Water with Excess Electric Charge

Leandra P. Santos, Telma R. D. Ducati, Lia B. S. Balestrin, Fernando Galembeck

Institute of Chemistry

University of Campinas, Campinas, S.P., Brazil 13083-970

phone: (55) 19-3521-3080

e-mail: fernagal@iqm.unicamp.br

Abstract— **Water dropped from a biased metal needle and stored within a Faraday cup contains net excess electric charge. Positive (negative) water is obtained from a positive (negative) needle and its charge largely exceeds the Rayleigh limit. Water drops become water threads at V<-9.5 kV, even under much lower field strengths than those used in electrospray, electrowetting or electrospinning experiments. Surface tension of electrified water decreases as the charge modulus increases. Water drops falling through a biased non-contacting metal ring also acquire charge but with opposite sign to the metal potential, in agreement with a recent model for the electrification of insulators or isolated metals, based on charge transfer coupled to water evaporation, adsorption and desorption.**

I. Introduction

Even though electrostatic phenomena and their consequences are everywhere, knowledge about this topic is still rather empirical [1,2]. Correlation of fundamental ideas of the atomic-molecular theory with the experimental observations of insulating materials electrostatics still presents many gaps [3]. Important questions have not yet been answered, and the most important one is the identity of the charge carriers in dielectrics, as well as their detection. According to Schein, *"Most researchers believe that insulator charging is a surface phenomenon. Creating a reproducible surface and obtaining experimental reproducibility among laboratories has been a challenge."* [1]. Therefore, there is no widespread consensus about electrostatic phenomena and reproducible experiments are not often reported, even in the simplest of cases of contact electrification and triboelectrification.

Lack of knowledge of electrostatic charging and dissipation mechanisms is not restricted to materials science. Geophysical research has not yet produced an effective model for atmospheric electricity phenomena [4], which is certainly related to the frequent casualties and property losses during electric storms.

Our research in this area began with the discovery of electrostatic patterns on polymer latex surfaces due to excess ion concentration. These electrostatic patterns were first observed using scanning electric potential microscopy (SEPM)/Kelvin force microscopy (KFM) [5,6], based on Kelvin method for non-contact potential measurement [7], and electric force microscopy (EFM) [8], which are operating modes of scanning probe microscopy (SPM) [7,9,10] derived from atomic force microscopy (AFM). Coupled with

transmission electron microscopy based on electron energy-loss spectroscopy (EELS-TEM) and transmission electron microscopy based on electron spectroscopy images (ESI-TEM), the results showed that excess static charges in colloidal polymers are associated to cation or anion concentration excess [11-13], such as K^+, Na^+ e $R-SO_4^-$ ions introduced in the emulsion polymerization process [14].

Braga *et al.* [15] and Herzog *et al.* [16] used TEM and KFM to study poly[styrene-(2-hydroxyethyl methacrylate)] (PS-HEMA) latex. The dispersed particle morphology is approximately spherical, but capillary adhesion forces and dehydration deform the particles after drying. KFM images show core-shell structures, where the shell is more positive than the core. Identification of the charge carriers in PS-HEMA was done with KFM and ESI-TEM [13]: negative charges come from the initiator, which are persulfate residues incorporated to the ends of polymer chains, trapped inside the particles. On the other hand, the counter-ions (K^+) are clustered on the outer part of the particles, forming a positively charged shell. The asymmetrical charge distribution imparts an electric multipole character to the latex particles [17].

Teixeira-Neto *et al.* also verified the formation of core-shell structures in poly(styrene-*co*-acrylamide) (PS-AAM) latex [18], using KFM. Nevertheless, this latex presents a very complex behavior: the particles show pronounced positive electric potential on one side only, suggesting the formation of an electric dipole aligned with one mica crystallographic axis. This was explained considering that: (a) latex particles are plastic electric multipoles or dipoles and (b) the surface plane of mica is anisotropic.

Electric potential distribution in thermoplastics was also observed in another KFM study. Polyethylene (PE) and polypropylene (PP) surfaces show irregular electrical potential patterns, with great contrast [12]. Topography and electric potential images were simultaneously acquired with variable degrees of correlation, indicating that the topography and electric pattern of the sample are independent.

PE monoliths were also macroscopically studied. Burgo *et al.* [19] verified that the higher the humidity of the system, the faster the charge dissipation in low density polyethylene (LDPE), until an equilibrium value of *ca.* (-4,6±0,7) V is reached. Dissipation rates and the equilibrium potential were ascribed to water cluster formation with excess negative charge while water is adsorbed or absorbed on LDPE.

Other macro- and microscopic evidence led to the hypothesis that the atmosphere is a charge reservoir for dielectrics due to the partition of OH^- e H^+ groups and adsorption of water at the solid-air interface. Local electric potential and specific water ion-dielectric surface interactions determine the relative amounts of OH^- e H^+ adsorption and, therefore, the extent of charging of the solid.

A Kelvin probe was used to verify the excess of induced charges in macroscopic samples of cellulose under the influence of an external electric potential [20]. An excess of negative charge is accumulated when cellulose is under positive electric potential, and is dissipated when the electric potential is reduced to zero. Cellulose electric charge uptake and dissipation rates are strongly dependent on the atmospheric humidity and corroborate the dielectric charging model based on H^+ e OH^- adsorbed ions partition.

KFM calibration experiments with a silica surface coated with microlithographed gold electrodes showed the great influence of relative humidity on the formation of charge patterns on silica thin films grown on silicon [21]. Under high humidity, formation as well

as dissipation of charge on silica surfaces is more pronounced.

More recently, analysis of non-crystalline Stöber silica and aluminum phosphate surfaces [22] showed that humidity changes affect the electric potential, even when they are in an isolated and electrically grounded environment. Under high humidity, silica becomes negative and aluminum phosphate becomes positive, confirming the importance of specific interactions. Surfactants deposited on mica also showed an atmospheric humidity-dependent charging [23].

While the complex charge distribution patterns shown by dielectrics are stable in some cases, in other cases they change under external forces. Most materials have a net charge different than zero, showing that the paradigm of electroneutrality of chemical substances should be reviewed, as proposed by Whitesides *et al.* [24].

Recently, charging of electrically insulated metals during adsorption and desorption of water vapor was demonstrated, as well as the existence of an electric double layer at solid-gas interfaces in the presence of humidity, and paving the way for atmospheric electricity harnessing - one of the most sought-after scientific objectives [25].

Partition of ions resulting from the dissociation of water in solid-liquid interfaces is well-known and is responsible for the charging of many solids, as shown by surface charge or zeta potential measurements. Curiously, solid-gas and liquid-gas interfaces have not been treated in the same way, considering the existence of ions in any natural atmosphere and in many laboratory conditions. The only case in which charge partition at the solid-gas interface was studied in sufficient detail was thermionic emission [26], where electrons form a cloud of space charge next to a heated metallic filament. Many of the above results can be well understood considering the existence of an electric double layer at the solid-gas and liquid-gas interfaces, where the diffuse layer extends throughout the gas phase.

Recent reports show electrostatic patterns on some electret surfaces, obtained by charge accumulation due to surface ion transfer [27]. Whitesides *et al.* [24] explained that contact charging between dielectric materials happens due to the asymmetrical partition of OH^- in the adsorbed water layers at the interface of non-ionic insulating materials. OH^--specific adsorption at the water-air and water-oil interfaces is well-established in the literature [28].

On the other hand, Bard *et al.* recently described polymer tribocharging experiments with polytetrafluoroethylene (PTFE), poly(methyl methacrylate) (PMMA), nylon, and polyethylene (PE), and the results were attributed to tribochemical formation of positive and negative electron holes at the polymer surface [29,30].

Water adsorption effect on dielectric charging has been known since long and this was the subject of Schrödinger's PhD Thesis [31]. However, a passive role is usually assigned to adsorbed water, helping to dissipate charges due to its intrinsic conductivity [32], which can be further increased by its ability to solvate surface ions. Another factor that is often mentioned is that water molecules under the influence of an external electric field are oriented, contributing to water polarization.

Our work hypothesis is as follows: electrostatic phenomena under atmospheric conditions have an important atmospheric ion contribution [33], as added to the contribution of ions derived from charged water adsorbed on surfaces. Atmospheric ions are charge carriers that migrate under influence of electric fields, and are distributed inside an electric

potential gradient, according to Poisson-Boltzmann equation [34]. They are adsorbed on liquid and solid surfaces and can be electrochemically discharged on metallic and semi-conducting surfaces.

Since the atmosphere between the surface of the Earth and the ionosphere is subject to great electric potential gradients, one can expect the water contained in electrically isolated containers to be non-electroneutral. This idea is in apparent conflict with the principle of electroneutrality [35], but this is solved by considering that pure water is electroneutral under zero potential and non-neutral under any non-zero potential, to satisfy the thermodynamic equilibrium condition as defined by the electrochemical potential (1).

Thus, water in the atmosphere or adsorbed on surfaces under non-zero electric potential, has always excess concentration of H^+ e OH^- ions to satisfy Eq. 1:

$$\mu_i = \mu_i^0 + RT \ln a_i + z_i FV \quad (1)$$

where μ_i is the electrochemical potential of the ion i, μ_i^0 is the standard electrochemical potential of i, R is the gas constant, T is the temperature, a_i is the activity of i, z_i is the valency, F is Faraday's constant and V is the electric potential affecting i. According to (1), water should have an excess of H^+ under negative electric potential, and an excess of OH^- under positive potential.

Non-neutrality of water has been previously reported in the literature. An MIT group showed that water from different sources is always negatively charged [36]. Pollack and Ovchinnikova [37] recently demonstrated an electrolysis experiment where water stored charge and an electric current could be measured for 10 min after the electrodes were shut down. They concluded that macroscopic bodies of water can separately store electric charges, but their interpretation of the experimental results led to intense questioning by Corti and Colussi [38], initiating a strong discussion [39].

Formation and stability of electrified water drops and jets have also attracted a lot of attention and many open questions remain, even focusing only on the fundamental qualitative aspects. Lord Rayleigh already studied jets from levitated microdroplets and predicted that water drop jets should be observed when the ratio X given by Eq. (2) exceeds unity [40].

$$X = \frac{Q^2}{(64\pi^2 \varepsilon_0 \gamma_0^3)} \quad (2)$$

where Q is the drop charge, ε_o is vacuum permittivity, γ is surface tension and r_o is the drop radius. Charging of water droplets, either pendant or free, has been studied in detail previously by Saunders and many others [41 and the relationship between charge, droplet size, solvent surface tension, and the Rayleigh limit in electrospray has been extensively examined by, among others, Beauchamp [42], Taflin [43] and Gomez [44]. In a recent work the jets were observed at $X = 1$ and the authors concluded that renewed investigation would be necessary to explain the complex hydrodynamics of this century-old problem [45].

According to Ahadi and Konnermann, in electrospraying for mass spectrometry, "the final step that generates free analyte ions from highly charged nanodroplets remains enigmatic." [46] These authors found in a molecular dynamics study that ions may be accu-

mulated at the interior of an electrospray droplet, while orientation polarization of water molecules then acts to transfer the excess charge to the droplet periphery.

These difficulties are at least partly due to the concurrent but not identical effects of electric field and electric potential. Electric fields produce forces causing shape distortion and motion of electrified bodies. Large electric fields are obtained even using low potential differences, provided distances within the experimental setup are sufficiently small [21]. On the other hand, it is possible to bring an isolated body to high positive or negative potential but under low field, within a large Faraday cage.

This work describes the preparation, storage and characterization of electrified water by using two different procedures. Many results presented here should be published shortly [47].

II. Experimental Section

A. Setup

A Cole Parmer 74900-00 syringe pump, calibrated to ±0.001 mL prior to use, was used to form drops of MilliQ deionized water (resistivity: 18 MΩcm). The water was pumped through a stainless steel needle (internal diameter ϕ_i=1.60 mm, outer diameter ϕ_o=2.00 mm).

The drops were collected in a Faraday cup connected to the input of a Keithley 6514 electrometer. The Faraday cup is a pair of copper concentric cylinders (ϕ_i = 2.1 and 3.4 cm, lengths L = 19.0 and 20.0 cm, respectively) containing a glass test tube or an aluminum pail (ϕ_{top} = 27.0 cm, ϕ_{bottom} = 18.5 cm, height h = 23.0 cm) isolated within a large Faraday cage made by lining a 3 x 3 x 2.6 m^3 room with aluminum foil or screen and galvanized steel screen. The aluminum pail within the shielded room was used to obtain a minimum one-meter distance between the electrified needle tip and any grounded objects, to minimize the electric field.

A ±1 kV (Keithley 2410) or a 0 to −10 kV (Instrum, São Paulo) power supply were used to bias the needle and also a metal ring (ϕ_i = 1.90 cm, L = 2.0 cm). The Instrum power supply was calibrated using the Keithley 6514 instrument as the standard and using a megaohm resistance bridge built using resistors measured to ±100 Ω using the Keithley electrometer.

A Kruss Easydrop DSA20 instrument was used to measure water surface tension by the hanging drop shape technique [34]. In this case, grounded surfaces are at 5.5 cm from the hanging drop and the electric field strength for a drop biased to1 kV is in the 200 kV/m range.

B. Procedure

Charge was accumulated within the Faraday cup during experiments performed within the large Faraday cage (Figure 1), according to the following steps:

a) the charge baseline is recorded, while water is not flowing and the needle is neither biased nor grounded (1 min);

b) water flows through the unbiased and ungrounded (floating) needle (1 min);

c) water flows while the needle is biased to 0 V using the power supply (1 min);

d) water continues to flow but the needle is biased to the desired V within the +1000 to

-9000 V range of the two used power supplies (4 min, except for -9000 V: 2 min);
   e) the same as c);
   f) the same as b);
   g) the same as a).

Drop volume, obtained by measuring the pumped water volume and the number of drops, can be used to calculate the drop radius, drop weight and water surface tension (Figure 2), using the drop-weight method [34] with the usual corrections [48].

Charged water drops are also obtained when they are released from a grounded needle and pass through the center of a biased, non-contacting, metal ring. In this case, there is no interface between water and the biased metal, since they are always separated by air.

III. RESULTS AND DISCUSSION

Figure 1 shows that water dropped from an electrified needle at 33.3 mL/h and collected in a Faraday cup carries excess charge with the same sign as the needle voltage.
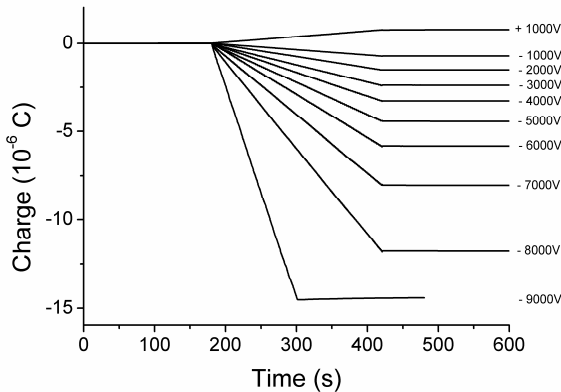

Fig. 1. Charge accumulated within the Faraday cup by collecting water dropping from a needle under different needle voltages.

Plots of charge of electrified water per unit surface area of the drops and per unit volume of water are shown in Figure 2. Water drop charge increases as the needle bias voltage increases, while drop radius and surface tension decrease. When the voltage exceeds -9 kV, water drops emerging from the needle are deformed into Taylor [49] cones, forming elongated jets, as observed in electrospinning and electrospray experiments. Moreover, small water droplets are sprayed out of the main jet, as in electrospray experiments used in mass spectrometry, even though the electric fields at drop surfaces are always less than 10 kV/m, much lower than the 500 kV/m or higher fields used in mass spectrometry and electrospinning.
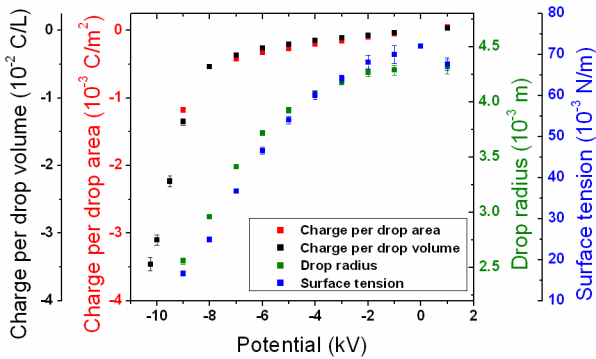
Fig. 2. Water drop charge per unit area and per unit volume, drop radius and calculated surface tension as a function of needle electric potential. Error bars are always plotted but in some points they are smaller than the symbol. Minimum distance between needle tip and surrounding grounded surfaces was 1.1 m, to minimize electric field strength.

Water drop charging can also take place by exposing water to the electrostatic potential created through air by a non-contacting biased electrode. Figure 3 shows that charge acquired by water pumped at 64.1 mL/h passing though a positive ring is negative, and vice-versa, and is highly reproducible, linear and symmetrical. This is evidenced by the cancellation or *titration* of positive and negative charges during this experiment.
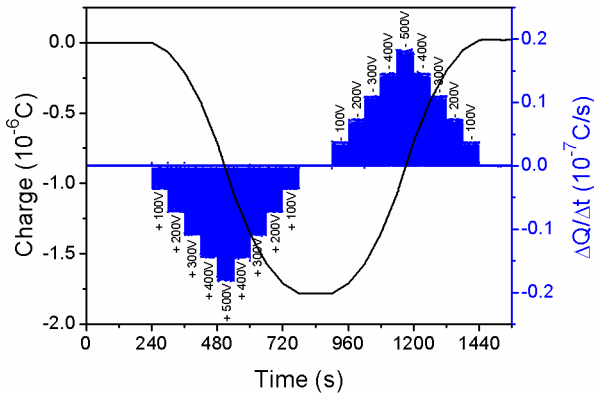

Fig. 3. (Black) Accumulated charge within the Faraday cup by collecting water dropping from a grounded needle and passing through the center of a non-contacting biased ring. (Blue) Electric current of individual drops, calculated dividing charge increments by the corresponding time interval.

A grounded metal plate was positioned next to the water drop hanging from a needle to verify the effect of surrounding objects and electric fields on the surface tension measurements. A scheme of the geometrical arrangements used together with the measurement results are shown in Figure 4. The electric field between the grounded plate and the electrified drop distorts the surface tension results if the grounded plate is within a few centi-

meters from the water drop. Therefore, reliable surface tension measurements are neces-
sarily obtained under low electric fields, meaning that the electrified water drops should
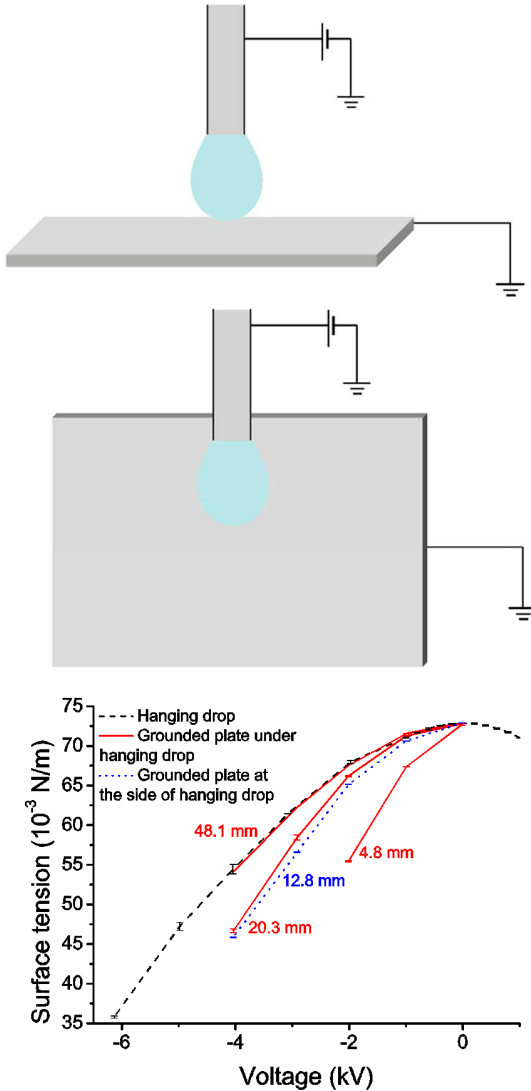be held as far as possible from any grounded surface.

Fig. 4. Top: Schematic description of the geometrical arrangement of a grounded metal plate near the water
drop hanging from a needle. Bottom: Plots of γ of a hanging water drop vs. *V* obtained by changing the posi-
tion of the grounded metal plate.

These experiments reveal the importance of the electric field strength. The distance be-
tween grounded metal surfaces and the hanging drop in the drop weight apparatus is al-
most fixed and it amounts to 5.5 centimeters only. This causes a deformation in the drop
shape and thus an apparently lower surface tension than measured under much lower

fields.

Electrostatic effects on the surface tension of liquids have already been considered in the literature [50] but considering dipolar liquids without net excess charge. These authors found that increasing the applied field tends to reduce the thermodynamic surface tension, but at the rather strong field of $E \cong 10^8$ V/m, when dielectric breakdown already takes place for many systems.

Water with excess charge shows spontaneous increase in surface area below −9.5 kV, stretching into threads and dividing spontaneously in smaller droplets. Droplet spontaneous deformation or subdivision is aided by surrounding electric fields and its dependence with the field may be assessed by plotting the apparent surface tension measured under a given voltage but decreasing distance to a grounded object, as shown in Figure 4.

Spontaneous water surface area increase is opposed to the usual minimum area expected under gravity for a water drop but it is consistent with the idea of a negative surface tension, according to Eq. (3),

$$\left(\frac{\partial G}{\partial A} \right)_{p,T,n} = \gamma \quad (3)$$

where G is Gibbs energy and A is the surface area.

Important authors like Tolman and Harkins [51,52] raised the idea of "negative surface tension" which is not frequently found, but it was it is found in current literature [53-55] and it can help to solve some hitherto pending questions.

A central question is the significance of the Rayleigh ratio as a predictor of drop stability. Results (Figure 5) calculated from data shown in Figure 2, evidence that the Rayleigh limit is largely overcome in experiments done under low Weber number, this means, under slow liquid flow and low electric field strength. This is quite different from the findings from various authors summed up by Kebarle and Verkerk in their review on electrospray mass spectrometry [56]. Thus, it is essential to have large electrode distance and thus low electric field strength together with slow liquid flow, to obtain water with large excess charge. Under the 1-3 cm electrode distances used in electrospray, liquid drop distortion and breakdown is mainly due to the large resulting electric fields. This was previously hinted at by Taflin and co-authors [43].

There is an analogy between water charging in the air with charge accumulation at the water/mercury interface in electrocapillarity. The usual Gibbs isotherm treatment for surface tension in an electrified interface leads to Eq. 4:

$$\left(\frac{\partial \gamma}{\partial \phi} \right)_{T,\mu} = -q \quad (4)$$

where q is the excess charge per surface area. Surface tension and surface charge are both known but $\Delta\phi$, the potential difference between the liquid and the atmosphere is not accessible due to the difficulty in measuring electric potential in a bare gas phase. This was calculated [47] using $q(\gamma)$ data described above, yielding $\Delta\phi(V)$ results shown in Fig. 5.
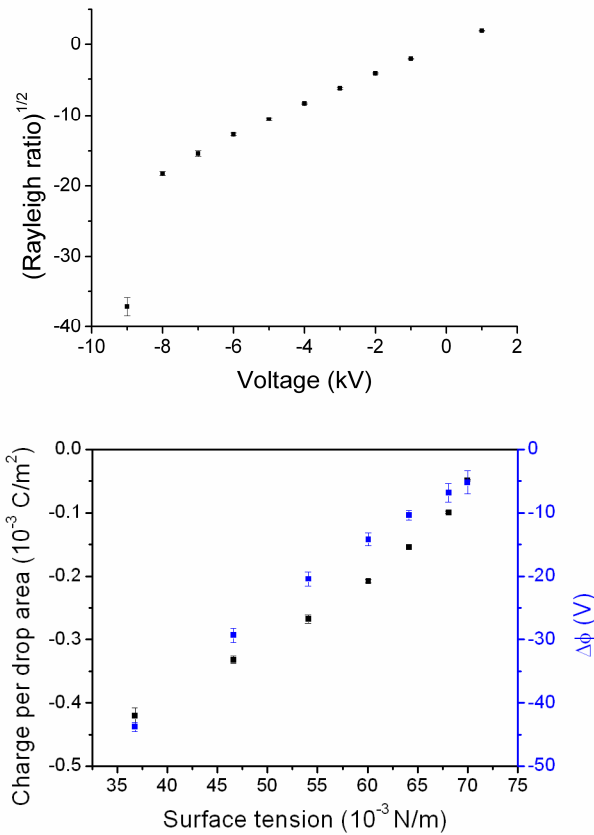
Fig. 5. Top: Square root of the Rayleigh ratio (X in Eq. 2) for water drops formed slowly (33.3 mL/h) and under low fields at various needle voltages. Bottom: Potential difference across the water-air interface (calculated using Eq. 4) and water drop charge per unit area, as a function of the surface tension.

The potential difference between the electrified drop and the surrounding atmosphere is thus much smaller than the voltage applied to the water drop.

Water charging mechanisms are distinct in the two cases (Figure 6):

1) When it is in direct contact with a positive needle, water acquires positive charge because negative ions (OH^-, HCO_3^- and others) are attracted to the metal surface, where they are discharged [Eq. (5)].

$$2OH^- \rightarrow H_2O + \tfrac{1}{2}O_2 + 2e^- \quad (5)$$
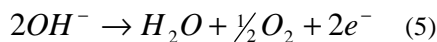
Consequently, excess H^+ ions are left behind and are transported by dropping to the interior of the Faraday cup. If the metal needle is negative, H^+ ions are discharged and the water drops leaving the metal needle have excess negative charge (Figure 6a).
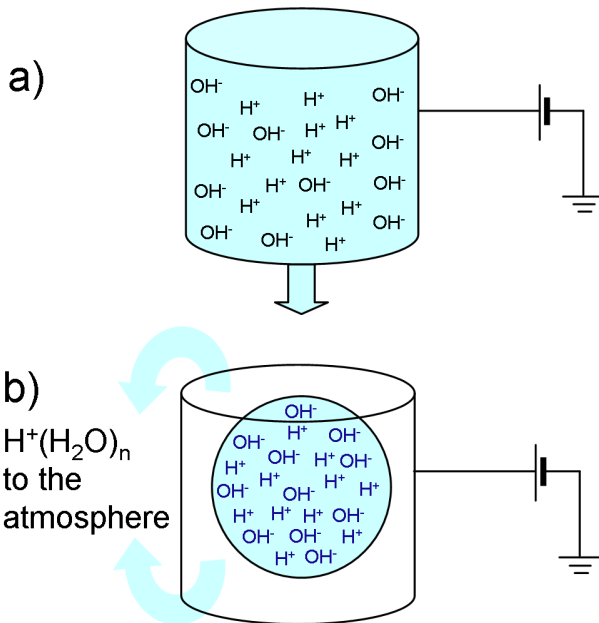
Fig. 6. Schematic descriptions of charge build-up on water. a) Water dropping from a biased needle. b) Water dropping from a grounded needle but passing through a non-contacting biased ring.

2) Conversely, when a neutral water drop formed in a grounded needle passes through the center of a positively biased metal ring, the electrochemical potential of H^+ ions increases and these ions leave the drop, associated to water molecule clusters. The falling drop therefore becomes negatively charged (Figure 6b). This is direct proof of ion evaporation which is one of the competing models for charged droplet formation in electrospray [57,58].

The mechanism described in Figure 6a is also applicable to the first step in the production of gas-phase ions from electrolyte ions in solution, within the model presented by Kebarle and Verkerk for electrospray mass spectrometry [41], but it does not require the presence of any ions beyond H^+ or OH^-, when highly purified water is used as the solvent.

IV. CONCLUSION

Simple and well-defined experimental setups were used to obtain non-electroneutral water. Charge acquired by static water drops and bulk water is well in excess of the Rayleigh limit under low electric fields and slow water flow. Electrified water surface tension is lowered, evidencing a decrease in surface water cohesion due to electrostatic repulsion. Recognition of these facts should contribute to further understanding and applications of various electrostatic phenomena taking place in the presence of liquid or adsorbed water. The phenomena described in this work should have a strong effect on water dispersion colloidal properties, on water solvency and phase transitions, including atmospheric phenomena [59], since surface tension is strongly connected to cohesion of solids and liquids.

REFERENCES

[1] L. B. Schein, "Recent progress and continuing puzzles in electrostatics," *Science*, vol. 316, pp. 1572-1573, 2007.

[2] A. G. Bailey, "The charging of insulator surfaces," *J. Electrostat.*, vol. 51, pp. 82-90, 2001; G. S. P. Castle, "Contact charging between insulators," *J. Electrostat.*, vol. 40-41, pp. 13-20, 1997.

[3] E. Németh, V. Albrecht, G. Schubert and F. Simon, "Polymer tribo-electric charging: dependence on thermodynamic surface properties and relative humidity," *J. Electrostat.*, vol. 58, pp. 3-16, 2003; J. L. Davidson, T. J Williams, A. G. Bailey and G. L. Hearn, "Characterisation of electrostatic discharges from insulating surfaces," *J. Electrostat.*, vol. 51, pp. 374-380, 2001; G. Chen, Y. Tanaka, T. Takada and L. Zhong, "Effect of polyethylene interface on space charge formation," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 11, pp. 113-121, 2004; G. Chen, T. Y. G. Tay, A. E. Davies, Y. Tanaka and T. Takada, "Electrodes and charge injection in low-density polyethylene - Using the pulsed electroacoustic technique," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 8, pp. 867-873, 2001; M. D. Hogue, C. R. Buhler, C. I. Calle, T. Matsuyama, W. Luo and E. E. Groop, "Insulator-insulator contact charging and its relationship to atmospheric pressure," *J. Electrostat.*, vol. 61, pp. 259-268, 2004; N. Duff and D. J. Lacks, "Particle dynamics simulations of triboelectric charging in granular insulator systems," *J. Electrostat.*, vol. 66, pp. 51-57, 2008; K. S. Choi, M. Yamaguma and A. Ohsawa, "Experimental study on electrostatic hazards in sprayed liquid," *Jpn. J. Appl. Phys.*, vol. 46, pp. 7861-7864, 2007; A. A. Park and L. S. Fan. "Electrostatic charging phenomenon in gas-liquid-solid flow systems," *Chem. Eng. Sci.*, vol. 62, pp. 371-386, 2007.

[4] B. Vonnegut, "The atmospheric electricity paradigm," *Bull. Am. Meteorol. Soc.*, vol. 75, pp. 53-61, 1994; J. H. Helsdon Jr, S. Gattaleeradapan, R. D. Farley and C. C. Waits, "An examination of the convective charging hypothesis: Charge structure, electric fields, and Maxwell currents," *J. Geophys. Res.*, vol. 107, article number 4630, 2002.

[5] H. O. Jacobs, H. F. Knapp and A. Stemmer, "Practical aspects of Kelvin probe force microscopy," *Rev. Sci. Instrum.*, vol.70, pp. 1756-1760, 1999.

[6] F. Galembeck, C. A. R. Costa, "Electric Scanning Probe Techniques: Kelvin Force Microscopy and Electric Force Microscopy," In *Encyclopedia of Surface and Colloid Science*; P. Somasundaran, Ed. New York: Dekker Encyclopedias, 2006.

[7] M. Nonnenmacher, M. P. O' Boyle and H. K. Wickramasinghe, "Kelvin probe force microscopy," *Appl. Phys. Lett.*, vol. 58, pp. 2921-2923, 1991.

[8] P. S. O. Patrício, L. A. Cury, G. G. Silva and B. R. A. Neves, "Electric force microscopy investigation of a MEH-PPV conjugated polymer blend: Robustness or frailty?," *Ultramicroscopy*, vol. 108, pp. 302-308, 2008.

[9] H. O. Jacobs, H. F. Knapp and A. Stemmer, "Surface potential mapping: A qualitative material contrast in SPM," *Ultramicroscopy*, vol. 69, pp. 39-49, 1997.

[10] G. Binning, C. F. Quate and C. Gerber, "Atomic force microscope," *Phys. Rev. Lett.*, vol. 56, pp. 930-933, 1986.

[11] C. A. Rezende, R. F. Gouveia, M. A. da Silva and F. Galembeck, "Detection of charge distributions in insulator surfaces," *J. Phys. Condens. Matter*, vol. 21, article number 263002, 2009.

[12] A. Galembeck, C. A. R. Costa, M. C. V. M. Silva, E. F. Souza and F. Galembeck, "Scanning electric potential microscopy imaging of polymers: Electrical charge distribution in dielectrics," *Polymer*, vol. 42, pp. 4845-4851, 2001.

[13] M. Braga, C. A. R. Costa, C. A. P. Leite and F. Galembeck, "Scanning electric potential microscopy imaging of polymer latex films: Detection of supramolecular domains with nonuniform electrical characteristics," *J. Phys. Chem. B*, vol. 105, pp. 3005-3011, 2001.

[14] F. Galembeck, C. A. R. Costa, A. Galembeck and M. C. V. M. Silva, "Supramolecular ionics: Electric charge partition within polymers and other non-conducting solids," *Anais da Academia Brasileira de Ciências*, vol.73, pp. 495-510, 2001.

[15] M. Braga, "Formação de filmes a partir de látexes de poliestireno, induzida por vapores de solventes," M.Sc. dissertation, University of Campinas, Institute of Chemistry, Brazil, 2003.

[16] A. L. H. Cardoso, "Síntese e caracterização de látex copoliméricos de poli[estireno-co-(metacrilato de butila)]," M.Sc. dissertation, University of Campinas, Institute of Chemistry, Brazil, 1994.

[17] A. H. Cardoso, C. A. P. Leite, F. Galembeck, "Latex particle self-assembly and particle microchemical symmetry: PS HEMA latex particles are intrinsic dipoles," *Langmuir*, vol. 15, pp. 4447-4453, 1999.

[18] E. Teixeira-Neto and F. Galembeck, "Substrate effect on latex particle self-arraying: a SEPM study," *Colloids Surf. A*, vol. 207, pp. 147-154, 2002.

[19] T. A. L. Burgo, "Indução e dissipação de cargas em dielétricos: evidências do papel da atmosfera como reservatório de cargas," M.Sc. dissertation, University of Campinas, Institute of Chemistry, Brazil, 2009.

[20] L. C. Soares, S. Bertazzo, T. A. L. Burgo, V. Baldim and F. Galembeck, "A new mechanism for the electrostatic charge build-up and dissipation in dielectrics," *J. Braz. Chem. Soc.*, vol.19, pp. 277-286, 2008.

[21] R. F. Gouveia, C. A. R. Costa and F. Galembeck, "Electrostatic patterning of a silica surface: A new model for charge build-up on a dielectric solid," *J. Phys. Chem. B*, vol. 109, pp. 4631-4637, 2005; R. F. Gouveia, C. A. R. Costa and F. Galembeck, "Water vapor adsorption effect on silica surface electrostatic patterning," *J. Phys. Chem. C*, vol. 112, pp. 17193-17199, 2008.

[22] R. F. Gouveia and F. Galembeck, "Electrostatic charging of hydrophilic particles due to water adsorption," *J. Am. Chem. Soc.*, vol. 131, pp. 11381-11386, 2009.

[23] J. S. Bernardes, C. A. Rezende and F. Galembeck, "Morphology and self-arraying of SDS and DTAB dried on mica surface," *Langmuir*, vol. 26, pp. 7824-7832, 2010; J. S. Bernardes, C. A. Rezende and F. Galembeck, "Electrostatic patterns on surfactant coatings change with ambient humidity," *J. Phys. Chem. C*, vol. 114, pp. 19016-19023, 2010.

[24] L. S. McCarty and G. M. Whitesides, "Electrostatic charging due to separation of ions at interfaces: Contact electrification of ionic electrets," *Angew. Chem. Int. Ed.*, vol. 47, pp. 2188-2207, 2008.

[25] F. Galembeck, T. R. D. Ducati, R. F. Gouveia and T. A. L. Burgo, "Processo de eletrização de materiais por adsorção/dessorção de água, produtos eletrizados pelo dito processo e uso dos mesmos," BR PI0905342-5, December 18, 2009; T. R. D. Ducati, L. H. Simões and F. Galembeck, "Charge partition at gas-solid interfaces: humidity causes electricity build-up on metals," *Langmuir*, vol. 26, pp. 13763–13766, 2010.

[26] E. L. Murphy and R. H. Good, "Thermionic emission, field emission, and the transition region," *Phys. Rev.*, vol. 102, pp. 1464-1473, 1956.

[27] L. S. McCarty, A. Winkleman and G. M. Whitesides, "Ionic electrets: Electrostatic charging of surfaces by transferring mobile ions upon contact," *J. Am. Chem. Soc.*, vol. 129, pp. 4075-4088, 2007; L. S. McCarty, A. Winkleman and G. M. Whitesides, "Electrostatic self-assembly of polystyrene microspheres by using chemically directed contact electrification," *Angew. Chem. Int. Ed.*, vol. 46, pp. 206-209, 2007; H. O. Jacobs and G. M. Whitesides, "Submicrometer patterning of charge in thin-film electrets," *Science*, vol. 291, pp. 1763-1766, 2001.

[28] A. Gray-Weale and J. K. Beattie, "An explanation for the charge on water's surface," *Phys. Chem. Chem. Phys.*, vol. 11, pp. 10994-11005, 2009; T. W. Healy and D. W. Fuerstenau, "The isoelectric point/point-of-zero-charge of interfaces formed by aqueous solutions and nonpolar solids, liquids, and gases," *J. Colloid Interface Sci.*, vol. 309, pp. 183-188, 2007; J. K. Beattie, A. M. Djerdjev and G. G. Warr, "The surface of neat water is basic," *Faraday Discuss.*, vol. 141, pp. 31-39, 2009; J. K. Beattie, "The intrinsic charge on hydrophobic microfluidic substrates," *Lab Chip*, vol.6, pp. 1409-1411, 2006.

[29] C. Liu and A. J. Bard, "Electrons on dielectrics and contact electrification," *Chem. Phys. Lett.*, vol. 480, pp. 145-156, 2009; C. Liu and A. J. Bard, "Electrostatic electrochemistry: Nylon and polyethylene systems," *Chem. Phys. Lett.*, vol. 485, pp. 231-234, 2010.

[30] C. Liu and A. J. Bard, "Electrostatic electrochemistry at insulators," *Nat. Mater.*, vol. 7, pp. 505-509, 2008; C. Liu and A. J. Bard, "Chemical redox reactions induced by cryptoelectrons on a PMMA surface," *J. Am. Chem. Soc.*, vol. 131, pp. 6397-6401, 2009.

[31] E. Schrödinger, "Über die Leitung der Elektrizität auf der Oberfläche von Isolatoren an feuchter Luft," Ph.D. Thesis, University of Vienna, Austria, 1910.

[32] A. E. Seaver, "Surface resistivity of uncoated insulators," *J. Electrostat.*, vol. 63, pp. 203-222, 2005.

[33] M. L. Huertas and J. Fontan, "Evolution times of tropospheric positive ions," *Atmos. Environ.*, vol. 9, pp. 1018-1026, 1975.

[34] A. W. Adamson and A. P. Gast, *Physical Chemistry of Surfaces*, 6th ed., New York, NY: Wiley, 1997.

[35] IUPAC. (2006). Gold Book [Online]. Available: http://goldbook.iupac.org/E01992.html

[36] M. S. Amin, T. F. Peterson and M. Zahn, "Advanced Faraday cage measurements of charge and open-circuit voltage using water dielectrics," *J. Electrostat.*, vol. 64, pp. 424-430, 2006.

[37] K. Ovchinnikova and G. H. Pollack, "Can water store charge?," *Langmuir*, vol. 25, pp. 542-547, 2009.

[38] H. R. Corti and A. J. Colussi, "Do concentration cells store charge in water? Comment on Can water store charge?," *Langmuir*, vol. 25, pp. 6587-6589, 2009.

[39] K. Ovchinnikova and G. H. Pollack, "Reply to Comment on Can water store charge?," *Langmuir*, vol. 25, pp. 11202-11202, 2009; H. R. Corti and A. J. Colussi, "Response to Reply to Comment on Can water store charge?," *Langmuir*, vol. 25, pp. 11203-11203, 2009.

[40] L. Rayleigh, "On the equilibrium of liquid conducting masses charged with electricity," *Phil. Mag.*, vol. 14, pp. 184-186, 1882.

[41] P. R. Brazier-Smith, M. Brook, J. Latham, C. P. R. Saunders and M. H Smith, "Vibration of electrified water drops," *Proc. Roy. Soc. Lond. A*, vol. 322, pp. 523-534, 1971.

[42] J. N. Smith, R. C. Flagan and J. L Beauchamp, "Droplet evaporation and discharge dynamics in electrospray ionization," *J. Phys. Chem. A*, vol. 106, pp. 9957-9967, 2002.

[43] D. C. Taflin, T. L. Ward and E. J Davis, "Electrified droplet fission and the Rayleigh limit," *Langmuir*, vol. 5, pp. 376-384, 1989.

[44] A. Gomez and K. Tang, "Charge and fission of droplets in electrostatic sprays," *Phys. Fluids*, vol. 6, pp. 404-414, 1994.

[45] D. Duft, T. Achtzehn, R. Müller, B. A. Huber and T. Leisner, "Coulomb fission - Rayleigh jets from levitated microdroplets," *Nature*, vol. 421, pp. 128-128, 2003.

[46] E. Ahadi and L. Konermann, "Surface charge of electrosprayed water nanodroplets: A molecular dynamics study," *J. Am. Chem. Soc.*, vol. 132, pp. 11270-11277, 2010.

[47] L. P. Santos, T. R. D. Ducati, L. B. S. Balestrin and F. Galembeck, "Water with excess electric charge," *J. Phys. Chem. C*, to be published.

[48] J. L. Lando and H. T. Oakley, "Tabulated correction factors for drop-weight-volume determination of surface and interfacial tensions," *J. Colloid Interface Sci.*, vol. 25, pp. 526-530, 1967.

[49] G. I. Taylor, "Disintegration of Water Drops in an Electric Field," *Proc. R. Soc. Lond. A*, vol. 280, pp. 383-397, 1964.

[50] V. B. Warshavsky, T. V. Bykov and X. C. Zeng, "Effects of external electric field on the interfacial properties of weakly dipolar fluid," *J. Chem. Phys.*, vol. 114, pp. 504-512, 2001.

[51] Tolman, R. C. "Colloids and negative surface tension," *Science* **1916**, *44*, 565-567.

[52] W. D. Harkins and Y. C. Cheng, "The orientation of molecules in surfaces. VI. Cohesion, adhesion, tensile strength, tensile energy, negative surface energy, interfacial tension, and molecular attraction," *J. Am. Chem. Soc.*, vol. 43, pp. 35-53, 1921.

[53] S. Facsko, T. Dekorsy, C. Koerdt, C. Trappe, H. Kurz, A. Vogt and H. L. Hartnagel, "Formation of ordered nanoscale semiconductor dots by ion sputtering," *Science*, vol. 285, pp. 1551-1553, 1999.

[54] S. J. Marrink and A. E. Mark, "Effect of undulations on surface tension in simulated bilayers," *J. Phys. Chem. B*, vol. 105, pp. 6122-6127, 2001.

[55] P. W. Tasker, "Surface energies, surface tensions and surface-structure of the alkali-halide crystals," *Phil. Mag. A*, vol. 39, pp. 119-136, 1979.

[56] P. Kebarle and U. H. Verkerk, "Electrospray: From ions in solution to ions in the gas phase, what we know now," *Mass Spectrom. Rev.*, vol. 28, pp. 898-917, 2009.

[57] J. V. Iribarne and B. A. Thomson, "Evaporation of small ions from charged droplets," *J. Chem. Phys.*, vol. 64, pp. 2287-2294, 1976.

[58] S. Nguyen and J. B. Fenn, "Gas-phase ions of solute species from charged droplets of solutions," *Proc. Natl. Acad. Sci. U.S.A.*, vol. 104, pp. 1111-1117, 2007.

[59] J. L. Katz, J. A. Fisk and V. M. Chakarov, "Condensation of a supersaturated vapor. 9. Nucleation on ions," *J. Chem. Phys.*, vol. 101, pp. 2309-2318, 1994.