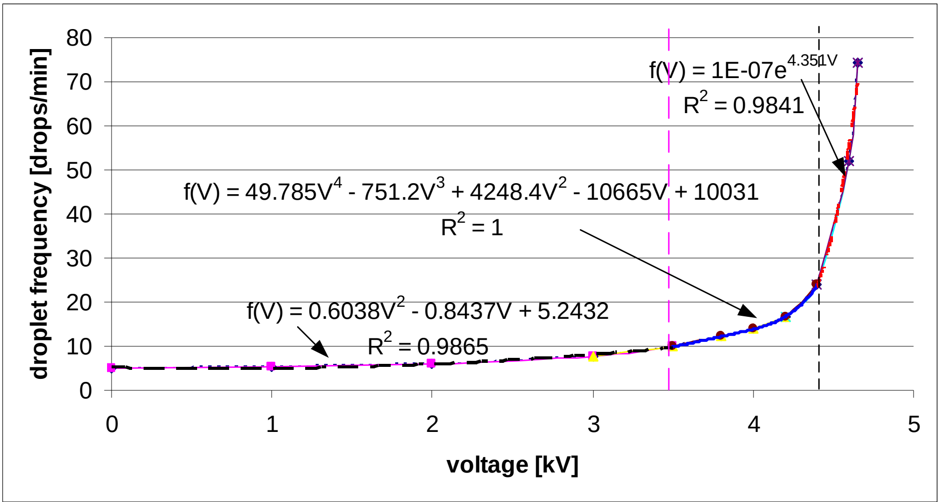

Fig. 5 General pattern of experimental data: three different regimes can be distinguished.

$$\frac{f_i(V+K_{1i})}{K_{2i}} = \frac{f_j(V+K_{1j})}{K_{2j}}, \qquad (3)$$

Given that $f_j(V, d_i)$ curves can be determined experimentally and coefficients K_{1i} and K_{2i} can be inferred as a calibration process, it appears that any other curve $f_k(V, d_k)$ corresponding to an arbitrary needle-plate distance d_k (with $d_{min}<d_k<d_{max}$) can be estimated based on the experimental variation of K_{1i} and K_{2i} with d and (2).

A relation giving the dependence of onset voltage V_{on} was given by Smith [11]

$$V_{on} = A\left(\frac{\gamma \cdot \cos\theta \cdot r_c}{\varepsilon_0}\right)^{1/2} \ln\frac{4d}{r_c} \qquad (4)$$

where γ is the surface tension of the fluid, θ is the half angle of the liquid cone at the tip of the capillary, r_c is the outer radius of the capillary, ε_0 is the electric permittivity of vacuum, and A is a proportionality constant. As in our experiments only d is variable, onset voltage varies linearly with the logarithm of needle-plate distance.

$$V_{on}(d) = a\ln d + b \qquad (5)$$

Our experimental data are in agreement with relation (5). Therefore, if $d_i<d_j$ it follows that $f_i(V, d_i)$ is on the left side of $f_j(V, d_j)$. As coefficient K_{2i} is experimentally smaller than K_{2j} relations (2) and (3) reflect experimental observations that the rate of change with voltage (for the same droplet frequency formation) for $f_i(V, d_i)$ is smaller than for $f_j(V, d_j)$.

For our capillary/needle and needle-plate investigated range a single curve appears to explain our data (Fig.). Three regions corresponding to different dripping regimes can be clearly distinguished. The first region with a small dependence on voltage appears to be explained by a second order polynomial variation of droplet formation rate with voltage. The second region appears to be explained by a forth order function of voltage, while the third region is explained to a certain extent by an exponential variation of droplet frequency emission with voltage.

V. Conclusion

Dripping regime was investigated in aqueous electrosprays. The droplet formation rate at the tip of a capillary/needle droplets in a needle-plate configuration was found to obey a scaling law given by relations (2) and (3) for the parameter range covered in our experiments. Accordingly, a single droplet frequency - voltage curve appears to be sufficient for characterizing electrospray development and three subregimes of the driping mode can be distinguished. It is believed that the present analysis can be useful for further investigation and design of aqueous electrosprays. Although our work indicates to a certain scaling law for aqueous electrosprays, additional data are needed in order to extrapolate the conclusions of the present study to other polar fluids, capillary diameter and capillary-counter electrode distances.

VI. Acknowledgements

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