

Electrospray Onset Study of Water-Ethanol Mixtures

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Abstract—The electrospray ionization (ESI) method is widely used in the analysis of biological molecules. The stable cone regime spray is usually obtained by the addition to the electrosprayed dipolar fluid of methanol or ethanol with the role of reducing the fluid surface tension. We investigate the spray onset voltages of water-ethanol mixtures of various concentrations starting from distilled water to pure ethanol. Positive or negative DC is applied separately in our measurements. The experimental setup allows for the study of nozzle-counter electrode gaps of up to 50 cm. Significant variations in the spray onset are observed and analyzed. Onset dependence is correlated to concentrations of water-ethanol binary mixtures. Smith's formula is assessed for the tested mixtures. The results of the study may be instrumental to electrospray electrode design and spray control.

I. INTRODUCTION

An electrospray can be generated by applying high voltage to a confined polar fluid having a small opening (often provided by a capillary nozzle). This method ensures liquid atomization by means of electrical forces. The electrospray has advantages over other mechanical means for spray generation. The droplet size of an ES can range from a few nm to the μm range. Moreover, size distribution is fairly constant and is controlled by the magnitude of the HV applied and the ES flow rate. In addition, the charged droplets better adhere to the sprayed surfaces and can be guided by means of electric field. ES is also a resourceful method for nano and micro particle production [1] as well as a highly uniform thin film deposition procedure [2].

The ES does not start below a certain voltage. Our experience shows that nozzles with smaller diameters have better defined ES onset than those with larger diameters, when ES inception is more of a process than a well-defined event (ES inception can be described better by a voltage range as opposed to a precise voltage). Also, smaller gaps between the capillary nozzle and the counter electrode will have more precisely defined voltage. ES onset is normally associated with a jump in ES current [3] (usually in the nanoampere

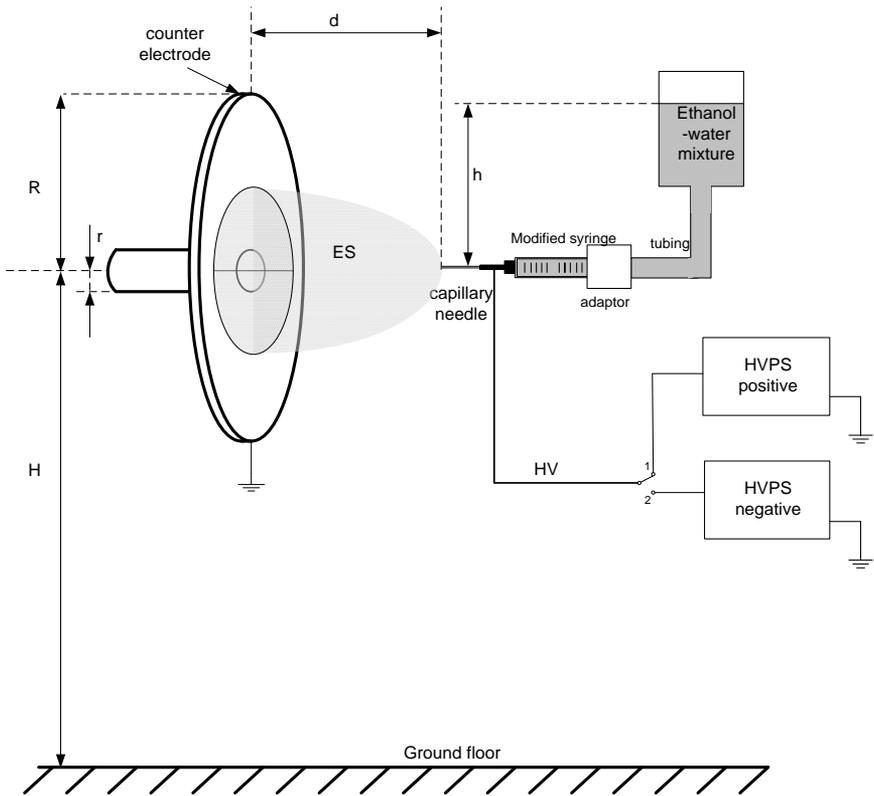


Fig. 1 Schematic of the experimental setup

range for micrometer size capillaries [4]). The frequency of the emitted droplets from the dripping regime to a continuous spray appeared in our experiments to be characterized by the same pattern [5]. Various ES regimes are reported in the literature [6-8]. In our measurements, ES onset voltage refers particularly to the dripping mode, which becomes visibly indistinguishable from the continuous emission of water droplets. The cone-spray is the most heavily investigated ES regime, particularly due to its suitability for ion generation in conjunction with mass spectrometry. However, other applications may involve larger tip-to-plate gaps than those employed for the cone-jet regime. Ethanol and methanol are commonly used for reducing the surface tension of other fluids in order to obtain the ES stable-cone regime particularly important for the ESI technique. In this study, we aim at characterizing the ESs of water-ethanol binary mixtures in terms of their dependencies on rather large tip-to-plate gaps, surface tension, and concentrations.

II. EXPERIMENTAL SETUP AND PROCEDURE

Fig. 1 shows the schematics of the experimental setup. The capillary nozzle is a blunt needle from Small Parts Inc. (p/n NE-271PL-10, S/S needle w/luer hub) 26G $\frac{1}{2}$ " (ID 0.26 mm, OD 0.46 mm). The needle is attached to a 3 mL BD Luer-Lok™ modified syringe

with positive plunger rod stop and tapered plunger rod design. The bottom part of the syringe was removed. Vinyl tubing (3/8" ID, 1/2" OD) was used to connect the syringe and the plastic fluid container on its central bottom side. A 14.5 cm long Polytetrafluoroethylene (Teflon) syringe adaptor holds the syringe to one end of a 1.5 m long rectangular rigid wood element (100 cm x 7cm x 2 cm). The syringe system can slide horizontally on a wood table equipped with a ruler for distance measurements. The system is 0.81 m above the laboratory floor. The counter electrode (ground electrode) is a stainless steel metal plate 35.56 cm (14") in diameter, 2.54 cm (1") center hole, 1.9 cm thick, which was axially held in horizontal position, coaxial with the needle, 0.81 m above the floor. The nozzle tip – counter-electrode distance was adjusted by translating the syringe system coaxially to the plate.

Our measurements were performed with the circular plate grounded and the nozzle/blunt needle connected either to the positive (Spellman HVPS, RHR40PN60, positive 0-40 kV 1.5 mA) or the negative (Glassman HVPS, 0-10 kV 30mA, PS/ER10R30-DM22) polarity of the HVPS.

In order to ensure consistency of voltage readings from the two power supplies a precision high voltage divider EMCO V1G (1000:1 voltage ratio) was used. Water-ethanol mixtures of various concentrations were prepared using distilled water and 200 proof ethanol obtained from Sigma-Aldrich (HPLC/spectrophotometric grade ethanol, Batch # 02496kk, Lot ID 09H07).

In all experiments, an unforced flow rate was ensured by the constant differential hydrostatic pressure (water-ethanol binary mixtures). The water-ethanol mixture reservoir is 9 cm in diameter and was connected to the modified syringe by a vinyl tube. The initial ethanol (100%) level above the needle tip was 10.2 cm and this hydrostatic pressure was maintained constant throughout the measurements.

A. Procedure

The distance between nozzle tip and counter electrode was set successively to 0, 1, 2, 4, 6, 8, 10, 15, 20, 25, 30, 35, 40, 45, and 50 cm for each tested water-ethanol mixtures. The onset voltage of the ES was determined for the positive and negative polarities applied to the nozzle. The onset voltage is defined in our paper as the voltage where there is a switch from the dripping mode to a continuous ES jet.

The ethanol concentrations (by volume) prepared were 0%, 5%, 10%, 20%, 40%, 60%, 80%, and 100%. Equivalent levels of fluid mixtures were calculated for each ethanol concentration employed in the experiments so that the 10.2 cm ethanol hydrostatic pressure at 25°C (785.7 N/m²) should remain constant. Calculation of the equivalent fluid height for a given ethanol concentration was performed starting from the observation that

$$\rho_1gh = \rho_1gh_1 + \rho_2gh_2 \quad (1)$$

where g is the gravitational acceleration, ρ_1 stands for specific mass of ethanol, ρ_2 stands for specific mass of water (at a given temperature $t^\circ\text{C}$), h stands for the initial ethanol level above the needle tip, h_1 and h_2 stand for ethanol and water, respectively, forming the equivalent fluid level above the needle tip at a given ethanol concentration c . The volume concentration of ethanol in water can be written as

$$c = \frac{Ah_1}{A(h_1 + h_2)} = \frac{h_1}{h_1 + h_2} \tag{2}$$

where A would be the cross-section area of a cylindrical volume. Solving for the equivalent fluid height ($h_e = h_1 + h_2$) gives

$$h_e = \frac{h}{c(1 - r_{we}) + r_{we}} \tag{3}$$

With $r_{we} = \frac{\rho_2}{\rho_1}$. Given the 25°C temperature in the lab the equivalent liquid column heights used are plotted in Fig. 2.

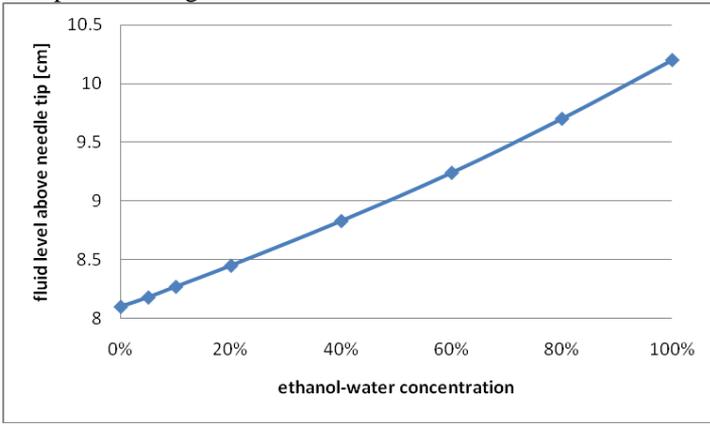


Fig. 2 Equivalent water-ethanol mixture’s height above the nozzle tip as a function of ethanol concentration (data points are the actual values used for measurements)

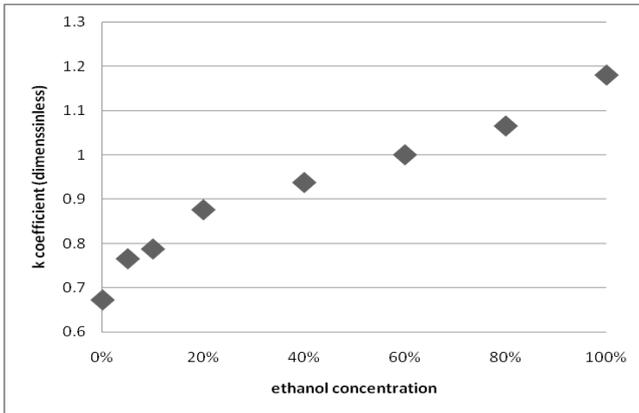


Fig. 3 Variation of the k coefficient with ethanol concentration

III. EXPERIMENTAL RESULTS AND ANALYSIS

ES onset voltage was recorded and plotted in Fig. 4 for all the studied water-ethanol mixtures. The nozzle-counter-electrode distance was measured in cm (horizontal axis) while the onset voltage was measured in kV.

A few characteristics of the experimental data appear clearly from the chart:

1. Onset voltages are lower for shorter nozzle-counter-electrode distances.
2. There are at least two distinct regions for each voltage-distance curve: a) one of sharp variation of onset voltage with distance (near the plate); b) one almost flat where only small variations of voltage with distance are observed.
3. The pure ethanol (100%) curve is the lowest (meaning that onset values are the lowest) while the pure water curve is the highest (meaning that it has the highest onset voltages).
4. For a given distance, the positive ES onset is always slightly lower than for the negative polarity, irrespective of ethanol concentration.
5. Ethanol concentrations up to 10% shift onset curves the most.

The high onset voltage of water is in agreement with the known fact that water has a relatively high surface tension [9]. Smith relation [10- 12] also predicts such a behavior:

$$V_{on} = A \left(\frac{\gamma \cdot \cos\theta \cdot r_c}{\epsilon_0} \right)^{1/2} \ln \frac{4d}{r_c} \quad (4)$$

(A is a constant, γ is the surface tension of the fluid, θ 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).

Given the apparent similar shape of the onset voltage – nozzle tip distance at different ethanol concentrations, an attempt was made to overlap the curves by scaling in the following way:

$$k_i V_{on}(c_i, d_{jc}) \approx V_{on}(c_{60\%}, d_{j60\%}) \quad (5)$$

where c_i is the ethanol concentration in water, d_j is the nozzle tip distance to the counter-electrode, $c_{60\%}$ is the 60% ethanol concentration, and k_i is a proportionality constant chosen so that it minimizes

$$S_i = \sum_j [k_i V_{on}(c_i, d_{jc}) - V_{on}(c_{60\%}, d_{j60\%})] \quad (6)$$

for each “i” individual curve. Coefficient k_i was calculated so that the sum in (6) was 0 with three decimals precision. The k coefficient was chosen as a global characterization parameter of onset variation with ethanol concentration. The 60% ethanol concentration curve was chosen closer to the 50% value. The variation of the k coefficient with ethanol concentration is shown in Fig. 3. A quasi-linear variation is observed at large concentrations, which is broken at low concentrations (less than 20%). The k coefficient shows that a quasi-linear scaling of 20% to 100% ethanol curves overlaps to a certain extent the 60% curve, while larger values (than those corresponding to a linear variation) of the scaling factor are needed at concentrations lower than 20%.

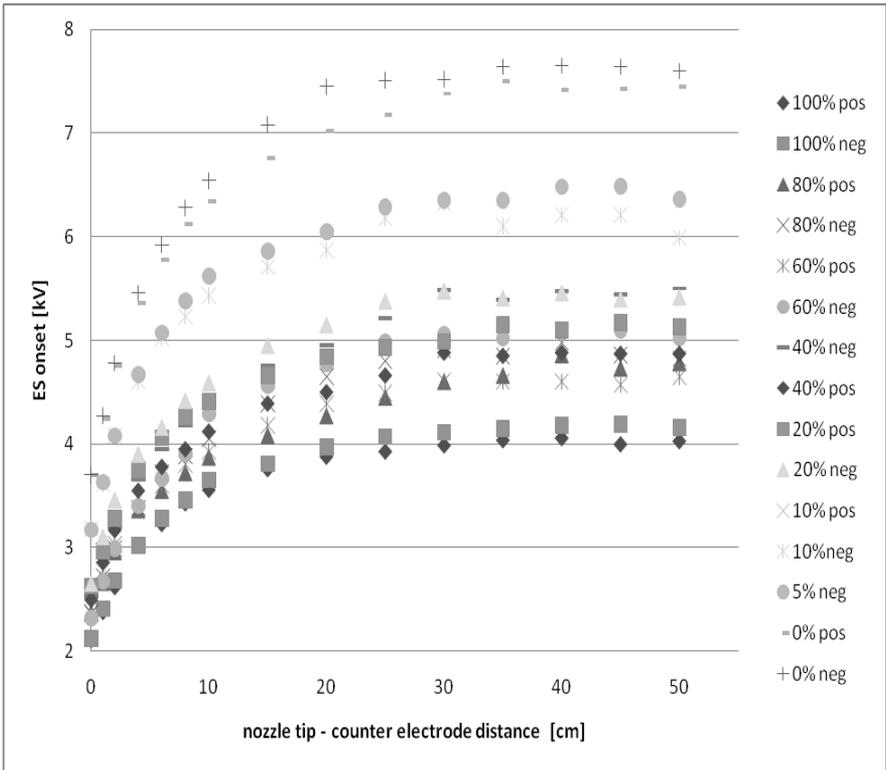


Fig. 4. Variation of ES onset voltage with ethanol concentration and nozzle tip-plate distance

The 60% curve and the average of all the scaled curves are plotted for comparison in Fig. 5. The overlapping of the two curves is fairly good (less than 5%) for most of the data range. Only three points on the chart had a variation between 5% and 8%. In semi-log coordinates (Fig. 6) the averages of the scaled data appear to have parabolic variation with a very good fit ($R^2 = 0.9979$, where R^2 is the coefficient of determination [13]) similar to the one provided by the actual 60% curve referenced.

A linear variation of onset voltage with the logarithm of the distance is predicted by Smith relation (4). However, the relation appears to hold well only for distances smaller than 20-25 cm, a conclusion that closely resembles our previous findings [14].

Surface tension data of water-ethanol mixtures were reported in [15] (concentrations calculated by mass). We converted the ethanol mass concentrations. The volume concentration of ethanol in water is defined as

$$c_v = \frac{V_1}{V_1 + V_2} \quad (7)$$

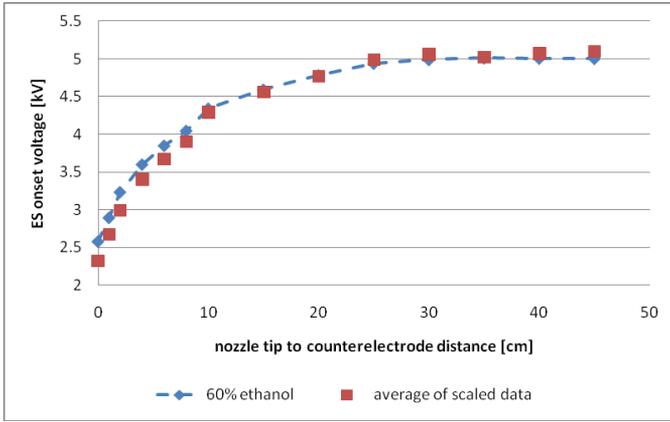


Fig. 5 Comparison of the average of scaled data sets and the 60% ethanol-water ES onset curve

where V_1 is the volume of ethanol and V_2 is the water volume in the water-ethanol mixture (volume $V_1 + V_2$). The mass concentration is defined as

$$c_m = \frac{m_1}{m_1 + m_2} = \frac{\rho_1 V_1}{\rho_1 V_1 + \rho_2 V_2} \quad (8)$$

where m_1 is the mass of ethanol and m_2 is the water mass in the water-ethanol mixture (of mass $m_1 + m_2$), ρ_1 and ρ_2 are the densities of ethanol and water, respectively ($\rho_1 = 785.22 \text{ kg/m}^3$ and $\rho_2 = 997.01 \text{ kg/m}^3$ at 25°C [16]). From (7) and (8) it follows that

$$c_v = \frac{1}{1 + \frac{\rho_1}{\rho_2} \frac{1 - c_m}{c_m}} \quad (8)$$

which was plotted in Fig. 7. Linear interpolation was used in order to determine the surface tension corresponding to the ethanol volume concentrations used in our experiments.

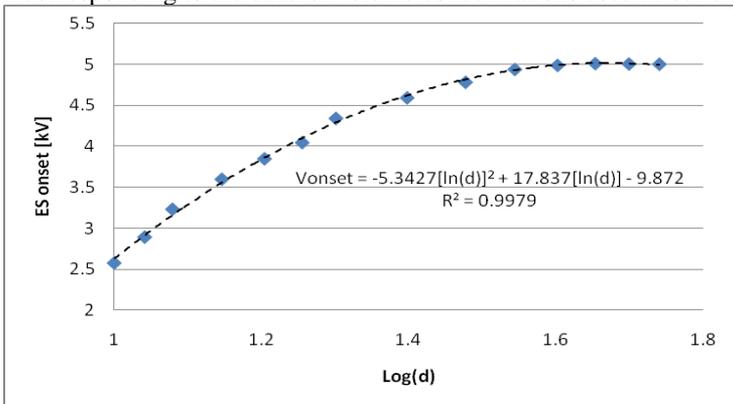


Fig. 6. Variation of average ES onset scaled voltage with tip-plate distance (semi-log scale) The point of reference has been chosen on the nozzle tip – center of counter-electrode axis 10 cm away from the initial origin of axis in order to allow log values to be plotted on the chart.

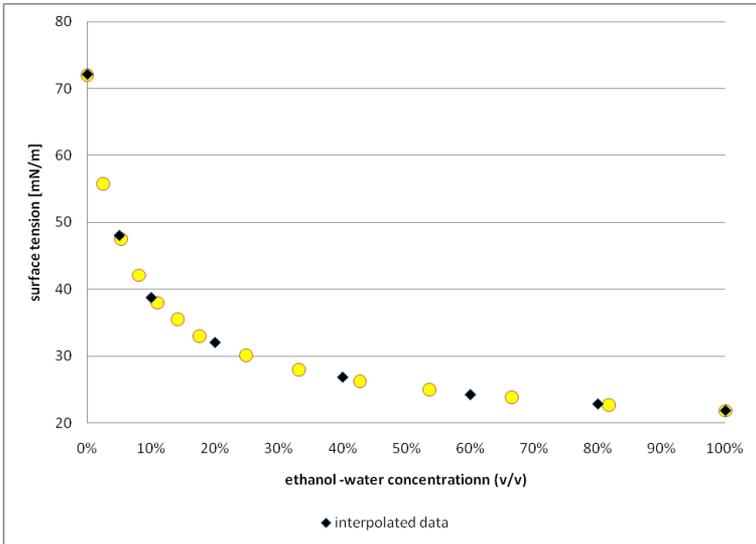


Fig. 7 Surface tension by volume concentration (calculated from mass concentrations in [15]). Interpolated data are the data points used in our experiments

Interpolated data is also plotted in Fig. 7. Noticeably, the largest variation of the surface tension with ethanol concentration happens at volume concentrations lower than 20-25%. The surface potential data obtained were used for plotting the coefficient k against surface tension in Fig. 8. The largest variation of the coefficient is observed for values of 20 mN/m to 40 mN/m (the most sensitive surface tension region of the water-ethanol mixtures).

The ES voltage onset data series were measured for a given ethanol concentration and nozzle tip to counter-electrode distances varying from 0 to 50 cm. It is well known that ES is sensitive to many parameters which cannot be perfectly controlled, but they do influence onset voltage and spray development. A cross-section ES onset data series specific to a certain inter-electrode distance can be obtained. However, the relative errors may be significantly larger than for the initial data series, still allowing for qualitative conclusions. Fig. 9 shows the variation of onset voltage with surface tension inferred values for specific inter-electrode distances (0, 2, 4, 8, 15, 30, and 45 cm) along with the associated power regression lines. It appears from the chart that a larger surface tension is associated with larger onset voltages of the water-ethanol mixtures. As previously argued, data appear more scattered; however, the power regression coefficient is consistently very close to $\frac{1}{2}$ (an average of 0.4524 with a standard deviation

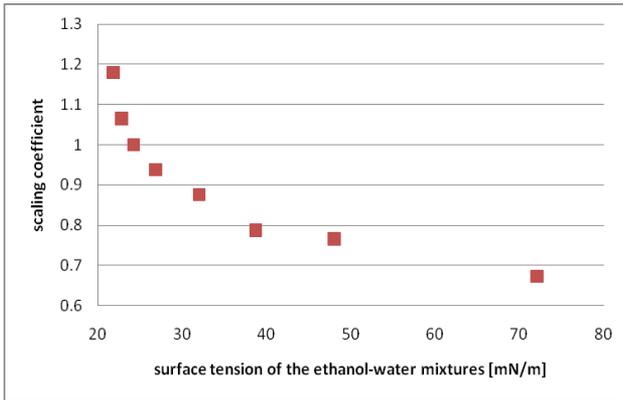


Fig. 8 Variation of the k coefficient with surface tension

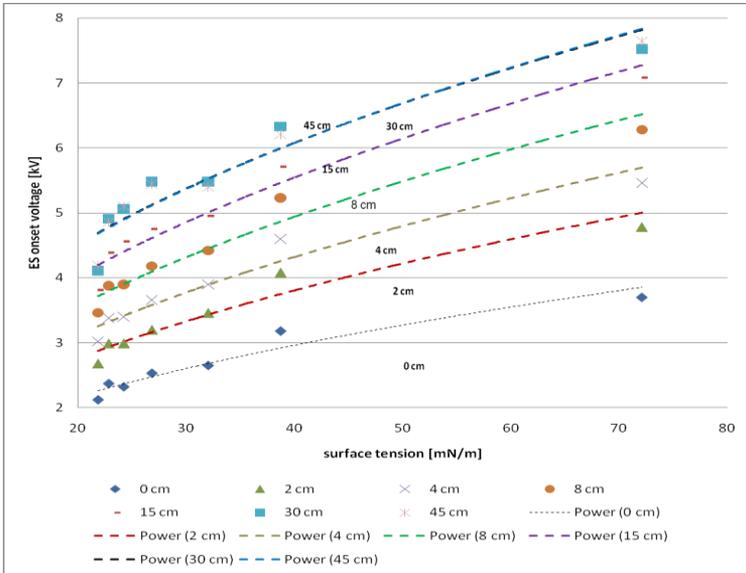


Fig. 9 Variation of onset voltage with surface tension of water-ethanol mixtures (data and power regression lines)

3.93%). This dependence of V_{on} with $\gamma^{1/2}$ is predicted by Smith's theoretical relation (4). Fig. 9 also shows that the onset voltage dependence on the surface tension of the mixture is more pronounced at low inter-electrode distances than at larger distances. The 30 cm and 45 cm regression lines essentially overlap; therefore, the 30 cm distance appears as a saturation point/curve in terms of $V_{on} - \gamma$ dependence.

IV. CONCLUSIONS

ES onset voltage characteristics of water-ethanol mixtures of various concentrations were investigated using blunt needle 26G 1/2" (ID 0.25 mm, OD 0.46 mm) as capillary

nozzles. The ethanol concentration was varied from 0% to 100% and the ES onset voltage was recorded for tip-plate distances ranging from 0 to 50 cm. Both positive and negative polarities were applied to the nozzle. Unforced ES was generated at a hydrostatic pressure of 785.7 N/m^2 which was maintained constant irrespective of the ethanol concentration used. More abrupt changes in onset voltage curves were obtained at low (lower than 20%) ethanol concentrations than at larger concentrations. The global characterization of the curves' shift by the coefficient "k" has resulted in more accurate similar conclusions. The "k" coefficient is most sensitive for surface tension values of 20 mN/m to 40 mN/m. The negative onset was always larger than the positive onset voltage, given that the other parameters were the same. The validity of Smith's theoretical relation was tested for accuracy for the used water-ethanol mixtures. A good correspondence was found for the dependence of V_{on} on $\gamma^{1/2}$. Moreover, the 30 cm distance appears as a saturation point in terms of $V_{\text{on}} - \gamma$ dependence. However, V_{on} dependence on $\ln(d)$ was confirmed only for a limited range ($d < 25 \text{ cm}$). The results of this work may be used for ES optimization of water-ethanol electrospray parameters. In addition, the onset characteristics, if calibrated, may allow ES to be used for alcohol concentration measurements.

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