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Experimental Investigation of Scaling Laws for Electro spraying: Dielectric Constant Effect

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ABSTRACT. Experiments were performed to investigate the effect of liquid dielectric constant on existing scaling laws for the electro spraying process. The variations of the droplet size and the emitted current were measured as a function of the dielectric constant for the electro spray operating in the cone-jet mode. Eight different solvents with dielectric constants, κ , ranging from 12.5 to 182 were tested. The residue particle size distributions were measured using a TSI scanning mobility particle sizer, (SMPS). The produced liquid droplet sizes were then calculated from the known solution concentrations. The results show that: (1) For the produced droplet size, D_d , experimental data are in agreement with the scaling law ($G(\kappa) = 1.66\kappa^{-1/6}$) proposed by Gañán-Calvo et al. (1994) for solvents with high dielectric constants. The derivation in low dielectric constant cases may be that the assumption of Gañán-Calvo (1994) on the characteristic length may not hold for the present system; (2) for the emitted current, I , experimental data deviate from those given by Fernández de la Mora and Loscertales (1994) except for the case of benzyl alcohol. The difference may be partially explained by the use of different electrolytes. A larger deviation is found in comparing with the equation, $f(\kappa) = 6.46\kappa^{1/4}$, provided by Gañán-Calvo et al. (1994). The reasons may be due to the inapplicable characteristic length assumption and the role of ion drifting current in the total emitted current. Based on the experimental data collected, some problems are pointed out regarding the criteria proposed in the previous studies for predicting the minimum liquid feed rate. A formula is given based on these data to estimate the maximum feed rate and to explain the observations reported in Chen et al. (1995). *AEROSOL SCIENCE AND TECHNOLOGY* 27:367–380 (1997) © 1997 American Association for Aerosol Research

INTRODUCTION

Electro spraying (or electrohydrodynamic spraying) is capable of producing monodisperse aerosols in the size range from 5 nm and up to 100 μm when operating in the cone-jet mode (Vonnegut and Neubauer, 1952; Cloupeau and Prunet-Foch, 1989; Fernández de la Mora et al. 1990; Rosell-Llompart et al. 1994; Gomez and Tang,

1991 and 1994; Loscertales and Fernández de la Mora, 1993; Gañán-Calvo et al. 1994; Chen et al. 1995). It can produce submicron aerosols with high concentration, typically on the order of 10^6 particle cm^{-3} or higher depending on the particle size range. In general, aerosols from the electro spray are more monodisperse and with higher concentration than the conventional

method of evaporation-condensation-DMA classification. They have many technological applications, e.g., material synthesis and microcontamination.

There are many factors that can affect the produced droplet size and the emitted current (which in turn could affect the mean particle charge). They include the geometrical configuration and the static pressure of spraying chambers, the conditions of the capillary sprayer (geometry and wettability), the surrounding gas properties, the liquid properties (electrical conductivity, K ; density, ρ ; viscosity, μ ; surface tension, γ ; and dielectric constant, κ), and the liquid feed rate Q . If the system setup and environmental conditions are defined, the remaining factors are the liquid properties and the feed rate.

Scaling laws are needed for characterizing a defined electrospray system. It enables the produced droplet size and the emitted current to be better correlated with all the factors involved, and provides better understanding of the mechanisms involved in the process. Two conclusions can be made from previous studies: (1) the produced droplet size is linearly proportional to $(Q\tau)^{1/3}$ for a specific solution (where τ is the charge relaxation time defined as $\kappa\epsilon_0/K$), and the slope of the straight line is considered to be a function of κ only; (2) the emitted current can be scaled with $(\gamma KQ/\kappa)^{1/2}$ for each solution and again the constant in this scaling is believed to be a function of κ only. Two approaches have been used to obtain the relations between Q and K , i.e., in the studies of Fernández de la Mora and Loscertales (1994) and Gañán-Calvo (1994). Review of these two approaches and the results derived in each approach are given in the next section. It can be seen from the review that the difference between them is on the functional form of the dielectric constant. The purpose of the present study is to investigate these functional forms with experimental data obtained from our electrospray system.

REVIEW OF EXISTING SCALING LAWS FOR ELECTROSPRAYING OF POLAR LIQUIDS IN THE CONE-JET MODE

Two scaling laws are available for electrospraying of polar liquids in the cone-jet mode. The main concepts behind these scaling laws are described below.

The scaling laws provided by de la Mora and Loscertales (1994), and Rosell-Llompart et al. (1994) are based on the dimensional analysis of all the parameters involved in the electrospraying process, namely, electrical conductivity (K), liquid surface tension (γ), liquid absolute viscosity (μ), liquid density (ρ), relative dielectric constant (κ) of liquids, and the feed rate (Q). Three nondimensional parameters (κ , η , and Π_μ) have been identified. The η parameter is defined as $(\rho Q/\gamma\tau)^{1/2}$ and η^2 represents a dimensionless flow rate, where τ is the charge relaxation time and is defined as $\kappa\epsilon_0/K$. The Π_μ parameter is defined as $(\gamma^2\rho\tau)^{1/3}/\mu$ which is inversely proportional to the viscosity. The current emitted from the cone-jet mode can then be scaled as $I/\gamma(\epsilon_0/\rho)^{1/2} = i(\kappa, \eta, \Pi_\mu)$. As a result of current measurements for six different polar liquids, it was concluded that the emitted current was insensitive to liquid viscosity over the range studied $0.022 < \Pi_\mu < 0.25$ and $I/\gamma(\epsilon_0/\rho)^{1/2}$ could be further reduced to $i(\kappa, \eta)$. By analyzing their experimental data, the authors concluded that

$$\frac{I}{\gamma(\epsilon_0/\rho)^{1/2}} = f(\kappa)\eta \quad \text{or} \quad (1a, b)$$

$$I = f(\kappa) \left(\frac{\gamma K Q}{\kappa} \right)^{1/2}.$$

By the same approach for the emitted current, the authors argued that the jet diameter d_j should be scaled first as $d_j/r^* = \Omega(\kappa, \eta, \Pi_\mu)$, where $r^* = (Q\tau)^{1/3}$ is the charge relaxation length. Based on the available experimental evidences, the authors suggested that the entire jet structure

should be independent of Π_μ except for the extreme and $d_j/r^* = \Omega(\kappa, \eta)$. This proposition was confirmed by a few incomplete photographs of ethylene glycol jets ($\Pi_\mu = 1.2$; $\kappa = 38.7$; $0.51 < \eta < 2.0$). Extending the knowledge for the uncharged jet, $D_d/d_j = \alpha_u(J)$ and $J = d_j \gamma \rho / 2 \mu^2$ and assuming similar jet breakup processes between the charged and uncharged conditions, $D_d/d_j = \alpha(J)$ with $J = \Pi_\mu^2 \eta^{2/3} d_j / 2 r^*$ for the charged jet breakup. Consequently, D_d/d_j can be written as $\alpha(\kappa, \eta, \Pi_\mu)$ and D_d/r^* should be a function of κ, η , and Π_μ . Through the droplet size distribution measurements using the aerosizer (API), the authors concluded that it was best to produce droplets in the region where η was close to 1, because only two peaks (main droplets and much smaller satellites) were shown in the measured size spectra when operating in this region. Then Q_{\min} could be derived from this observation as $Q_{\min} = \tau \gamma / \rho = \kappa \epsilon_0 \gamma / \rho K$. Under this condition, D_d (main droplet size) could be scaled with r^* because $\Omega \alpha$ is a weak function of Π_μ and κ was kept constant in their study. Therefore, the effect of dielectric constant on D_d/r^* remained unexplored. In general, the authors proposed that

$$\frac{D_d}{r^*} = G(\kappa) \quad \text{or} \quad D_d = G(\kappa) r^*. \quad (2a, b)$$

Gañán-Calvo (1994) published a scaling law based on the nondimensional analysis of the one dimensional governing equations for electrostatic and flow fields in the near region of the jet emitted from a liquid cone. In the derivation for polar liquids, the characteristic jet radius, r_j , the jet slenderness, $\delta (= r_j/L_j$, where L_j is the characteristic jet length), and the dimensionless current, λ , were chosen as

$$r_j = \left(\frac{Q \epsilon_0 \kappa^{1/2}}{\pi^2 K} \right)^{1/3}; \quad \delta = \frac{\epsilon_0 \gamma}{\rho K Q};$$

$$\lambda = \frac{I \kappa^{1/4}}{(8 Q K \gamma)^{1/2}}. \quad (3a, b, c)$$

If L_j is small as compared to other geometrical lengths, it was assumed that the spraying process is unaffected by the outer boundary conditions and consequently λ could be considered as a constant. Consequently, the author concluded that

$$I = k_I \kappa^{1/4} \left(\frac{\gamma K Q}{\kappa} \right)^{1/2}; \quad (4a, b)$$

$$D_d = k_d \kappa^{-1/6} (Q \tau)^{1/3}.$$

By taking the argument that the minimum flow rate occurred at the condition that the electrical relaxation time τ is in the order of the hydrodynamic residence time of the liquid in the jet L_{jj}^2/Q , the condition $\kappa^{1/2} \delta \sim 1$ was concluded and $Q_{\min} \sim \kappa^{1/2} \epsilon_0 \gamma / \rho K$. The scaling law proposed by Gañán-Calvo (1994) was further confirmed in the work of Gañán-Calvo et al. (1994) using the data measured by the PDA (phase doppler anemometer) and the values of k_I and k_d were found to be 6.46 and 1.66, respectively.

The comparison of these two scaling laws derived from two different arguments is summarized in Table 1. Both scaling laws give D_d , I , and Q_{\min} the same power function relation with the parameters K , γ , ρ , and Q . The major difference is in the functional forms of κ (dielectric constant). The main objective of this study is therefore to clarify the functional forms of κ in the scaling laws with our electrospraying setup.

EXPERIMENTAL SETUP AND TEST SOLUTIONS

The experimental setup, shown schematically in Fig. 1, is the same as that described in our previous paper (Chen et al. 1995). In this study, the CO_2 sheath flow was used only when pure water was used as the solvent because of its high surface tension and the resulting high voltage needed for electrospraying. The compressed air flow was fixed at 2.0 lpm^{-1} . The produced droplets were quickly transported into the neutralization chamber which contained two 5 mCi ^{210}Po radioactive sources mounted on the

TABLE 1. Comparison of the Scaling Laws Proposed by Fernández de la Mora et al. (1994) and Gañán-Calvo et al. (1994)

D_d :	produced droplet size	Q :	feed flow rate
I :	current emitted	\bar{K} :	liquid electrical conductivity
τ :	charge relaxation time ($\kappa\epsilon_0/K$)	κ :	dielectric constant
γ :	surface tension	k_I, k_d :	1.66, 6.46 (constants)
ρ :	liquid density	Q_{\min} :	minimum feeding flow rate
Fernández de la Mora (1994)		Gañán-Calvo (1994)	
D_d	$G(\kappa)(Q\tau)^{1/3}$	$k_d\kappa^{-1/6}(Q\tau)^{1/3}$	
I	$f(\kappa)\left(\frac{\gamma K Q}{\kappa}\right)^{1/2}$	$k_I\kappa^{1/4}\left(\frac{\gamma K Q}{\kappa}\right)^{1/2}$	
Q_{\min}	$\frac{\kappa\epsilon_0\gamma}{\rho K}$	$\frac{\kappa^{1/2}\epsilon_0\gamma}{\rho K}$	

opposite walls of the chamber. The bipolar ions from the radioactive sources were capable of reducing the charge level on the produced droplets to the equilibrium charge distribution. In the neutralization chamber, the size of the droplets were further reduced by evaporation. The residue particle size distributions were then measured by the scanning mobility particle sizer (SMPS) which consisted of a TSI 3071 differential mobility analyzer (DMA) and a TSI 3025A ultrafine condensation particle counter (UCPC). The aerosol and sheath flow rates used for the DMA were 2.0 and 20.0 l pm⁻¹, respectively, and the UCPC was operated at high flow rate mode of 1.5 l m⁻¹.

Eight different solvents with dielectric constants ranging from 12.5 to 182 were chosen in this study. The purity of all the solvents was higher than 99.5% by volume. Their properties are listed in Table 2. Two properties were common among the selected solvents: (1) all solvents were miscible (or slightly miscible) with water. This property allowed us to use them in the preparation of the 0.091% sucrose solutions easily. During preparation, 1 cm³ solution of 10% (by volume) sucrose in ultrapure water was mixed with each 100 cm³ solvent. The electrical conductivity of the final solutions was controlled by the adding a trace amount of nitric acid; (2) the boiling

points of the solvents were sufficiently low so that they could evaporate from the solution droplets. It allows us to correctly measure the size of the residue sucrose particles without error from possible unevaporated solvents.

The electrical conductivity of the final solutions were measured by a Cole-Palmer digital conductivity meter. Table 3 lists the electrical conductivity of all the solutions sprayed. The relative errors in measuring the electrical conductivity of the solutions are no more than 2%. Note that there is no test solution with electrical conductivity less than 200 μΩ⁻¹ cm⁻¹ for formamide and *n*-methyl formamide. It is because the original solvents had electrical conductivity of 270 μΩ⁻¹ cm⁻¹ for formamide and 419 μΩ⁻¹ cm⁻¹ for *n*-methyl formamide. In order to make sure that there were no residue particles formed from the impurity of the original solvents, solutions with the same electrical conductivity but without sucrose solute were prepared first using the same buffer solutions. Then, the solutions were electrosprayed and the size distributions were measured. The background concentration was always less than 10 particles cm⁻³ compared to 10⁶ particles cm³ for the sucrose residue particles, indicating that the impurity was negligible. The surface tension was measured by a Fisher Surface

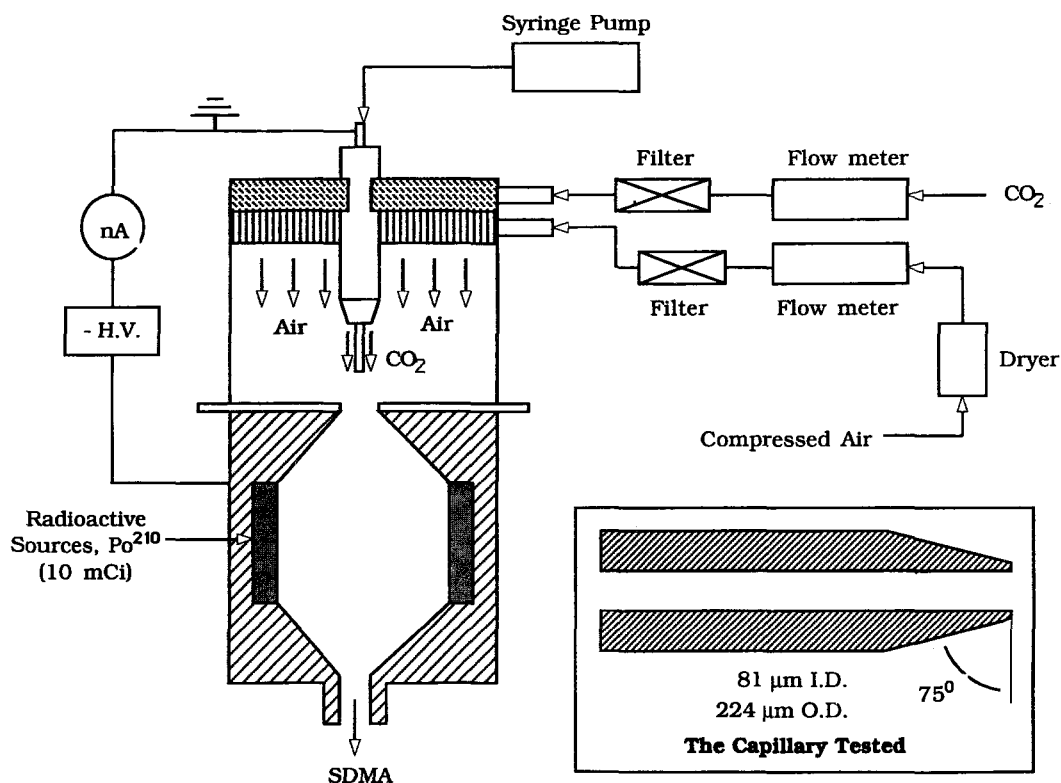


FIGURE 1. Schematic of experimental setup of electrospray unit.

Tensiometer (Model 20). The relative error was found to be less than 2% in comparison with the values listed in Table 2. We were unable to check directly the dielectric constants of the final solutions. However, with the impurity being less than 1% by volume for the final solutions, they should be close to the values listed in Table 2.

In order to test the scaling laws over a wider particle size range, the minimum and the maximum liquid feed rates for each test solution were explored. For each run listed in Table 3, the liquid feed rate was changed and the size distribution was measured for each change in order to locate the minimum and maximum. The maximum feed rate was defined as the flow rate before the start of jet bifurcation as indicated by Rosell-Llompарт et al. (1994). The mini-

mum feed rate was limited by the liquid pump oscillation and the evaporation rate of test solutions. The relative error of liquid feed flow rates were kept no more than 5%. Under this circumstance, the determination of minimum feed rates of solvents with high vapor pressure, e.g., alcohol, 60% water + 40% alcohol, and 85% water + 15% alcohol, were difficult to define due to the high evaporation rate.

RESULTS AND DISCUSSION

The main objective of the study is to investigate the effect of dielectric constants on the scaling laws for the produced droplet size and emitted current in the cone-jet mode of the electrospray process. The following subsections will address this effect and other experimental observations. Some

TABLE 2. Properties of Test Solvents at 25°C in this Study^a

Solvent	γ : solvent surface tension κ : solvent dielectric constant		μ : solvent viscosity ρ : solvent density		
	γ (dyne/cm)	κ	μ (cP)	ρ (g/cm ³)	b.p. (°C)
Benzyl alcohol	39.45	12.51	5.69	1.04127	205.45
Alcohol	21.90	24.55	1.0826	0.78493	78.30
Ethylene glycol	47.37	37.70	17.87	1.11	197.54
60% water + 40% alcohol	31.1 ^c	41.28 ^d	—	—	—
85% water + 15% alcohol	44.0 ^c	60.89 ^d	—	—	—
Water	71.81	78.36	0.89025	0.99705	100.00
Formamide	58.15	111 ^b	3.302	1.12915	210.5
n-methyl formamide	39.46	182.4	1.65	0.9988	180–185

^aData (at 25°C) taken from Riddick, J. A., et al. "Organic solvents: Physical properties and methods of purification," 4th ed., 1986.
^bat 20°C
^cAdamson, A. W., "Physical chemistry of surfaces," 5th ed., 1994.
^dMoriyoshi et al. "Static dielectric constants of water + ethanol and water + 2-methyl-2-propanol mixtures from 0.1 to 300 MPa at 298.15 K," *J. Chem. Eng. Data*, (1990), 35:p. 17–20.

remarks on the prediction of the minimum and maximum liquid feed rates will be discussed based on our experimental results.

Produced Droplet Size

Figure 2 shows the produced droplet size as a function of $(Q\tau)^{1/3} = (r^* = (Q\kappa\epsilon_0/K)^{1/3})$ for each test solvent. Note that the relative error associated with r^* is no more than 2%. It is evident that for each solvent the droplet size is proportional to r^* before jet bifurcation in the cone-jet mode. This observation is consistent with previous results of other investigators when their electro-spray units were well functioned. In order to obtain the functional form of $G(\kappa)$ in the scaling law given in Eq. 2, the slope of

the straight line fit of the data using the least-squares regression analysis for each solvent is plotted against its dielectric constant. The result is shown in Fig. 3. The criteria of 95% confidence interval is used to obtain the error bars shown in the figure. Included in the same figure is the equation obtained by Gañán-Calvo et al. (1994). The scaling law of Gañán-Calvo approaches our experimental data in the high dielectric constant range. Relatively good agreement is observed when the dielectric constant is higher than 80. However, detectable deviation is observed for solvents with low dielectric constants.
The best fit of our experiments data using the least-squares regression analysis is also shown in the figure. The fitted function

TABLE 3. Measured Electrical Conductivity, K, of Different Solutions

(Unit: $\mu\Omega^{-1}/\text{cm}$)					
	Run#1	Run#2	Run#3	Run#4	Run#5
Benzyl alcohol	8.5	23.8	68.0	153	293
Alcohol	93.0	189	300	414	
Ethylene glycol	70.8	173	368	726	
60% water + 40% alcohol	41.0	135	459		
85% water + 15% alcohol	43.0	86.0	234	446	
Water	57.0	109	227	496	
Formamide	270	307	535		
n-methyl formamide	419	585	890		

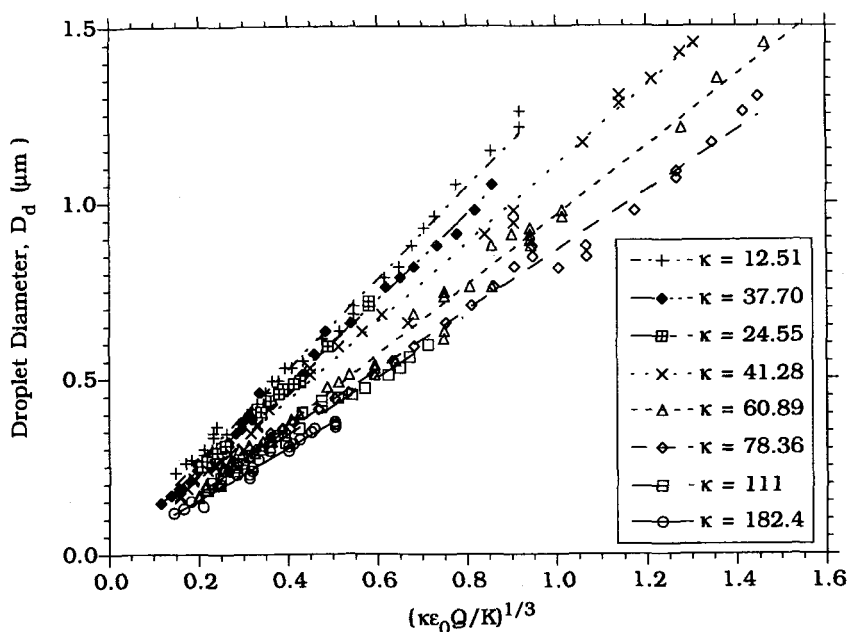


FIGURE 2. It shows the linear functional relationship between produced droplet size, D_d , and $r^* = (\tau Q)^{1/3}$, where $\tau = K \epsilon_0 / K$ (r^* : charge relaxation length) for each test solvent.

is in the form of $G(\kappa) = 10.87\kappa^{-6/5} + 4.08\kappa^{-1/3}$. Consequently, the jet diameter should be scaled as $G(\kappa)(Q\tau)^{1/3}$ if we accept the experimental observations of previous investigators (e.g., Jones and Thong, 1971; Cloupeau and Prunet-Forch, 1989; Gomez and Tang, 1991; Gomez, 1993). They found that D_d/d_j is almost a constant except in some extreme conditions which can be extrapolated to our relatively small electrospray setup. The present setup gives stronger effect of dielectric constant on the produced droplet size than that predicted by Gañán-Calvo (1994) in the low dielectric constant range. It indicates that his model which is purely based on the jet is not adequate to describe the cone-jet mode completely. During the experiment we observed that the jet length was on the order of the capillary size (i.d. = 81 μm) with our microscopic system when the liquid feed rate was close to the maximum. This observation contradicts the assumption made by

Gañán-Calvo (1994) that the process is localized (independent of outer boundary conditions) if the characteristic length L_j is much smaller than other geometrical dimensions in the setup. Our study clearly shows that the existence of the cone needs to be considered. Further, the dielectric constant seems to have relatively small influence on the droplet sizes when high dielectric constant solvents are sprayed.

In Fig. 3, the viscosity effect on the produced droplet size is seen to be minor for the case of ethylene glycol. The effect can be better described using Π_μ given by Fernández de la Mora et al. (1994). The value for ethylene glycol ranges from 0.12 to 0.27, while no obvious viscosity effect is shown in the case of benzyl alcohol with its Π_μ value ranging from 0.32 to 0.75. Consequently, the inviscid asymptote of the jet breakup appears to occur when Π_μ value is greater than 0.3. This observation is consistent with the data presented by Rosell-

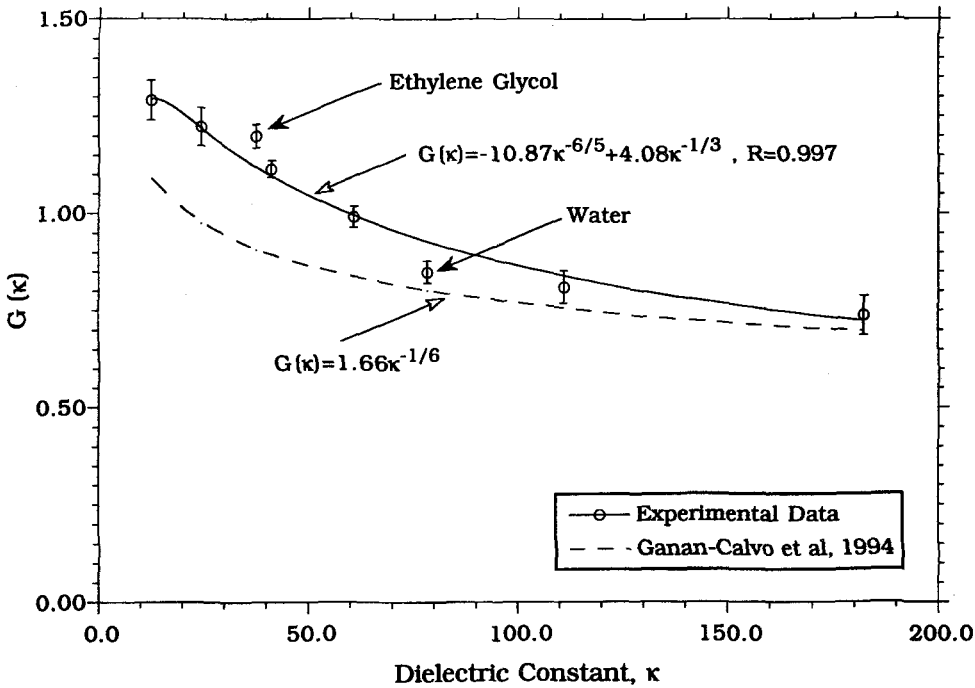


FIGURE 3. Comparison of the experimental $G(\kappa)$ with that proposed by Gañán-Calvo et al. (1994).

Llompart et al. (1994). They observed that Π_μ should be greater than 0.1 for the inviscid asymptote of the jet breakup by electro-spraying triethylene glycol (3EG) and tetraethylene glycol (4EG). The difference between these two values could be attributed to the different aerosol sizing instruments used in the two studies.

Spraying Current

Figure 4 shows the emitted current, I , as a function of $(\gamma KQ/\kappa)^{1/2}$. The linear correlation between I and $(\gamma KQ/\kappa)^{1/2}$ for each solvent is consistent with the previous studies (e.g., Cloupeau and Prunet-Foch, 1989; Fernández de la Mora et al., 1994; Gañán-Calvo et al., 1994; Chen et al., 1995). It is evident that the emitted current can be linearly correlated with $(KQ)^{1/2}$ for each solvent. Note that the relative error associated with $(\gamma KQ/\kappa)^{1/2}$ is less than 3% and

the relative error in measuring emitted current is less than 4%.

To identify the functional form of $f(\kappa)$ in the scaling law shown in Table 1, the slope of the straight line fit to the data using the least-squares regression analysis for each solvent is plotted against its dielectric constant, κ . The result is shown in Fig. 5. The error bars shown in the figure are obtained using the criteria of 95% confidence interval. In the same plot, the curves representing the equation given by Gañán-Calvo et al. (1994) and the experimental data of Fernández de la Mora et al. (1994) are included. The trend of the experimental data are closer to the data of Fernández de la Mora et al. (1994) in the low dielectric constant range. Good agreement is obtained for the case of benzyl alcohol. When compared with the ones estimated by Gañán-Calvo et al. (1994), larger deviation is detected in the entire dielectric constant range tested.

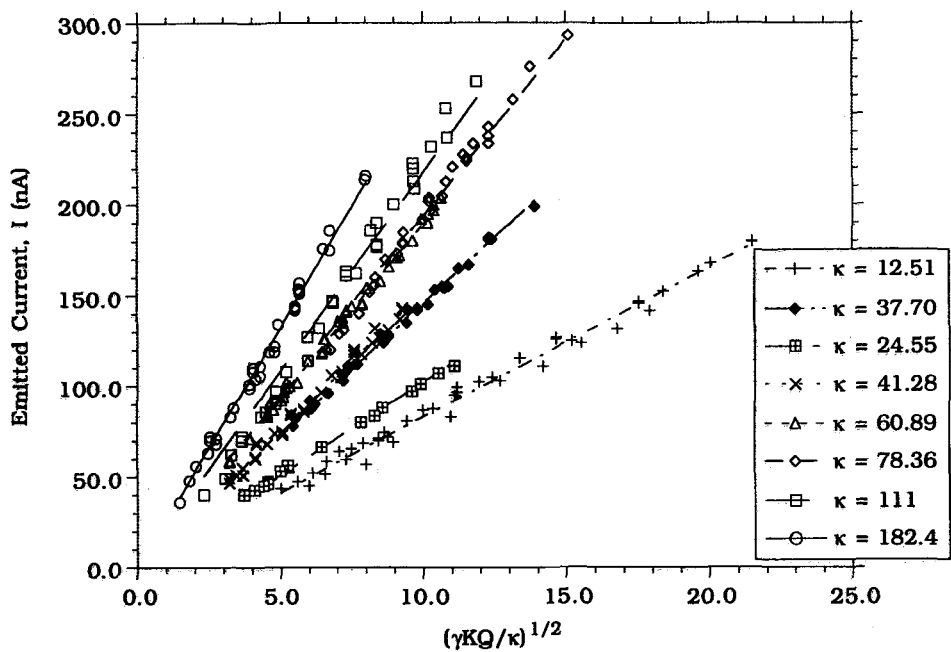


FIGURE 4. It shows the linear correlation relation between emitted current, I , and the nondimensional parameter $(\gamma K Q / \kappa)^{1/2}$ for each test solvent.

In the work of Fernández de la Mora et al. (1994), $f(\kappa)$ approaches a constant value as κ increases. Our experimental data show a gradual increase of $f(\kappa)$ in the entire κ range tested. The difference between the two observations could be in part due to the additives which are used to control the electrical conductivity of the solutions. In principle, the total current consists of convective current by the fluid flow and conductive current by ions in solutions. The former is governed by the physical process in the electrospray. The latter is dependent on the additives which provide ions in the solutions, and on the electric field. Different additives contribute different ion species in the solutions, and their ion mobilities could be substantially different from each others even though the solvent is kept

the same. For example, H^+ mobility is eight times higher than that of Li^+ in pure water. In our work, NH_4^+ is used, which provides H^+ and NO_3^- in solutions. $LiCl$ is selected as the additive by Fernández de la Mora et al. (1994), which gives Li^+ and Cl^- in the solutions. Based on the order-of-magnitude comparison, the total current contributed by different ion species could vary from 25% for H^+ to 15% for Li^+ for the cases of water. However, this effect cannot explain the observations of higher currents for ethylene glycol and lower currents in high dielectric constant range by Fernández de la Mora et al. (1994). Large deviation between our experimental data and the equation of Gañán-Calvo et al. (1994) is observed for the entire κ range. The difference may be partially due to (1) the inapplicable assumption made in the theory of Gañán-Calvo (1994) (dis-

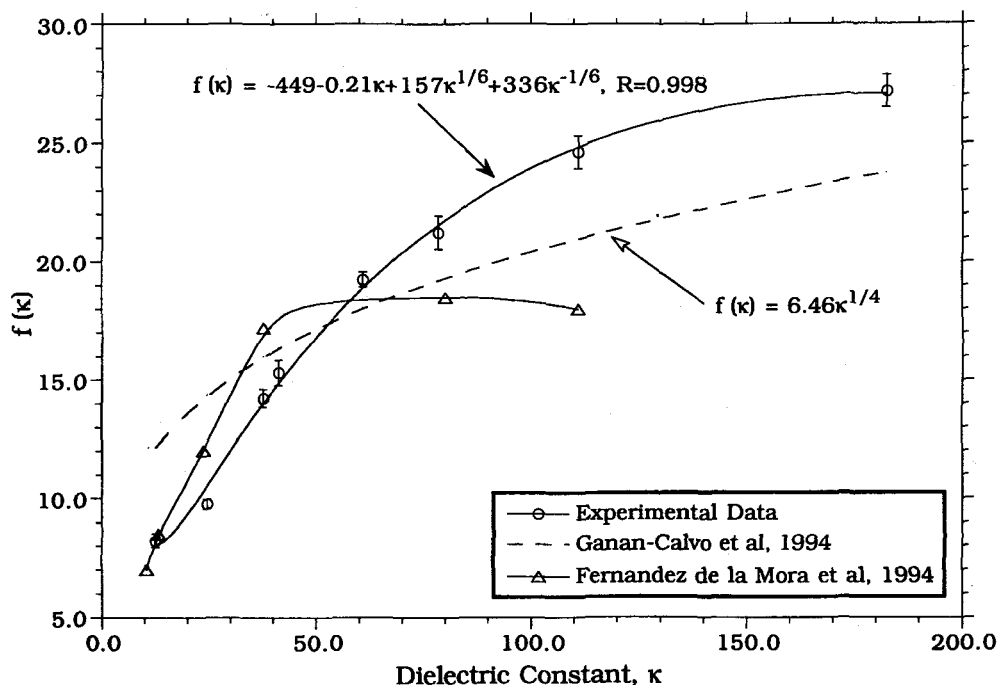


FIGURE 5. Comparison of the experimental $f(k)$ with the experimental data from Fernández de la Mora et al. (1994) and that proposed by Ganán-Calvo et al. (1994).

cussed in the previous section); and (2) the different additives used to adjust the electrical conductivity of test solutions.

The best fit of our data using the least-square regression analysis is in the functional form of $f(\kappa) = -449 - 0.21\kappa + 157\kappa^{1/6} + 336\kappa^{-1/6}$. The functional form is only valid in the dielectric constant range tested with nitric acid as the additive. The above discussion shows that the fitted equation may not be the same if different additives are used to control the electrical conductivity of solutions. To obtain consistent data in one study, the same additive should be used in all solutions. Further, it is important to consider incorporating the ion mobility effect in the scaling laws.

Finally, although we observed the viscosity effect on the produced droplet size, there was no detectable viscosity effect on the emitted current for the cases of ethylene glycol. The Π_μ value in our work is in the range of 0.12–10. The result is consistent

with what was observed by Fernández de la Mora et al. (1994), which showed no viscosity effect in the wider Π_μ range (from 0.022 to 12).

Some Remarks on the Operating Envelope (Minimum and Maximum Liquid Flow Rates)

For characterizing the performance of the electrospray system for producing monodisperse aerosol, it is necessary to know its operating envelope. In general, there are many factors which could affect the operating envelope of a defined electrospray setup. They include the geometry of the spray chamber, the capillary sprayer (geometry and wettability), the arrangement of the electrodes, the surrounding gases and pressure level, the liquid feed rate, the electrical conductivity of solutions, the evaporation rate of solutions, among others. However, if all the external factors are kept

the same, the operating envelope should be based primarily on the properties of solutions and the liquid feed rate.

In our previous work (Chen et al., 1995), we obtained the operating envelope (which was shown in Fig. 9 of that paper) of our setup when spraying aqueous solutions. The envelope was within the shaded area of Q vs. K plot. For the minimum flow rate, KQ product was approximately kept constant. Two criteria based on experimental observations were proposed (described in Section 2) to calculate the minimum feed flow rate. The last row in Table 1 shows that the difference between them is again on the dielectric constant, κ . The common feature is that KQ should be held constant for each specified solvent. We will try to clarify these two criteria in the following discussion.

A similar trend of KQ being a constant for the maximum flow rate condition was also observed in Chen et al. (1995). There was no explanation on this phenomenon by

previous researchers. In this section we intend to give its explanation and to provide a way to estimate the maximum feed rate.

On the Minimum Liquid Feed Rate. Figure 6 gives D_d/r^* as a function of η ($= (Q\rho K/\gamma\kappa\epsilon_0)^{1/2}$), similar to that of Rosell-Llompart et al. (1994). The data are shown to scatter around a constant value of D_d/r^* for each solvent. The first point (left-hand most point) for each group of κ value data represents η_{\min} . For low dielectric constant solvents, i.e., $\kappa < 38$, η_{\min} is close to 1.0. For high dielectric constant solvents, e.g., for formamide and *n*-methyl formamide, η_{\min} can be as low as 0.4. Using the criteria ($\eta_{\min} \sim 1.0$) given by Rosell-Llompart et al. (1994), the estimated minimum flow rate can be higher than the actual rate by a factor of 6. It seems reasonable to use the criteria given by Gañán-Calvo (1994) for high dielectric constant, because his Q_{\min} estimation is always smaller than that given by Rosell-Llompart

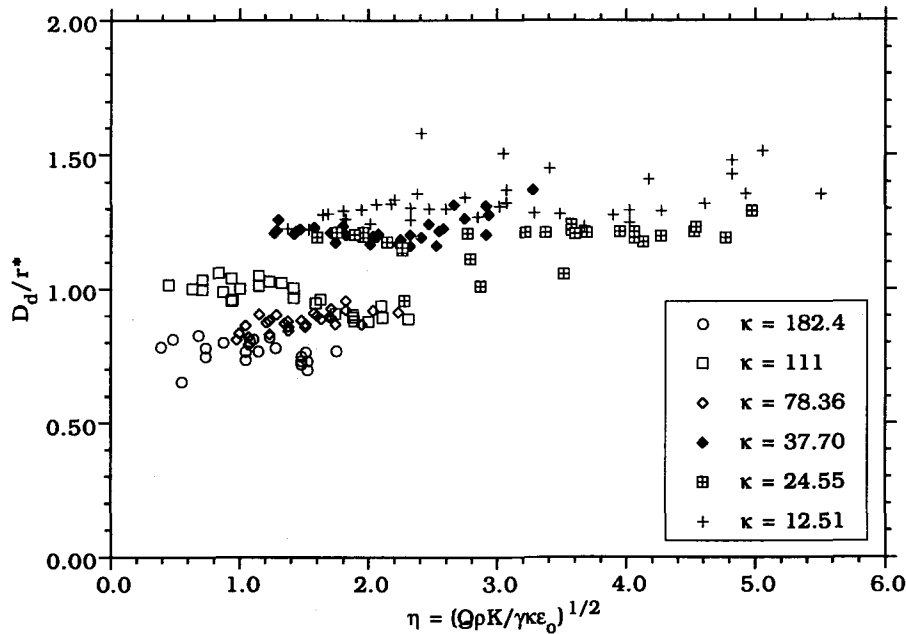


FIGURE 6. Normalized droplet size (with the charge relaxation length, r^*) as a function of the nondimensional parameter.

et al. (1994) by a factor of $\kappa^{1/2}$ according to Table 1. However, its usage tends to overpredict the minimum flow rate for the solvents with low dielectric constant.

On the Maximum Liquid Flow Rate. As was discussed previously, we observed that KQ_{\max} is nearly constant for spraying aqueous solutions. This was not discussed by previous researchers. In order to investigate the produced droplet size in the region close to the maximum feed rate, we plot D_d/R^* vs. η in Fig. 7. R^* is the inertial characteristic length derived from the balance between the dynamic pressure ($\rho u^2/2$) associated with the flow velocity, u , at the cone (assumed to be a sink flow; $u \sim Q^2/\gamma$), and the capillary pressure (of the order of γ/r). Taking R^* as the characteristic length for high liquid feed rate cases was first discussed by Fernández de la Mora et al. (1990, 1994) and Rosell-Llompart et al. (1994). From the plot, it can be clearly shown that D_d/R^* approaches one con-

stant ($\sim 0.5 = k_c$) as η is increased for all test solvents. A similar constant value was obtained in Rosell-Llompart et al. (1994) for electrospraying relatively high viscosity solvents (3GE and 4GE). This results in $D_d = k_c R^*$ for the maximum flow rate condition. Since D_d could be represented as $G(\kappa)r^*$ (in Section 4), the following equation can be derived,

$$Q_{\max} K = \left(\frac{G(\kappa)}{k_c} \right)^3 \left(\frac{\kappa \epsilon_0 \gamma}{\rho} \right). \quad (5)$$

From this derivation, the observation that KQ holds constant at the maximum flow rate condition for spraying aqueous solutions (Chen et al., 1995) is clearly demonstrated.

This equation implies that there are two characteristic lengths competing in the electrospraying process: the charge relaxation length, $r^* = (Q\tau)^{1/3}$, the inertial length, $R^* = (\rho Q^2/\gamma)^{1/3}$. For low liquid

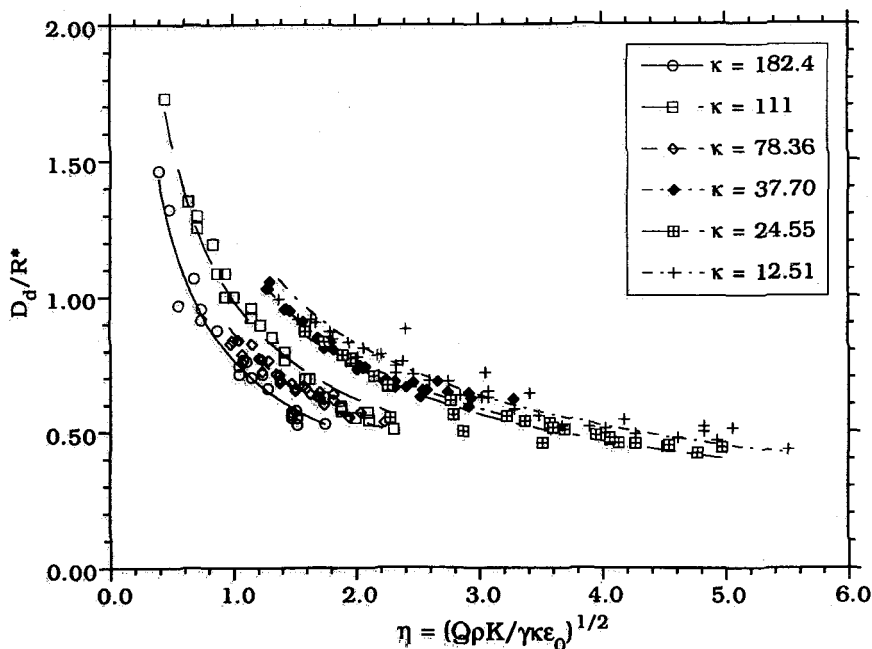


FIGURE 7. Normalized droplet size (with the inertial length, $R^* = (\rho Q^2/\gamma)^{1/3}$) as a function of the nondimensional parameter, η (defined as $(\rho Q K / \gamma \kappa \epsilon_0)^{1/2}$).

feed rate, the jet diameter emitted from the liquid cone could be scaled with r^* because it is the dominating characteristic length and also for the produced droplet size. As the flow rate increases, both the inertial length ($\sim Q^{2/3}$) and the charge relaxation length ($\sim Q_{1/3}$) increase. The increment of the inertial length is more than that of the charge relaxation length. This implies that the inertia effect is becoming dominant as the flow rate increases. When the inertia length is on the order of charge relaxation length (about a factor of two compared to the charge relaxation length), jet bifurcation is likely to occur. As a result, size spectra with multiple modes are produced.

Although Eq. 4 can be used to predict Q_{\max} , it only provides an approximate answer. Table 4 shows the comparison of the predicted and measured $Q_{\max}K$ values. The difference is within 20%. The agreement is reasonable. For precise estimation of Q_{\max} , more understanding on the electrospray process is needed.

CONCLUSIONS

In this study, the effect of liquid dielectric constant on existing scaling laws for the electrospraying process were investigated experimentally. Eight different solvents with dielectric constants, κ , ranging from 12.51 to 182.4 were tested. The results show that (1) the produced droplet size, D_d , for the

present system could be represented as $G(\kappa)r^*$ with $G(\kappa) = -10.9\kappa^{-6/5} + 4.08\kappa^{-1/3}$, $r^* = (Q\tau)^{1/3}$, and $\tau = \kappa\epsilon_0/K$. For solvents with high dielectric constants, the experimental data are in good agreement with the scaling laws ($G(\kappa) = 1.66\kappa^{-1/6}$) proposed by Gañán-Calvo et al. (1994). One of possible explanations for the deviation in low dielectric constant cases may be that Gañán-Calvo's assumption of the characteristic length of the jet emitted from the cone tip always being small compared to the geometrical lengths may not hold for our system. During our experiment it was observed that the length of the jet could be on the order of the capillary diameter when the liquid feed rate is close to the maximum; (2) the emitted current, I , could be formulated by $f(\kappa)(\gamma KQ/\kappa)^{1/2}$ with $f(\kappa) = -449 - 0.21\kappa + 157\kappa^{1/6} + 336\kappa^{-1/6}$, where γ is the surface tension of solutions. The trend of the experimental data is in closer agreement to those given by Fernández de la Mora et al. (1994) for low dielectric constant. Good agreement was only obtained for the case of benzyl alcohol. The deviation in the high dielectric constant range could possibly be explained by the different additives used (HNO_3 in our work and LiCl in their work) to control the electrical conductivity of solutions. When comparing with the equation, $f(\kappa) = 6.46\kappa^{1/4}$, provided by Gañán-Calvo et al. (1994), a larger deviation was observed in the entire dielectric constant range tested. The difference could be partially attributed to the inapplicable assumption in characteristic length described earlier and the role of ion drifting current in the total emitted current.

In constructing the operating envelope, one should exercise some cautions if any one of the criteria for minimum liquid feed rate (listed in Table 1) is used. If the criterion proposed by Rosell-Llompart et al. (1994) for high dielectric constant solvents is used, it could result in a factor of 6 higher feed rate than the measured values. The criterion introduced by Gañán-Calvo (1994) could possibly overestimate the minimum flow rate by a factor of 6 for low

TABLE 4. Comparison of $Q_{\max}K$ for Different Solvents

(Units Q : $\mu\text{l min}^{-1}$, K : $\mu\Omega^{-1}\text{cm}^{-1}$)		
Solvent	Calculated (Eq. 4)	Experiment ^a
Benzyl alcohol	50	61
Alcohol	48	55
Ethylene glycol	88	79
Water	200	170
Formamide	160	150
<i>n</i> -methyl formamide	150	140

(Q_{\max} : the max. liquid feed rate; K : electrical conductivity of solutions.)

^aListed experimental data are the average of all the data from the runs with the same solvent.

dielectric constant solvents. For the maximum liquid feed rate, Eq. 5 is derived in the present study. The formula explains the observation in Chen et al. (1995) that $Q_{\max}K$ is approximately held constant when electro spraying aqueous solutions.

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