Electrospray characteristics of aqueous KCl solutions with various electrical conductivities

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Abstract

In the present experimental study, the effects of electrical conductivity on electrospraying procedure are investigated. A metallic nozzle with 600 μm ID as high voltage electrode and a stainless steel ring as a ground electrode were employed. Experiments were carried out in still room temperature. Four different aqueous KCl solutions were sprayed in various high voltages and flow rates. Results confirm that spraying modes changes with conductivity variation. For forming a cone shape, emerging from the nozzle, required applied electric field decreases with conductivity increasing. Results also revealed that conductivity of dispersed solution acts a main role on forming and elongation of the cones in electrospraying procedure. The size and velocity of emanated droplets are also investigated in order to gaining some insight to the electrospraying phenomenon.

Introduction

Electrospraying of liquids is a well-established process for producing submicron particles. This spraying method (also known as electro hydrodynamic atomization) is a process in which high electric field is employed to disperse a liquid. High voltage is applied to a liquid supplied through an emitter (usually a metallic capillary). In electrospraying, the shear stress caused by the electric force applied to the surface of liquid, elongates the liquid meniscus formed at the tip of a capillary, to the form of a cone and/or a jet which then deforms and disrupts into droplets due to interplay of electrical and mechanical forces. In this method no additional purely mechanical energy is applied to spray the liquid. Electrohydrodynamic spraying (EHD spraying) has wide range of applications including fine resolution electrohydrodynamic printing [20, 3], biomedical application especially drug delivery system [29, 23], powder production [9, 11] and producing stable emulsions [13, 16, 21].

Early works on the electrified surfaces has been done by Zeleny in 1917[24]. In 1969, Taylor conducted some experiments in electrified jets [22]. Cloupeau and Prunet-Foch introduced cone jet as one the modes which expects to have monodisperse produced droplets in 1989 [5]. Fernandez de la Mora and his coworkers investigated the droplets diameter and the current emitted from electrosprays in the well-known cone jet mode [8]. They also studied the effect of physical parameters like electrical conductivity, viscosity, liquid density and the feed rate on the electrospraying in cone jet mode [12]. Experimental observation of the dielectric constant effect on the cone jet mode spraying has also been investigated by D. R. Chen et al [4]. They proposed some scaling laws between produced droplets and dielectric constants.

For other values of electric field and feed rates, some other regimes, different from cone jet mode, appears on the tip of nozzle [14]. Cloupea and Prunet-foch (1990) studied these electrospraying modes and present the classification based on their observation. Subsequently, they [7] reviewed electrospraying modes and clarified some ambiguous concepts of spraying modes which were arising from multiplicity of spraying functioning modes. Astable modes of spraying are other modes which attract growing interest in the recent years [1, 2, 19]. These modes of spraying occur in the transition between three axial modes of spraying (Dripping, Pulsating and cone-jet).

The physical parameters in the electrospraying process have an undeniable role in manipulation of produced droplets. Viscosity as one of these parameters was studied by Ku and Kim [15]. They investigated produced droplet diameter and compared their results with existing scaling laws which demonstrated an evident discrepancy in some of cases. Role of electrical conductivity on the electrospraying modes remains incomplete or even poorly understood. However, there is high volume of reports regarding relationship between electrical conductivity with cone jet mode of spraying but there are still ambiguous parts related to other modes of spraying. The authors tried to clarify the effect of electrical conductivity on the modes of spraying in first chapter of their results. In the present study, the results are divided to three parts: the first part is the role of electrical conductivity on spraying modes. The second part pertains to the behaviour of the emerged menisci at the tip of nozzle for different conductivities. The last part of study is about the droplet diameter and droplet emerging velocity in pulsating cone jet mode for different conductivities. Most of the Electrospray (ES) publications to date are related to

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droplet diameter in the cone jet mode and disregards to the droplet produced in the other modes of spraying like pulsating cone jet mode and the velocity of these drops. In this work, authors strive to present an image for behaviour of produced droplets in pulsating cone jet mode. Droplet emerging velocity which is studied in the third part of results section is an important criterion for describing the behaviour of droplets when colliding to a solid surface and this also has wide range of applications including printing [17,20].

Experimental Methods

In order to investigate the electrospraying process experimentally a setup, consisting of a metallic nozzle with inner diameter of o.6 mm and a metallic ring with 30 mm in inner diameter, was developed. The ring was fixed 25mm below the nozzle tip .A schematic illustration of the experimental apparatus is presented in Fig. 1 In this experimental setup, the nozzle is used as high voltage electrode by connecting it to the high voltage power supply and the ring is employed as grounded electrode. The liquid, going to be sprayed, was fed to the nozzle by means of a syringe pump through an insulator tube. Combined effects of gravity, back pressure in the tube and the electric forces cause the liquid to discharge vertically downstream through the nozzle toward the ring electrode. Tangential Electric stresses resulted in spraying of the liquid in different so-called electrospraying modes.

In order to study the effects of electrical conductivity on electrospraying phenomena, KCl was dissolved in distilled water. Adding KCl extremely changes electrical conductivity of water. The conductivity of water and aqueous KCl solutions were measured by conductivity-Meter (EZTECH AZ- 8361). Measured amount are noted in table 1.

Table 1
Electrical conductivity of dispersed solution.

Materials	Distilled water (0.00 Molal)	KCl solution (0.01 Molal)	KCl solution (0.10 Molal)	KCl solution (1.00 Molal)
Conductivity (S/m)	0.042E-3	1.634E-3	11.82E-3	108.620E-3

It is noteworthy that with adding KCl the permittivity of water does not change, therefore during the experiments this property was assumed constant [26]. Also the changes in amount of viscosity [28] and surface tension [25] are negligible in comparison with the changes in conductivity.

Pictures of the liquid meniscus and cones at the nozzle tip were captured by a digital CCD camera (20D Canon) with range of 1000 to 8000[1/s] shutter speed. In order to achieve better visualization and focus on the nozzle tip, 500 mm macro lens was installed to the camera. The camera was fixed in front of the nozzle tip and regarding to the desired type of photography a cooled light supply or a stroboscope with 5000-11000 flash/min exposure times was employed.

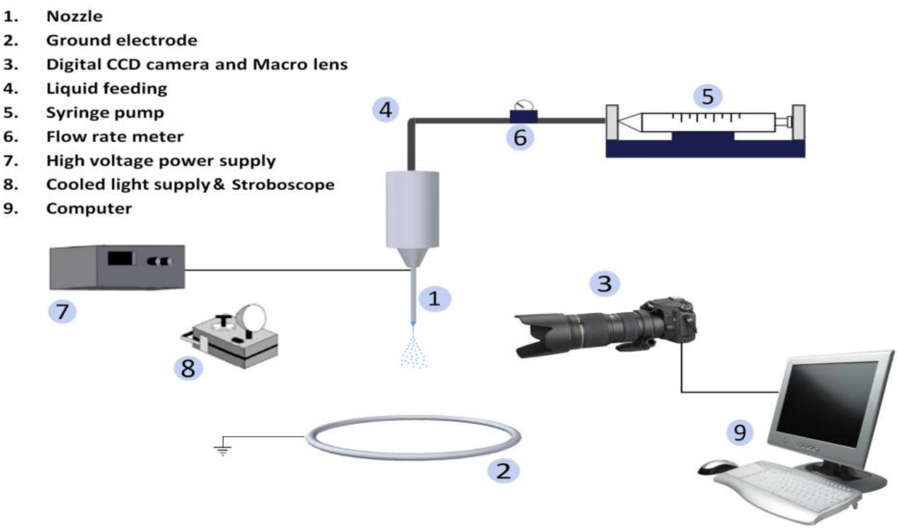


Figure 1 Schematic illustration of the experimental apparatus

Summary and Conclusions

The efficacy of electrical conductivity on the electrospraying process has been divided by the path of spraying into three parts: 3.1. Before liquid ejection from from nozzle 3.2. At the tip of the nozzle and 3.3. After emission from the nozzle.

3.1 effect of conductivity on electrospraying modes

Spraying modes of distilled water and KCl solutions are studied experimentally. Fig. 2 shows the modes of ES for different applied voltages. As shown in Fig. 2, six well-known modes are observed in this study. For different voltages and conductivities of liquid, the modes of spraying are reported. The dripping mode was the preliminary mode of spraying. This mode occurs when the electric forces on the surface are not strong enough to make a distinctive mode but the increase in dripping frequency and reduction of drop size due to voltage growth are the main characteristics of this mode. For rather higher applied voltages, the oscillating jet mode, which is an unstable mode, is the last observed mode. In this mode, the swirling of jet front and the vigorous lashing are the main features. The cone jet mode occurred in 0.1 molal KCl solution for the first time. With conductivity rising, charge density at the tip of nozzle increases and leads to diminishing of discharging voltage. The discharging voltage is the voltage in which the nozzle, as high voltage electrode, discharges to the ring as a ground electrode via the air medium. For example the discharging phenomenon for 0.1 and 1 molal KCl solution happens in 12kV and 10kV applied voltage, respectively. As shown in Fig. 2, electrical conductivity plays an important role in producing different modes of spraying in the same applied voltage. In a particular applied voltage due to different charge densities for different liquids, unequal electric forces occur at the nozzle tip, reulting in different modes of spraying.

Furthermore, the flow rate as another important characteristic of ES modes has been studied. The effect of flow rate on spraying modes is presented in Fig. 3. As shown in this figure, in this range of flow rates, the effect of flow rate on altering the spraying behaviour is negligible compared to effect of applied voltage. In the minimum amount of applied voltage, the modes of spraying experience no considerable change during flow rate increasing, and this behavior clearly exists in the higher voltages. Without considering the suction effect of spraying, the volume flow rates is illustrated in the figures.

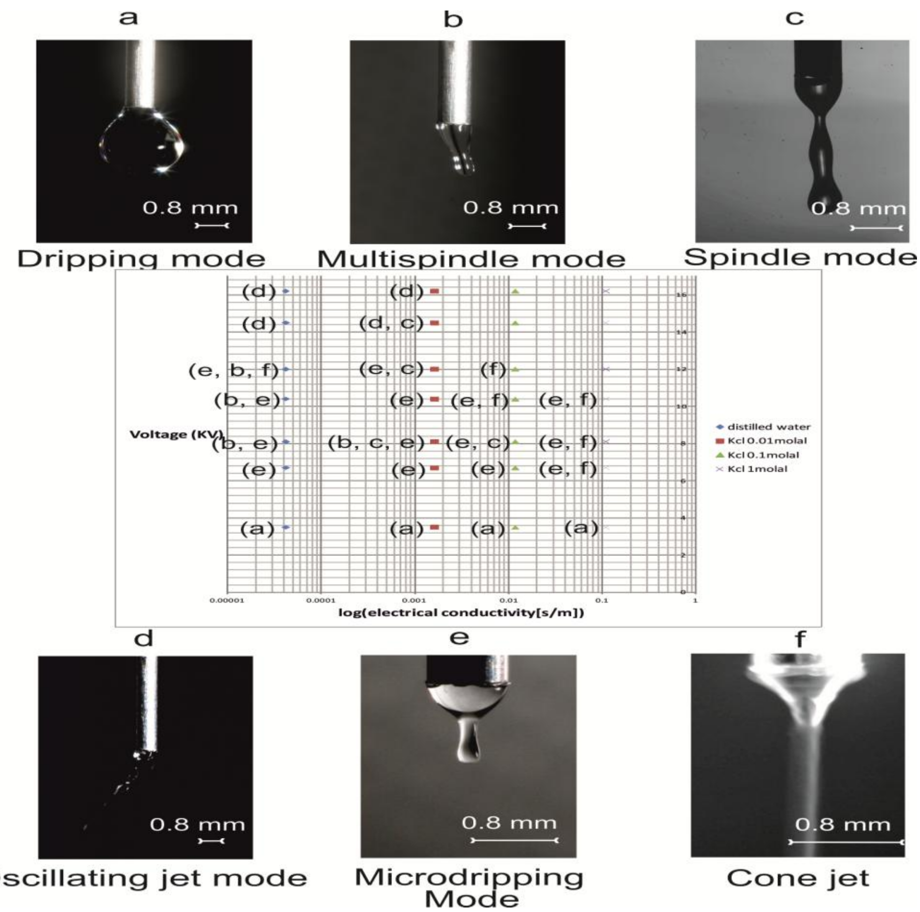


Figure 2 Electrospraying modes for different KCl solution in different applied voltage

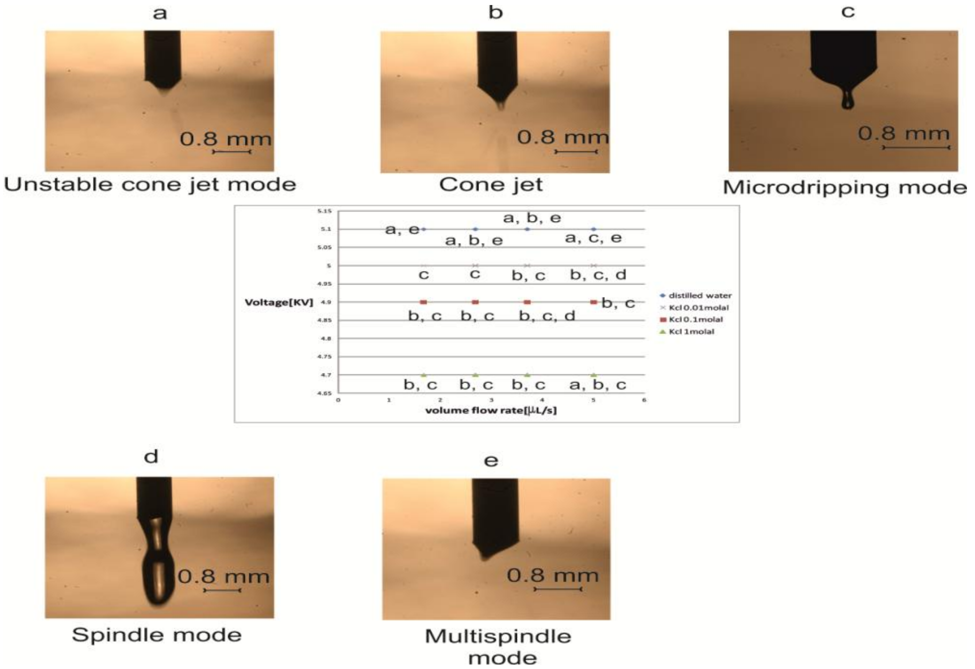


Figure 3 Modes of spraying with different flow rates and various voltages

3.2 Effect of conductivity on the cone of the capillary

In order to study the role of the electric field, in which the cone shape is observed at the nozzle tip, three parameters were defined as follows:

$$t_c = \sqrt{\frac{\rho l^3}{\gamma}} \qquad [1]$$

$$t_e = \frac{\varepsilon}{\sigma} \qquad [2]$$

$$\alpha = \frac{t_e}{t_c} \qquad [3]$$

α is the ratio of charge relaxation time to capillary timescale.
In these experiments, the flow rate is non-dimensional as follows:

$$\eta^2 = \frac{\rho K Q}{(\gamma \epsilon \epsilon_0)}$$

The onset voltage fluctuations versus α is depicted in fig. 4. This voltage for different KCl solutions decreases with rising of conductivity. Onset voltage in this study is defined as a voltage in which cone shape is observed.

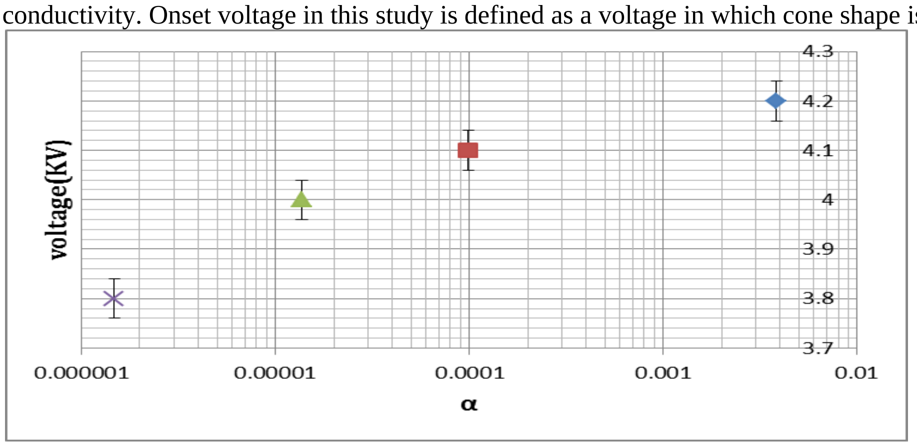


Figure 4 Onset voltage for different relaxation times

From theoretical point of view more conductive liquids can get more charge in a particular period of time. Increase in conductivity of dispersed phase leads to intensification of electric forces on the capillary due to more net charge. This process makes cone form in lower voltages on the capillary. For better understanding that how these forces act on the meniscus Fig. 5 is presented. According to this figure normal electric stresses are paramount factor in elongation of meniscies at the nozzle tip [18]. Owing to the fact that in higher amounts of conductivity these normal electric stresses intensify on the capillary the cone shape occurs in lower voltages.

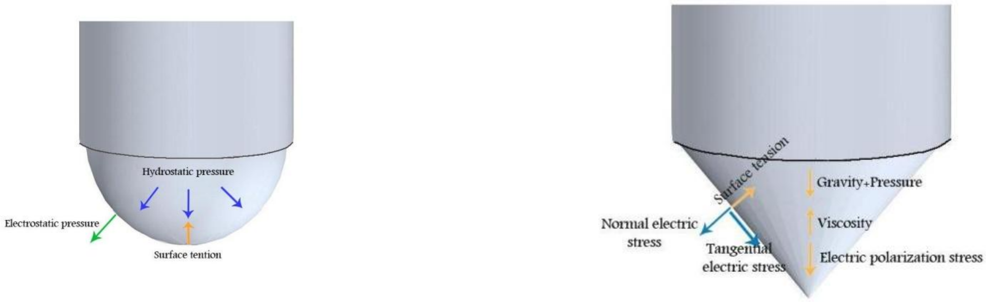


Figure 5 Schematic illustration of exerted force on the meniscus of the capillary

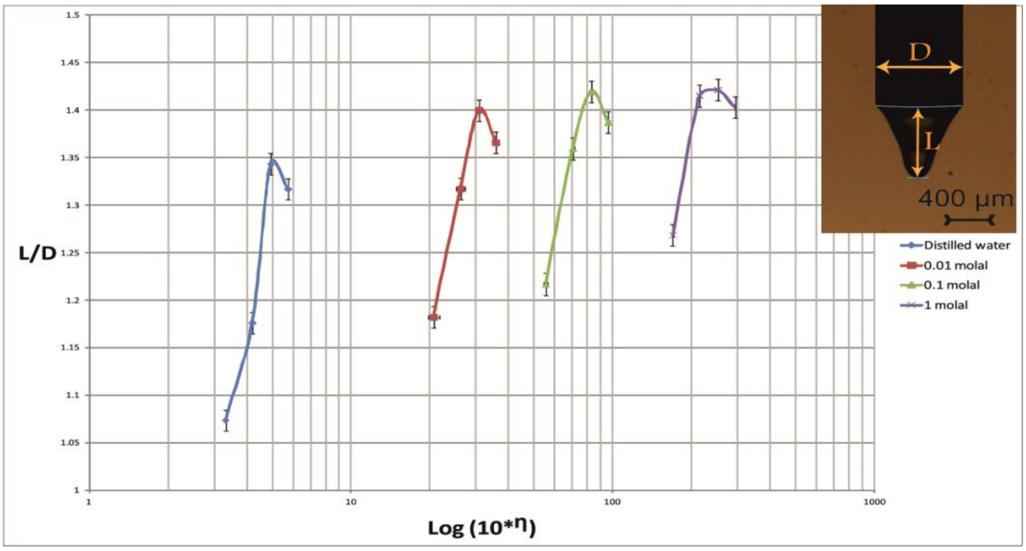


Figure 6 Fluctuation of non-dimensionalized cone length (L) versus non-dimensional flow rate for various conductivities. D is the nozzle outer diameter.

Figure 6 illustrates the variation of cone length in different non-dimensional flow rates. The cone stretches vertically downward due to higher EHD body force exerted on the cone due to more surface charge in the cases of higher KCl concentrations. Increasing of electrical conductivity emerges as extension on the menisci which is illustrated in Fig. 6.

The EHD body force can be expressed as follows [27]:

$$f_e = \rho_f E - \frac{1}{2} E^2 \nabla \varepsilon + \frac{1}{2} \nabla \left[E^2 \left(\frac{\partial \varepsilon}{\partial \rho} \right)_T \rho \right]$$

Mentioned force consists of three terms. The first term is coulomb force (electrophoretic) which exerts on positive and negative free charges, the second term is dielectrophoretic force, mainly depends on electric permittivity gradient, and the third term is electrostrictive force related only to compressible fluids. Here because of very large amount of electric charge which leads to very large electrophoretic forces, the dielectrophoretic term can be neglected. Also in this case study the third term is almost zero.

Owing to the fact that more the conductivity is more the charge is, in spraying of solutions with higher molality, the electrophoretic force increases and cone experiences more electrical forces leading to more vertical extension.

Another important point that can be obtained from fig. 6 is the effect of flow rate on the cone length.It is rational that hydrodynamic field intensification leads to more elongation of the cone menisci. The rate of cone length augmentation diminishes with increasing the conductivity of dispersed phase.

For better understanding the whole procedure Fig. 7 is prepared. This figure shows the cone length variation versus We/We(e). This non-dimensional number is defined as follows:

$$We = \frac{\rho U^2 d}{\sigma} \quad [5] \qquad We_e = \frac{\varepsilon E_0^2 L}{\sigma} \quad [6] \qquad \xrightarrow{[5],[6]} \qquad \pi = \frac{We}{We_e} = \frac{\rho U^2 d}{\varepsilon E_0^2 L} \quad [7]$$

This number illustrates the behavior of hydrodynamic field with respect to the electric field. As depicted in Fig. 8 cone elongates with We/We_e rising and the slope of variation diminishes with electric field reduction. This behavior shows the main role of electric field on the behavior of cone and the equilibrium between electric and hydrodynamic fields. As mentioned before, with regarding to the fact that in cone-shape mode the liquids with higher conductivity experience more exerted electric forces, the maximum cone elongation occurs in the case of 1 molal KCl solution.

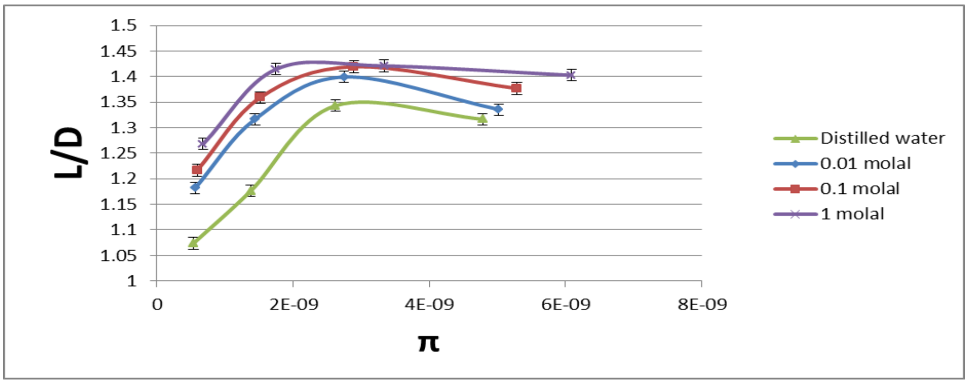


Figure 7 Length of the cone variation versus π

3.3 The behavior of emanated droplets and effect of conductivity

Studying the emanated droplets behavior in the response of different dispersed phase conductivities in the modes in which a cone is formed, is another aim of this paper. Due to growing interest of cone shaped modes of spraying, functioning cone shape mode in this section is pulsating cone jet mode.

As shown in Fig. 8, the droplet velocity initially increases and after a specific flow rate the drops velocities do not change appreciably. As another result, concluded from this figure, the drop velocity rises slightly with conductivity reduction. For higher conductivities because of the fact that the cone appears in lower voltages the electric field strength is less than cases with lower conductivity. And it is obvious that in solutions with lower KCl concentration due to less conductivity the surface charge diminishes [27]. Hence according to equation [1] in this phenomenon two main factors are interplaying: the first is electric field intensification and the other is surface charge density reduction. The observed behavior depicts the prevailing of electric field intensification factor. For example in spraying of water, having the minimum conductivity, the surface charge is the minimum amount and the cone appears in the highest voltage among other liquids so the electric field strength is maximum amount comparing to other sprayed liquids. As it is shown in the figure in spite of the lowest surface charge density the highest velocity refers to water because of highest electric field strength.

The electric field effect on the droplets velocity is shown in Table 2 showing the electrical Weber number We_e lessening with conductivity. Electrical Weber number (We_e) presents the behavior of electric forces with respect to the interfacial forces and diminishing of this number demonstrate the electric field shrinking effect, so it can be concluded that electrical forces act a main role in droplets velocity.

Droplet size variation versus applied electric field is illustrated in Fig.9 the droplet size increases with flow rate increment. According to the constant applied voltage in each concentration, droplet size soaring behavior arises from hydrodynamic force intensification which is in good agreement with previous work of the authors [27]. It is noteworthy that the diameters of observed droplets are in the range of 150-300 micrometer.

On the other hand raising conductivity leads to diminishing drop sizes which is related to more charge on droplets surfaces. Regarding to the fact that produced droplet charge depend on the applied electric field strength and electrical properties of liquids such as conductivity, the interaction between these parameters influence on the droplets sizes. More the conductivity of dispersed fluid is, less the droplet size is.

The mode of spraying changes from microdripping in low flow rates to pulsating cone jet mode in higher flow rates. In this flow rate range, distilled water does not show any significant increase in droplet size but the KCl solutions soaring behaviour is much higher than what the distilled water is and this process shows the effect of increasing charge on the augmentation of drops sizes.

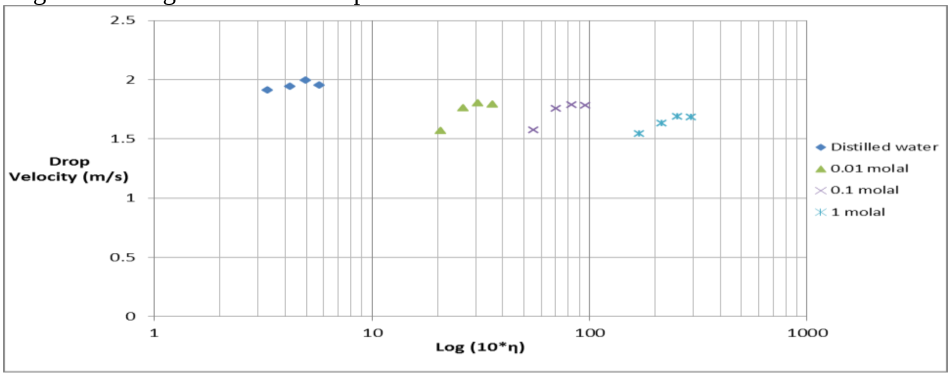
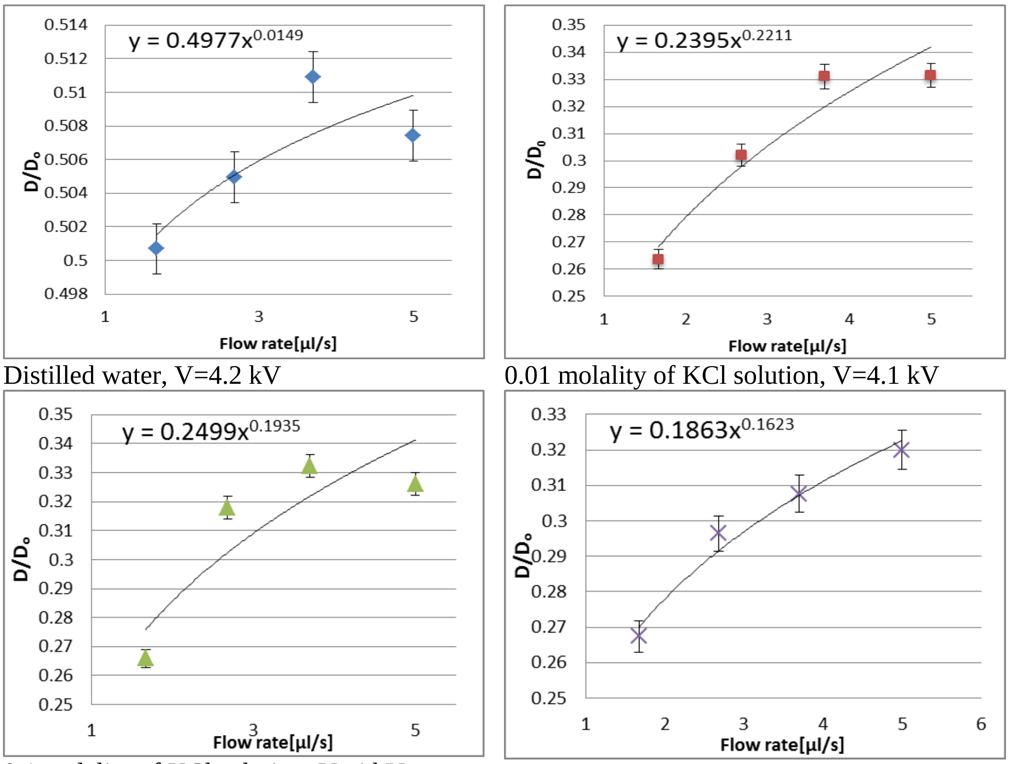


Figure 8 droplet velocity variation versus flow rate for different dispersed solution

Table 2. The variation of Electrical Weber number versus Conductivity

Conductivity (s/m)	0.0420 E-3	1.634 E-3	11.820 E-3	110.620 E-3
Electrical Weber number	453.092	435.195	415.360	373.871



Distilled water, V=4.2 kV

0.01 molality of KCl solution, V=4.1 kV

0.1 molality of KCl solution, V=4 kV

1 molality of KCl solution, V=3.8 kV

Figure 9 Droplet size variaton versus flow rate for four different dispersed solutions

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