

# On the EHD Atomization Mechanism

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Several scaling laws having different functional forms have been proposed in the literature for relating diameters of spray drops to liquid flow rate for an EHD spray nozzle operating in a stable cone-jet regime. According to these publications, liquid flow rate is the main operating parameter controlling the drop size.

An experimental study was performed in this work, using an EHD spray apparatus, in which three different liquid compositions were tested methodically, within their cone-jet parameters domains. Drop size distributions were measured using a Malvern 2600 laser light diffraction instrument. As a result of these measurements, it was found that drop size dependence on liquid flow rate can follow three distinct trends, which range from no dependence at some low flow rates to either a  $d_d \sim Q^{1/3}$  or  $d_d \sim Q^{2/3}$  proportionality, depending on liquids.

Based on a qualitative analysis of the results obtained, a functional form was proposed for scaling drop size with the net charge acquired by the liquid, not with the flow rate alone, according to which  $d_d \sim (Q/I)^{2/3}$ , and which consolidates all three drop size trends on a single basis if liquid charging kinetics is taken into consideration.

## 1. Introduction

This paper deals with a remarkable liquid atomization process that occurs when a liquid is fed at a relatively low rate through a capillary tube connected to a high electric potential, relative to the potential of a counter-electrode positioned in the vicinity of the capillary nozzle. In this process, the liquid forms a cone-shaped meniscus as it exits at the tip of the nozzle, frequently referred to as the “Taylor cone”, with a thin jet emanating from its apex. Under certain operating conditions, the jet breaks up vigorously at a relatively short distance from the nozzle, forming a diverging cloud of fine aerosol drops. Depending on liquid properties and process conditions, several other jet breakup modes can be achieved, such as those leading to systematic formation of monodispersed primary drops with diameters on the order of the jet diameter. While these breakup modes are not discussed in this paper, the subject of this study was the fine atomization mode of electrospray, when drops noticeably smaller than the jet diameter are produced.

The electro-hydrodynamic (EHD) atomization process has been studied intensively in the past by a number of researchers addressing various aspects of the physics involved, results of which have been published in the literature, e.g., [1] through [10], among others. Some of the studies were focused on experimental investigations in which pertinent spray characteristics were measured, such as the jet and drop diameters and the electric current carried by the charged drops away from the nozzle, while many other investigations were concerned mainly with theoretical derivations focused on modeling the electro-hydrodynamics of the Taylor cone and jet configuration. As a result of these studies, significant advancements have been made in the understanding of both the electric charge distribution on liquid surface and flow

velocity profile of the liquid, which explain the nature of the stability of the cone-jet geometric configuration, as well as an understanding of the effects of liquid properties on this behavior.

However, in spite of the progress made in the technical areas of electro-hydrodynamic phenomenology of electrospray operating in the cone-jet mode, understanding of the principal factors that govern this drop formation mechanism is limited. As a result, even though production of fine drops is the ultimate purpose of an EHD process, the laws that control drop size distribution of the spray produced in a cone-jet electrospray are not yet sufficiently explored.

To illustrate this knowledge gap, without attempting any comprehensive or in-depth review of the findings obtained in the previous research studies, Table 1 summarizes some of the well-known scaling laws published in the literature, which were proposed for predicting both the EHD jet diameter and representative spray drop diameter as respective functions of liquid properties and operating parameters. The purpose of this table is thus to demonstrate the disagreement in the functional forms of the equations proposed in the literature for describing these scaling laws.

Table 1. Principal Scaling Laws for EHD Jet and Drop Diameters

Ref	Jet Diameter	Drop Diameter	Comments
[1]	$d_j \propto r^* = \left( \frac{\epsilon \epsilon_0}{K} \right)^{\frac{1}{3}} Q^{\frac{1}{3}}$	–	$h = \left( \frac{rKQ}{\epsilon \epsilon_0} \right)^{\frac{1}{2}} < 1$ and small Re
[2]	$d_j \propto R^* = \left( \frac{r}{s} \right)^{\frac{1}{3}} Q^{\frac{2}{3}}$	–	$h \gg 1$ and large Re
[3]	Same as [1] and [2]	$d_{d\_min} = \left( \frac{s}{r} \left( \frac{\epsilon \epsilon_0}{K} \right)^2 \right)^{\frac{1}{3}} Q^{0.0}$	Existence of multimodal aerosol assumed; $d_{min}$ corresponds to $Q_{min}$ $d_{max}$ scales as $d_j$ in [1] and [2]
[4]	$d_j = \frac{2.0}{p^{\frac{2}{3}}} \left( \frac{r \epsilon_0}{sK} \right)^{\frac{1}{6}} Q^{\frac{1}{2}}$	$d_d = \frac{2.9}{p^{\frac{2}{3}}} \left( \frac{r \epsilon_0}{sK} \right)^{\frac{1}{6}} Q^{\frac{1}{2}}$	Rayleigh jet instability assumed for charged jets
[5]	–	$d_d = G(\epsilon) \left( \frac{\epsilon \epsilon_0}{K} \right)^{\frac{1}{3}} Q^{\frac{1}{3}}$	An empirical form of $G(\epsilon)$ is suggested, different from [1]
[6]	–	$d_d = \left( \frac{r}{s} \right)^{\frac{1}{3}} Q^{\frac{2}{3}} [0.37 + F(Q, V^*)]$	Voltage is found to affect EHD drop formation
[7]	$d_j \propto Q^{\frac{1}{2} + \frac{2}{3}}$	–	Findings from both experiment and theoretical analysis

In Table 1,  $d_j$  is the jet diameter,  $d_d$  is the drop diameter,  $Q$  is the volumetric flow rate,  $\rho$  is the density,  $s$  is the surface tension,  $\epsilon_0$  is the electric permittivity of vacuum,  $\epsilon$  is the electric permittivity coefficient for the liquid,  $K$  is the liquid conductivity, and  $V^*$  is non-dimensional voltage.

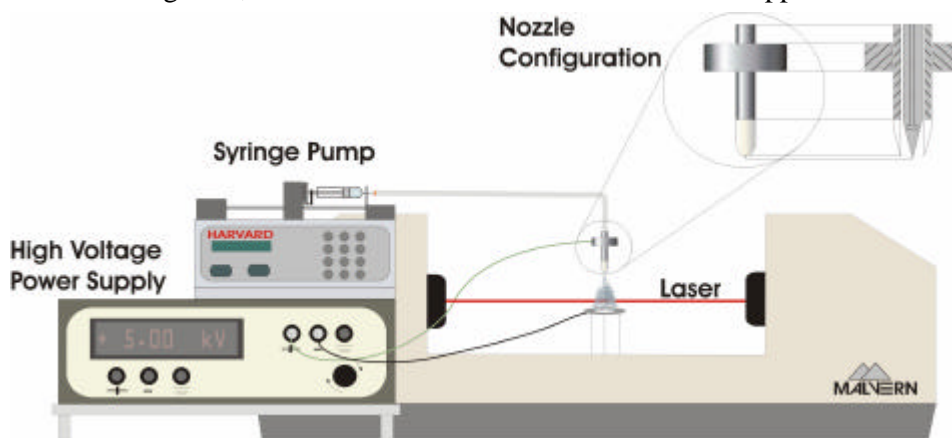
With the exception of several aspects of EHD phenomenology, which lie outside the scope of this paper, such as the effects of nozzle voltage and liquid viscosity on drop size, most published work has recognized that liquid flow rate through the nozzle is the only operating

parameter controlling the jet and drops diameters produced in the process. The effects of voltage, nozzle dimensions, and liquid viscosity have been found to be insignificant in most of the studies involving typical domains of parameters facilitating the cone-jet operating mode. As shown in the table, most correlations proposed for the effect of liquid flow rate on drop size indicate a power law relationship, with the main difference, however, being in the power law exponent that ranges from zero to  $2/3$  in most cases. It should be noticed also that while the jet diameter correlations were obtained in different studies using both the empirical observations and theoretical derivations, with the latter based on modeling the conditions for facilitating the stable cone-jet configuration, the drop size correlations were based on either fitting some experimental data or assuming that drop diameters are simply scalable with the jet diameters as described by Rayleigh's, for example, hydrodynamic instability of liquid jets [11]. In these studies, little attention was paid to the charge induction process in the liquid to be aerosolized, and the lack of liquid charging kinetics in the considerations may be responsible for the inconsistencies seen in the scaling laws.

The purpose of this paper is to present some experimental results obtained at Battelle on drop size distributions measurements for a cone-jet electrospray process, and propose a functional form that extends the laws governing the EHD drop formation mechanism.

## 2. Experimental study

Systematic experiments were performed in which three different liquid compositions were sprayed using an EHD nozzle. In these experiments, drop size distributions were measured for different rates of liquid flow through the nozzle. The nozzle had an insulating capillary tip, 1.3 mm I.D., with a metal needle extending 0.5 mm from the tip. The nozzle is diagrammed in Figure 1, which also shows a schematic of the test apparatus used.



**Fig. 1** Schematic of test apparatus.

A representative photograph of the EHD spray pattern obtained with a long working distance microscope is displayed in Figure 2. As the photograph shows, fine aerosol drops form from the EHD jet, having diameters smaller than jet diameter.

The needle was connected to the positive pole of a high-voltage DC power supply, while the negative pole of the power supply was connected to the counter-electrode. The counter-electrode was made of a metal ring having 10 mm outer diameter and 6 mm inner diameter, and positioned 12 mm below the nozzle. In all cases, the voltage was varied for each flow rate tested, so that drop size distributions were obtained for the entire range of EHD stable

cone-jet operating regime. However, no noticeable effect of voltage on drop size was observed within the range. Liquid flow rate was also varied in this testing, changing from the lowest to highest level within the ranges of stable operation. Current carried by the drops was not measured in these experiments.



**Fig. 2** EHD spray pattern.

Drop size distributions were measured using a Malvern Series 2600 laser diffraction instrument. Drop size distributions were relatively narrow, and each of the distributions was represented by a single volume-median diameter. Most of the tests were performed in replicates.

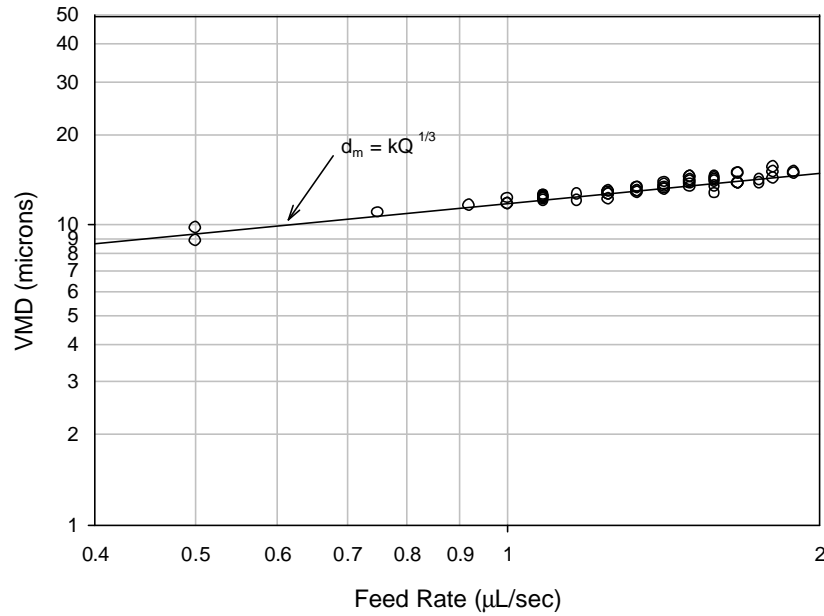
Three different liquid compositions were selected for this investigation because of their different aerosolization behavior with respect to the effect of flow rate on drop size distributions. The compositions were made of polyethylene glycol (PEG200 or PEG300), ethanol (EtOH), and deionized water (H<sub>2</sub>O). Pertinent physical properties of the test liquids were measured and are summarized in Table 2.

Table 2. Physical Properties of Test Liquid Compositions

No.	Liquid Composition	Surface Tension (N/m)	Conductivity (S/m)	Permittivity	Density (g/cm <sup>3</sup> )	Viscosity (centipoise)
1	55% PEG300, 10% EtOH, 35% H <sub>2</sub> O	0.041	2.421x10 <sup>-4</sup>	38	1.07	N/A
2	40% PEG 200, 60% EtOH	0.027	6.667x10 <sup>-4</sup>	21	0.919	4.12
3	20% PEG 200, 80% EtOH	0.023	2.688x10 <sup>-4</sup>	23	0.833	1.00

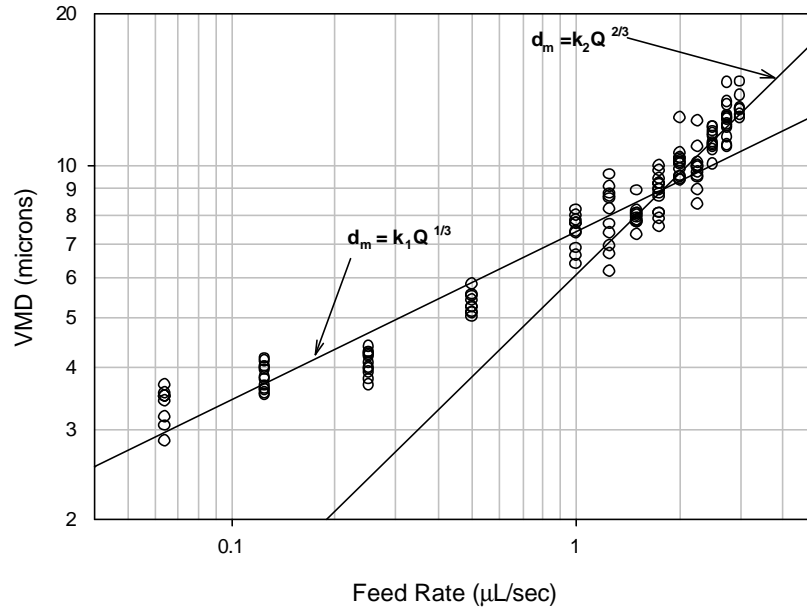
Figure 3 shows the results obtained for one of the test liquids composed of a mixture of PEG300 (55%), EtOH (10%), and H<sub>2</sub>O (35%). In this figure, the symbols represent individual test results, and the correlation line was obtained by best-fitting a  $d \sim Q^{1/3}$  function

to the test data. According to these results, drop size increases with  $Q^{1/3}$ , which agrees with a number of observations made by several other researchers in the field mentioned above.



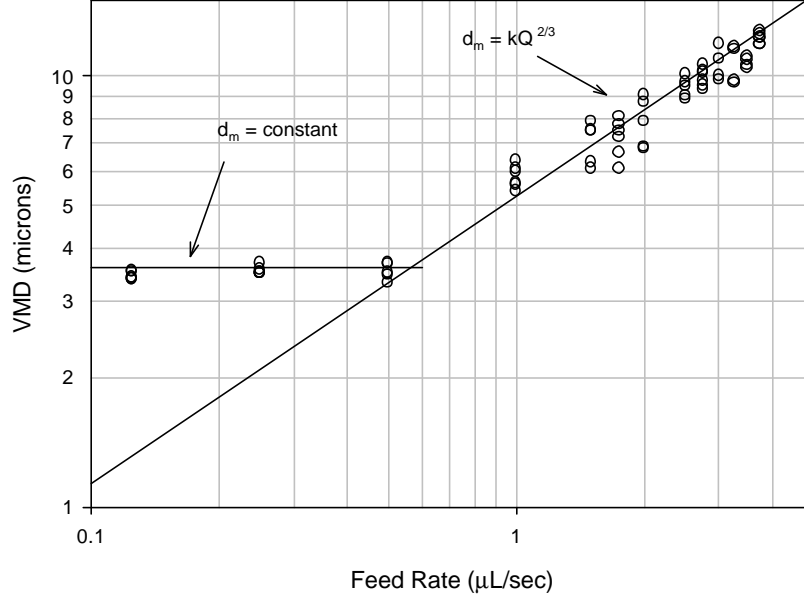
**Fig. 3** Composition 1 test results.

Another test liquid, however, composed of a mixture of PEG200 (40%) and EtOH (60%), displayed different aerosolization behavior, such as that shown in Figure 4. In this case, the  $d \sim Q^{1/3}$  dependence changes to a  $d \sim Q^{2/3}$  proportionality, at a flow rate of approximately 1.5 μL/sec.



**Fig. 4** Composition 2 test results.

Finally, the third test liquid composed of a mixture of PEG300 (20%) and EtOH (80%) exhibited no effect of  $Q$  on particle size at low flow rates up to approximately 0.5 μL/sec in our experimentation, beyond which the  $d \sim Q^{2/3}$  proportionality has been observed to emerge. Figure 5 illustrates this spray behavior.



**Fig. 5** Composition 3 test results.

### 3. Technical discussion

#### 3.1. Drop size scaling law

The results of experiments performed in this study show that depending on liquid properties and flow rate through an EHD nozzle, operating in a stable cone-jet regime, drop size dependence on flow rate can follow three distinct trends. These trends include the possibility of having no effect of liquid flow rate on drops volume median diameter, which may occur at some low flow rates, and either a  $d_d \sim Q^{1/3}$  or  $d_d \sim Q^{2/3}$  proportionality at some higher flow rates.

In an attempt to consolidate these different trends onto single common foundation, it is suggested that breakup of an EHD jet into spray aerosol is controlled, ultimately, not by liquid flow rate through the nozzle but by the net charge acquired by the liquid during its flow over the electrode. In this case, drop formation occurs in the cone-jet EHD aerosolization mode according to the following equation:

$$d_d = G(K, \epsilon, \sigma, \dots) \left( \frac{Q}{I} \right)^{\frac{2}{3}} \quad (1)$$

where  $I$  is the rate of charge induction in the bulk liquid prior to the aerosolization, which in fact is the current carried by the charged drops to the counter-electrode. The function term  $G(K, \epsilon, \sigma, \dots)$  comprises liquid properties that are considered important in this mechanism, with a dimension  $[C^{2/3} m^{-1}]$ . The exact form of the function was not explored in this study. If we assume that EHD drop formation occurs according to this equation, then we believe all three EHD aerosolization regimes can be explained by considering the charging kinetics of liquid in the nozzle.

Liquid charging occurs at the liquid/electrode interface where an electrochemical reaction takes place. If liquid charging kinetics is rapid enough (such as in case of high ionic conductivity), any liquid parcel arriving at the tip of the nozzle will be fully charged as long as its residence time in the vicinity of electrode is sufficiently long (i.e., low flow rate),

resulting in achieving the maximum possible charge induction in the liquid. Under these conditions, obviously,  $I \sim Q$ , so that  $d \sim (Q/I)^{2/3} = \text{const}$  is independent of liquid flow rate (first aerosolization mode depicted in Figure 5 for low flow rates).

When residence time of a liquid element in the nozzle becomes too short for achieving charge saturation, liquid charging process can reach its maximum rate in accord with the rate of charge transfer across the interface between liquid and the electrode. The rate of such electrochemical reaction is dependent on a number of characteristics, including structure of ions participating in the reaction, electrode material properties, and interface area available for charging. In this case,  $I = \text{const}$  regardless of liquid flow rate, resulting in the  $d \sim Q^{2/3}$  dependence, as shown for higher flow rates in both Figures 4 and 5.

If, on the other hand, charging of liquid occurs between these two bounding regimes, which is often the case, it is a diffusion-controlled electrochemical process with rate controlled by diffusion of ions and reaction products toward and away from the electrode, respectively. Depending on flow configuration, diffusion rate (or liquid charge rate  $I$ ) may increase with square root of liquid velocity (or as  $I \sim Q^{1/2}$ ), resulting in the  $d \sim Q^{1/3}$  dependence, as shown in Figure 3 and in Figure 4 at low flow rates. Apparently, when the mass transfer rate becomes as high as the maximum charge transfer rate across interface, the rate of electrochemical reaction at the interface once again becomes the limiting factor, and the  $d \sim Q^{1/3}$  dependence changes to  $d \sim Q^{2/3}$  as shown in Figure 3 at high flow rates.

### 3.2. Charging in the diffusion controlled regime

Many research studies published in the literature have concluded that electric current  $I$  carried by the spray drops is indeed proportional to  $Q^{1/2}$ , e.g., [1, 5, 8, 9]. As mentioned above, theoretical efforts leading to these conclusions were based on applying the principal conservations laws of physics and using some simplifying assumptions for describing the unique cone-jet pattern. (Note that while this proportionality was thus found to facilitate a stable EHD process, variations in the cone-jet configuration geometry have also been observed to occur in response to some deviations in operating conditions, e.g., voltage [6]). In spite of these studies, however, since liquid charging kinetics is not controlled by the electric and flow fields developing in the cone-jet region of the spray, the  $I \sim Q^{1/2}$  proportionality needs also to be explained independently, on kinetics basis. A possible explanation of this liquid charging kinetics can be found by considering the electric double layer (EDL) at the interface between liquid and electrode.

The application of an electrode to a liquid solution attracts both the anions and cations, creating a several nanometers thick EDL. The migration of ions from the bulk towards the electrode where they react is a slow process, so that ions *concentration polarization* occurs further out from the EDL, leading to formation of the Nernst diffusion layer with a thickness on the order of 0.1 mm [12]. Concentration of ions diffusing toward the electrode changes within this layer from their bulk to surface concentration (which can be as low as zero). The rate of ion migration is dependent on many flow independent characteristics, including concentration and charge of ions participating in the reaction, and ion diffusion coefficient. However, the thickness of the diffusion layer is a strong function of flow conditions [12].

The rate of mass transfer in a flowing liquid is proportional to the Sherwood number ( $Sh$ ):

$$I = \frac{dm_{\text{Charge}}}{dt} \propto k = Sh \times \left( \frac{D}{d} \right) \quad (2)$$

where:  $k$  is the mass transfer coefficient,  $D$  is the diffusion coefficient, and  $d$  is a characteristic dimension. The Sherwood number is a function of flow and fluid properties,

represented by the Reynolds (Re) and Schmidt (Sc) numbers). Because of the small thickness of the boundary layer, this diffusion process can be evaluated considering liquid flow over flat surface. For a flat plate, the Sherwood number takes the following form [13]:

$$Sh = 0.646 \cdot Re^{1/2} Sc^{1/3} \quad (3)$$

where:  $Re = \frac{U l \rho}{\mu}$ ,  $U$  is the flow velocity, and  $l$  is a dimension.

Then, from Equations 2 and 3, and since  $U \sim Q/A$ , where  $A$  is the cross-flow area, the rate of liquid charging in the diffusion controlled EHD regime is proportional to  $Q^{1/2}$ , i.e.,  $I \sim Q^{1/2}$ .

### 3.3. Consistency with the drop charge accommodation theories

The functional form of Equation 1 is consistent with the considerations of Rayleigh and Vonnegut and Neubauer [14], as also discussed in [10], who developed basic concepts for determining the amounts of electric charge that liquid drops accommodate. According to Rayleigh [10], the maximum charge ( $q_R$ ) that a droplet with diameter  $d_R$  can accumulate before it breaks up into smaller droplets, which occurs when electrostatic repulsion stresses exceed surface tension, is expressed as the following:

$$q_R = 8\pi \sqrt{\epsilon_0 \sigma} (0.5 d_R)^{3/2} \quad (4)$$

In contrast, Vonnegut and Neubauer [14] derived an approximate expression for the size of monodispersed drops that would form from an electrically charged liquid, basing their derivations on minimizing the total surface energy of the resulting aerosol. Limiting their analysis to the major surface energy contributions from surface tension and electric charge, they determined the “Vonnegut drop” diameter, with a charge coincidentally to be one half the Rayleigh limit:

$$q_V = 4\pi \sqrt{\epsilon_0 \sigma} (0.5 d_V)^{3/2} \quad (5)$$

For the purpose of this analysis, it should be realized that while both the  $q_R$  and  $q_V$  represent absolute droplet charge, the ratio  $I/Q$  in Equation 1 represents specific charge induced in a unit volume of liquid, i.e.,  $q = \rho d^3 I / 6Q$ . Subsequently, the following expression results for the Rayleigh and Vonnegut drops, respectively:

$$d_R = \sqrt[3]{9\epsilon_0 \sigma} \left( \frac{Q}{I} \right)^{2/3} ; \quad d_V = 2d_R \quad (6-a; b)$$

The consistency between the Equation 1 functional form and both Equations 6-a and 6-b supports the drop-size scaling law suggested in this paper.

With the purpose to assess the applicability of these correlations to the test results obtained in the experiments, the current carried by the spray was estimated using correlations published in the literature, since it was not measured in this work. Four different scaling laws were used for calculating the current, as indicated in Table 3. For the  $Q^{1/3}$  regression line shown in Figure 4, Table 3 shows ratio of measured drop diameters to the Vonnegut drop diameters, and electric charge carried by the drops as a fraction of the Rayleigh limit. According to Table 3, drop diameters formed in the experiments are comparable with the Vonnegut diameters, considering that the current used in Equations 6 was estimated using available correlations.



Table 3. Reduced Test Data vs. Vonnegut Diameter and Rayleigh Charge Limit

Correlation for current ( $I$ ) from:	Fraction of Vonnegut diameter	Fraction of Rayleigh limit
[9] - Gañán-Calvo (1994)	0.62	0.25
[1] - F. de la Mora (1994)	1.21	0.67
[15] - Gañán-Calvo (1997)	1.28	0.72
[4] - Gañán-Calvo (1999)	1.39	0.82

#### 4. Conclusions

An experimental study was performed using an EHD spray apparatus, in which three different liquid compositions were sprayed. The experiments were conducted varying liquid flow rate through the nozzle, and adjusting voltage level for achieving stable cone-jet operating regime. For each liquid, within its stable-operation domain of flow rates and voltages, drop size distributions were measured using a Malvern 2600 laser light diffraction instrument. The measurements were obtained, for each flow rate, using voltages that ranged from minimum to maximum boundaries of the domains. No effect of voltage on drop size distribution was noticed.

As a result of these measurements, it was found that drop size dependence on liquid flow rate can follow three distinct trends, which range from no effect at some low flow rates to either a  $d_d \sim Q^{1/3}$  or  $d_d \sim Q^{2/3}$  proportionality, depending on liquids.

Based on a qualitative analysis of the results obtained, a functional form was proposed for scaling drop size with the net charge acquired by the liquid, not with the flow rate alone, according to which  $d_d \sim (Q/I)^{2/3}$ . This relationship was found to consolidate all three drop-size trends on a single basis if liquid charging kinetics is taken into consideration.

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