

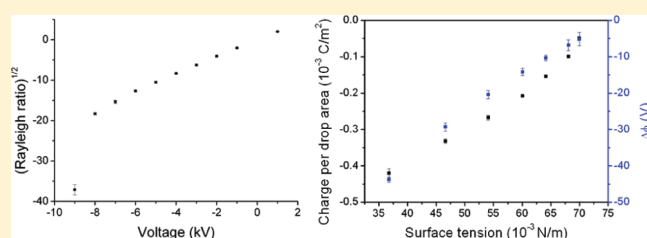
Water with Excess Electric Charge

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Supporting Information Web-Enhanced

ABSTRACT: Water dropping from a biased metal needle acquires net electric charge that can be stored within a Faraday cup. Positive (negative) water is obtained from a positive (negative) needle, and its charge largely exceeds the Rayleigh limit. Water drops transform into water threads at $V < -9.5$ kV, even under field strengths much lower than those used in electrospray, electrowetting, or electrospinning experiments. Surface tension of electrified water decreases as the positive or negative charge increases, but its density and viscosity are the same as those of neutral water. Water drops falling in the air through a biased noncontacting 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.



INTRODUCTION

The electroneutrality principle¹ expresses the fact that all pure substances carry a net charge of zero. However, real substances in the environment are usually under significant static potential gradients and thus under nonzero electric potential.² The electrochemical potential (μ) (eq 1) of ions under a given electric potential (V)

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

where μ_i^0 is the standard chemical potential, R is the gas constant, T is the temperature, a is the activity of the ion, z is the valency of the ion, and F is Faraday's constant, requires excess cation concentration under negative V and excess anion concentration under positive V , in conductors and insulators as well. However, assessment of V within the bulk of a nonconducting solid or liquid (Galvani potential) is often very difficult.

Many important phenomena take place when some substances are under strong electric fields. For instance, electrospraying, electrowetting, and electrospinning receive great attention since they are now very important in mass spectrometry and materials processing. Great effort has been put into modeling these phenomena and verifying the proposed competing models. Electrified water droplets are also found in thunderstorm clouds, inkjet printing, and the Wilson chamber. Moreover, electric fields also have a complex effect in nucleation phenomena.^{3,4}

Formation and stability of electrified bulk water, drops, and jets are still far from understood, 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.⁵

$$X = Q^2 / (64\pi^2 \epsilon_0 \gamma r_0^3) \quad (2)$$

where Q is the drop charge, ϵ_0 is vacuum permittivity, γ is surface tension, and r_0 is the drop radius. Charging of water droplets, either pendant or free, has been studied in detail previously by Saunders and many others,⁶ and the relationship between charge, droplet size, solvent surface tension, and the Rayleigh limit in electrospray has been extensively studied by, among others, Beauchamp,⁷ Taflin,⁸ and Gomez.⁹ 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.¹⁰

According to Ahadi and Konnermann, in electrospraying "the final step that generates free analyte ions from highly charged nanodroplets remains enigmatic."¹¹ These authors found in a molecular dynamics study that ions may be accumulated at the interior of an electrospray droplet, while orientational 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.¹² 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.

Quiescent excess charge in a bulk solid or liquid can be determined in the laboratory using the Faraday cup technique, but these measurements are not often done, even though Faraday cups are widely used as electron and ion detectors. On the other

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hand, charge determination in definite domains on a solid surface is now possible by using the scanning electric charge or potential measurement techniques derived from atomic force microscopy, like Kelvin force microscopy. However, these techniques are not yet routinely used in many laboratories.^{13,14}

There is abundant experimental data on excess concentration gradients due to local V gradients, especially in the areas of electrokinetic phenomena,¹⁵ electrochemical kinetics,¹⁶ and biophysics.¹⁷ Overall excess charge in electrets and dielectrics has also been intensely studied, but the nature and identity of charge carriers in these cases are still under discussion.^{18–29} Recently, Whitesides and coauthor proposed that contact charge in insulators is due to partition of OH^- ions derived from adsorbed water, at the contacting surfaces. Partition of water ions at isolated metallic surfaces is the driving force of hygro-electricity, which is metal charging due to atmospheric water adsorption.³⁰

Bulk water with excess charge has been previously mentioned in the literature. An MIT group found negative charge on water from different sources³¹ using Faraday cup measurements. On the other hand, results from Ovchinnikova and Pollack,²⁹ based on electrochemical experiments, provoked reactions from other authors triggering a strong debate.³²

In this work, we show that water with excess charge is obtained by using two different, simple, and reproducible procedures. In addition, the surface tension of electrified water is lower than the normal γ of water under ground V , but water density and viscosity do not change with net charge.

EXPERIMENTAL SECTION

Water drops were formed by pumping Milli-Q deionized water (resistivity: 18 $\text{M}\Omega\text{ cm}$) through a stainless steel needle (internal diameter $\phi_i = 1.60$ mm, outer diameter $\phi_o = 2.00$ mm). Water was pumped using a Cole Parmer 74900-00 syringe pump that was calibrated to ± 0.001 mL prior to use.

Water dropping from the needle was collected in a glass test tube located within Faraday cups connected to the input of a Keithley 6514 electrometer. One Faraday cup is a pair of copper concentric cylinders ($\phi_i = 2.1$ and 3.4 cm, lengths $L = 19.0$ and 20.0 cm, respectively), and the other is an aluminum pail ($\phi_{\text{top}} = 27.0$ cm, $\phi_{\text{bottom}} = 18.5$ cm, height $h = 23.0$ cm) isolated within a large Faraday cage made by lining a $3 \times 3 \times 2.6$ m³ room with aluminum foil or screen and galvanized steel screen. The aluminum pail within the shielded room was used to obtain a minimum 1 m distance between the electrified needle tip and any grounded objects.

The needle and also a metal ring ($\phi_i = 1.90$ cm, $L = 2.0$ cm) were biased using either a ± 1 kV (Keithley 2410) or a 0 to -10 kV (Instrum, São Paulo) power supply. 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 $\pm 100\ \Omega$ using the Keithley electrometer.

Water surface tension measurements by the hanging drop method³³ were made using a Kruss Easydrop DSA20 instrument. In this case, grounded surfaces are at 5.5 cm from the hanging drop, and the electric field strength for a drop biased to 1 kV is in the 200 kV/m range.

RESULTS

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. Figure 1 shows the charge accumulated

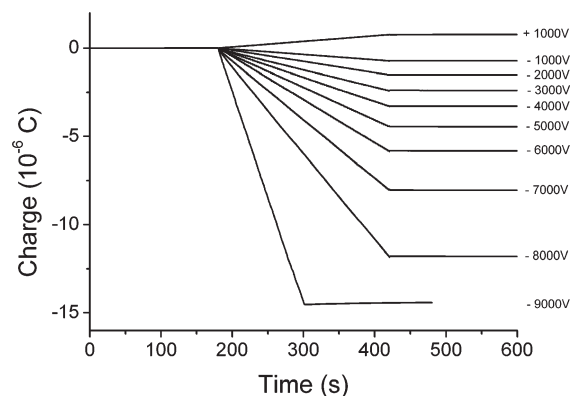


Figure 1. Charge accumulated within the Faraday cup by collecting water dropping from a needle under different needle voltages.

within the Faraday cup vs time during experiments performed within the large Faraday cage according to the following steps:

- the charge baseline is recorded, while water flow is stopped and the needle is neither biased nor grounded (1 min);
- water flows through the unbiased and ungrounded (floating) needle (1 min);
- water flows while the needle is biased to 0 V using the power supply (1 min);
- 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);
- the same as (c);
- the same as (b);
- the same as (a).

Table 1 gives a set of data extracted from the experiments shown in Figure 1.

Water collected under 0 ± 0.0002 V (Keithley), 6 ± 2 V (lowest output from the Instrum power supply), and from the floating needle still shows detectable charge, in the same range as the electrometer baseline drift.

Results obtained from duplicate experiments like those described in Figure 1 and Table 1 are in Figure 2. Figure 2 (top) shows the charge on electrified water per unit surface area of the drops and per unit volume of water: charge sign is the same as the needle bias voltage sign. By measuring the pumped water volume and the number of drops, it is possible to measure the drop volume that yields the drop radius, drop weight, and water surface tension (Figure 2, bottom), using the drop-weight method³³ with the usual corrections.³⁴

Water drop charge increases as the needle bias voltage increases, while drop radius and surface tension decrease. (A plot of the surface tension as a function of the charge per drop volume is shown in the Supporting Information.) When the voltage exceeds -9 kV, water drops emerging from the needle are deformed into Taylor cones, forming elongated jets as observed in electrospraying 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 these experiments. Video 1 (Web Enhanced Object, avi format, Xvid codec) shows water dropping from a biased needle (distance to ground >10 cm), and Figure 3 shows some representative pictures extracted from Video 1.

Table 1. Charge Accumulated in Each Step, Extracted from Figure 1

<i>t</i> /min ^a	step	accumulated charge/10 ^{−8} C under needle voltage/kV									
		1 ^b	−1	−2	−3	−4	−5	−6	−7	−8	−9
0–1	a	−0.2	−0.1	0.3	−0.9	−0.06	−0.04	0.3	0.3	0.2	0.2
1–2	b	−0.3	0.3	0.3	−0.04	−0.05	−0.06	−0.2	−0.3	−0.4	−0.4
2–3	c	−0.4	0.3	0.2	−0.03	−0.02	−0.09	−0.2	−0.1	−0.3	−0.4
3–7	d	74	−74	−152	−240	−330	−443	−586	−803	−1183	−1450
7–8	e	0.6	0.8	−0.6	2	1.6	−1.9	4	−1.2	6	3.2
8–9	f	−0.1	0.1	−0.03	−0.3	−0.4	−0.5	−0.6	−0.6	−0.7	4.1
9–10	g	−0.3	0.4	0.3	0.2	0.3	0.3	0.2	0.3	0.3	1.1

^a The duration of step d when needle voltage = −9 kV was 2 min. ^b Needle voltage measured using Keithley power supply (kV). Voltages between −1 and −9 kV were applied with the Instrum power supply.

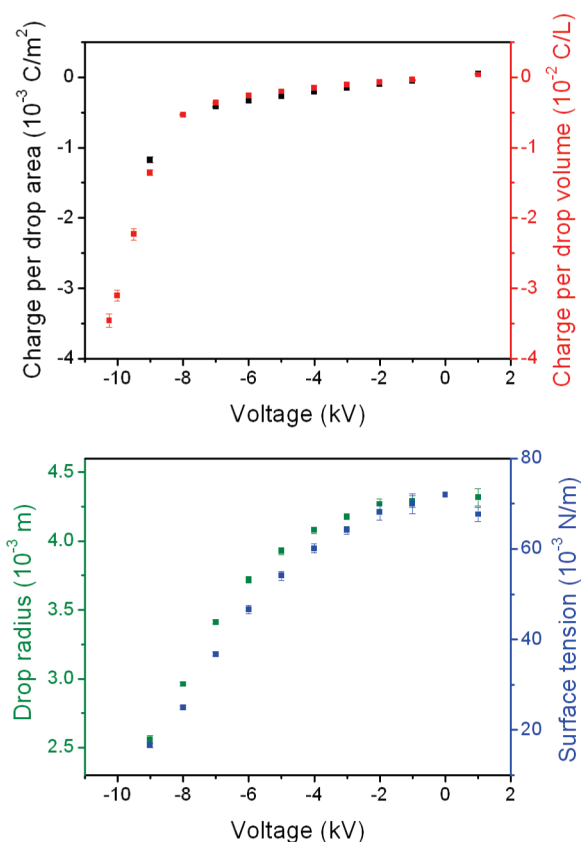


Figure 2. Top: Water drop charge per unit area and per unit volume as a function of needle electric potential. Bottom: Drop radius and calculated surface tension as a function of needle electric potential. Error bars are always plotted, but in some points they are smaller than the symbol. Minimum distance between needle tip and surrounding grounded surfaces was 1.1 m, to minimize electric field strength.

It is also possible to charge water drops released from a grounded needle by allowing them to pass through the center of a biased metal ring but without contacting it. In this case, there is no interface between water and the biased metal, since they are always separated by air. Figure 4 shows a typical result: charge acquired by water pumped at 64.1 mL/h passing through a positive ring is negative, and vice versa. The amount of charge thus obtained is shown in Table 2, in the same range as the data in Table 1.

Figure 4 shows the high reproducibility, linearity, and symmetry of charge acquisition by water subjected to an electrostatic potential. This is evidenced by the cancellation or titration of positive and negative charges during this experiment.

Thus, water drop charging can take place both by contacting an electrified metal or by exposing water to the electrostatic potential created through air by a noncontacting biased electrode.

Physico-chemical properties of water should change with its charging state, and this is verified by the decrease in drop radius shown in Figure 2 (bottom) that shows that electrified water surface tension is lower than electroneutral water. Water γ was also measured using the hanging drop shape technique, since this is conveniently applied to water drops hanging or dropping from an electrified needle. Typical experimental outputs of the hanging drop technique, for different sequences of needle bias voltages, are given in Figure 5. In these experiments, needle V was changed successively between desired values and ground, so that water γ at 0 V was checked during the whole experiment. Figure 5 shows a steady γ under 0 V (grounded needle) and a decreasing γ for water drops hanging from a positively or negatively biased needle. This shows the absence of any hysteresis or slow equilibration phenomena under the V and time scale used in these experiments.

Figure 5 also shows the volume of hanging drops as a function of time, using the same pictures taken for measuring surface tension. Drop volumes decrease linearly with time due to water evaporation, but the rate of volume change is unaltered by biasing the metal needle. In separate experiments (not shown), water within a glass pycnometer fitted with a NiCr wire did not show any meniscus displacement when the wire was biased. These two independent results show that water density is unaltered by charging, within $\pm 0.1\%$.

γ vs V data for needle voltages within the −1 to +1 kV range are plotted together in Figure 6, showing a concave parabola shape that closely resembles electrocapillary curves. Fitting the experimental points to a parabola yields eq 3, from which we can predict that γ should reach zero at ± 6.2 kV, becoming negative outside this range.

$$\gamma = aV^2 + bV + c \quad (3)$$

This is not in quantitative agreement with Figure 1, and the difference reveals the importance of the electric field strength, in these experiments. In the drop weight apparatus, the distance between grounded metal surfaces and the hanging drop is nearly fixed, and it amounts to 5.5 cm only. This causes a deformation in

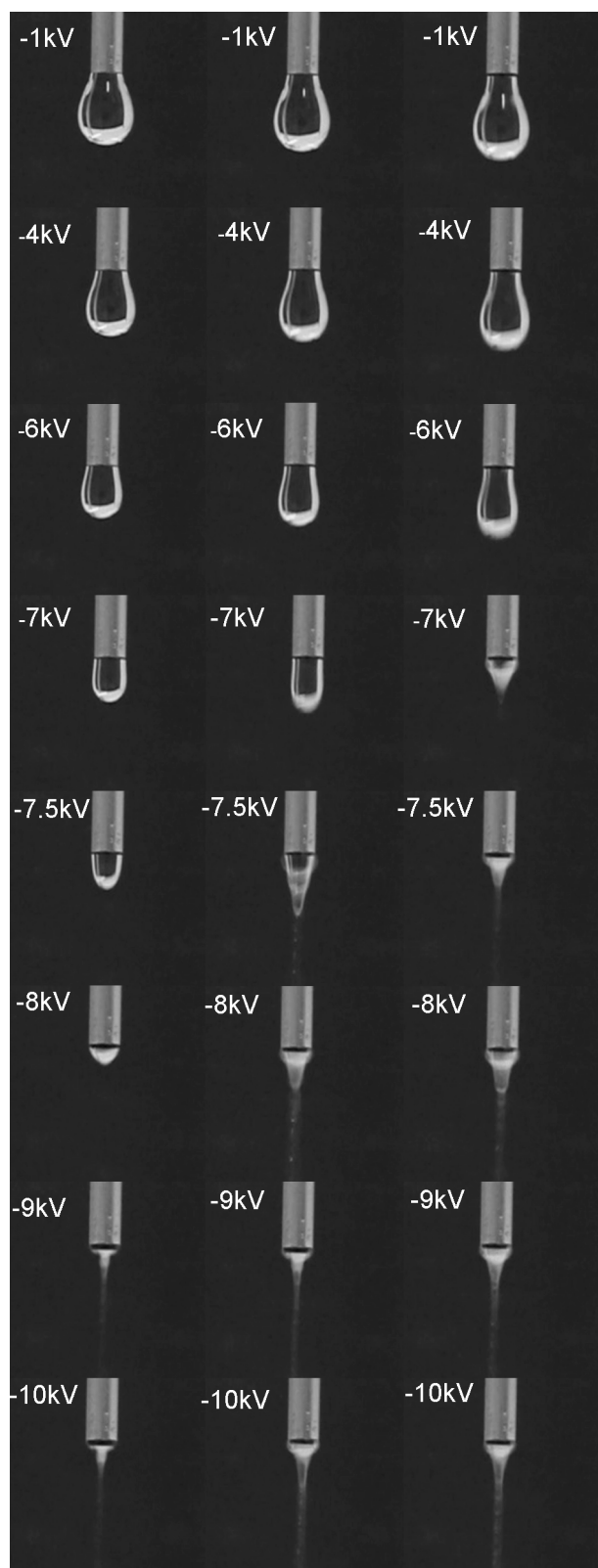


Figure 3. Water exiting the tip of a biased needle, showing Taylor cone formation, drop elongation, and Coulombic explosion at high V . Water flow: 64.1 mL/h. Distance from needle tip to the nearest grounded surface was ~ 10 cm. Extracted from Video 1. Pictures were chosen to represent interesting features, and time interval between them is not uniform.

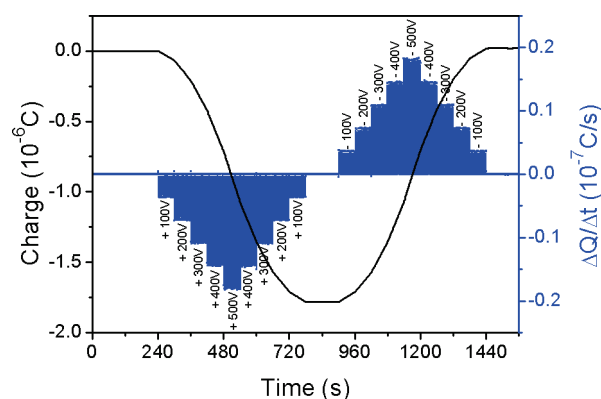


Figure 4. (Black) Accumulated charge within the Faraday cup by collecting water dropping from a grounded needle and passing through the center of a noncontacting biased ring. (Blue) Electric current of individual drops, calculated dividing charge increments by the corresponding time interval.

Table 2. Charge Accumulated in Water Dropping from a Grounded Needle and Through the Center of a Biased Metal Ring as a Function of V , Extracted from Figure 4

ring voltage/V	number of drops ^a	charge ^a /10 ⁻¹⁰ C
0	61 (60) (60)	5 (4.4) (1.4)
100	29 (31)	-668 (-718)
200	31 (31)	-1427 (-1428)
300	31 (30)	-2132 (-2072)
400	32 (30)	-2942 (-2759)
500	32	-3675
-100	31 (31)	720 (721)
-200	30 (31)	1387 (1433)
-300	30 (31)	2071 (2152)
-400	31 (31)	2858 (2864)
-500	33	3799

^a Values obtained in separate steps at the same V but in the decreasing branches are given in parentheses.

the drop shape and thus an apparently lower surface tension than measured under much lower fields.

To verify the effect of surrounding objects and electric fields on the surface tension measurements, these were repeated by positioning a grounded metal plate next to the water drop hanging from a needle. Figure 7 shows a scheme of the geometrical arrangements used together with the measurement results. The grounded plate and thus the electric field between it and the electrified drop distort the surface tension results if the grounded plate is within a few centimeters from the water drop. Thus, reliable surface tension measurements are necessarily obtained under low electric fields, this means, holding the electrified water drops as far as possible from any grounded surface.

DISCUSSION

Water with excess charge is easily obtained and kept under laboratory conditions, at room temperature and in contact with the atmosphere, using the two different methods described in this work.

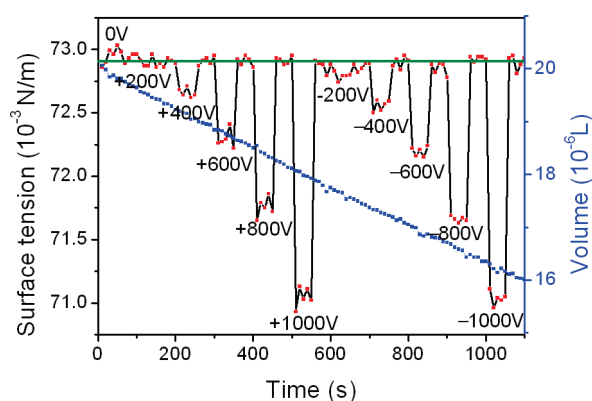


Figure 5. Consecutive γ measurements of a water drop hanging from a needle that was successively grounded and biased. Green line: average γ at 0 V. Distance between droplet and nearest grounded surface is 5.5 cm.

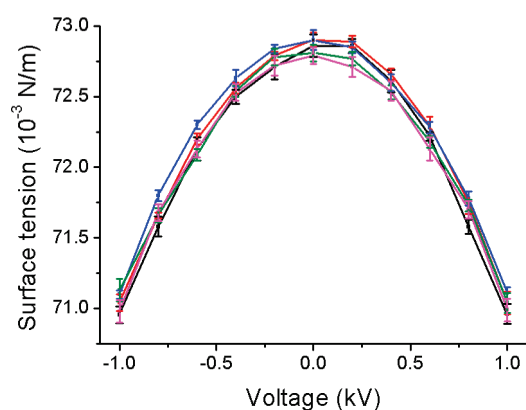


Figure 6. Plots of γ of a water drop hanging from a biased needle vs. needle V (quintuplicate runs). Distance between droplet and nearest grounded surface is 5.5 cm.

Electrostatic effects on the surface tension of liquids have already been considered in the literature³⁵ but considering dipolar liquids without net excess charge. These authors found that increasing the applied field tends to reduce the thermodynamical surface tension, but at the rather strong field of $E \approx 10^8$ V/m, when dielectric breakdown already takes place for many systems.

Below -9.5 kV, water with excess charge shows spontaneous increase in surface area, 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 7.

Spontaneous increase of water surface area is opposed to the usual minimum area for a water drop that is expected under gravity, but it is consistent with the idea of a negative surface tension, according to eq 4

$$\left(\frac{\partial G}{\partial A}\right)_{p,T,n} = \gamma \quad (4)$$

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

The idea of “negative surface tension” is not frequently found, but it was raised by important authors like Tolman and

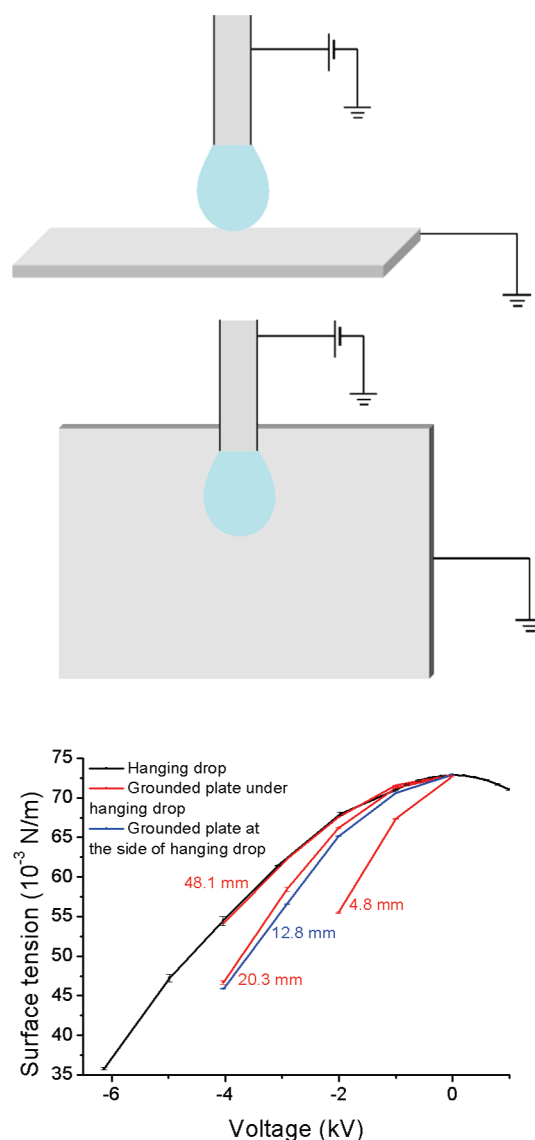


Figure 7. Top: Schematic description of the geometrical arrangement of a grounded metal plate near the water drop hanging from a needle. Bottom: Plots of γ of a hanging water drop vs V obtained by changing the position of the grounded metal plate.

Harkins,^{36,37} it is found in current literature,^{38–40} 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. Figure 8 shows results calculated from data shown in Figure 2, evidencing 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.⁴¹ 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 are mainly due to the large resulting electric fields. This was previously hinted at by Taflin and coauthors.⁸

There is an analogy between water charging in the air with charge accumulation at the water/mercury interface in

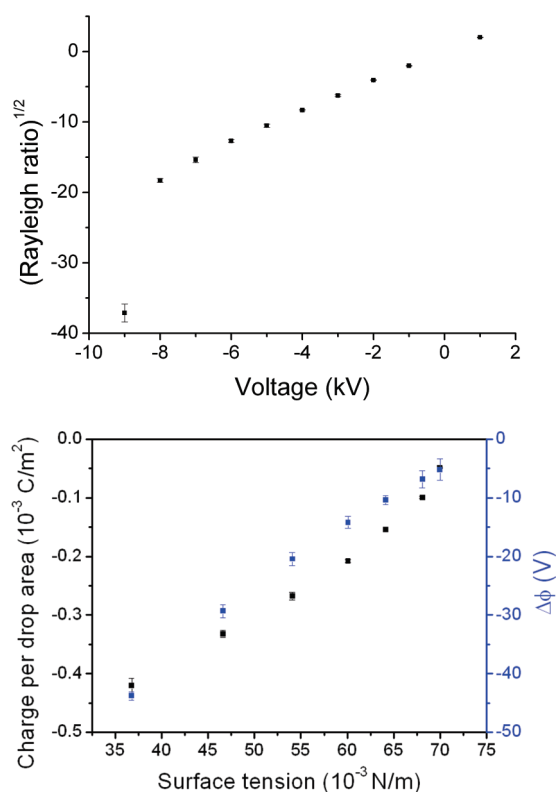


Figure 8. Top: Square root of the Rayleigh ratio (X in eq 2) for water drops formed slowly (33.3 mL/h) and under low fields at various needle voltages. Bottom: Potential difference across the water–air interface (calculated using eq 9) and water drop charge per unit area, as a function of the surface tension.

electrocapillarity. The usual Gibbs isotherm treatment for surface tension in an electrified interface leads to eq 5

$$\left(\frac{\partial\gamma}{\partial\phi}\right)_{T,\mu} = -q \quad (5)$$

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. However, we can calculate $\Delta\phi$ by solving eq 6

$$\Delta\phi = \int_{\gamma(V=0)}^{\gamma} -\frac{1}{q(\gamma)} d\gamma \quad (6)$$

where $q(\gamma)$ was obtained by regression of the experimental data for q and γ given in Figure 2, within the -1 to -7 kV applied voltage range.

The regression equation is

$$q(\gamma) = 0.24852\gamma^2 - 0.01656\gamma - 0.000112169 \quad (7)$$

Insertion of eq 7 into eq 6 gives eq 8

$$\Delta\phi = \int_{\gamma(V=0)}^{\gamma} -\frac{1}{0.24852\gamma^2 - 0.01656\gamma - 0.000112169} d\gamma \quad (8)$$

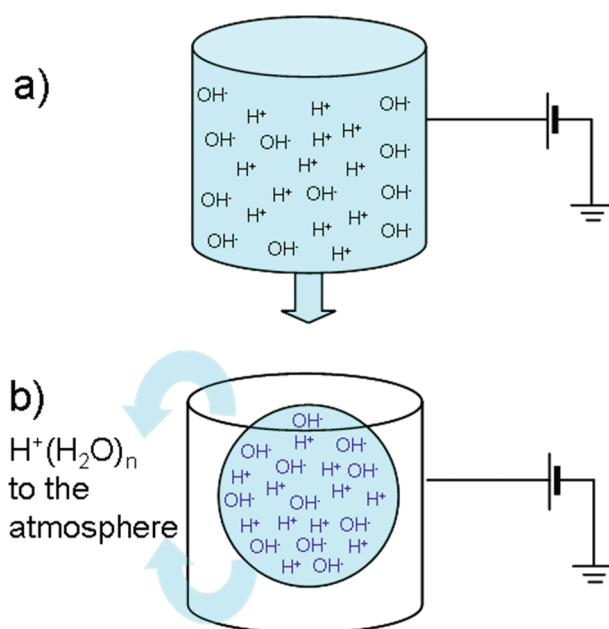


Figure 9. Schematic descriptions of charge buildup on water: (a) water dropping from a biased needle; (b) water dropping from a grounded needle but passing through a noncontacting biased ring.

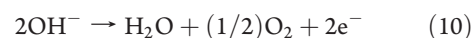
that can be integrated⁴² yielding (eq 9):

$$\Delta\phi = -50.915906 \ln \left| \frac{0.497048\gamma - 0.0362003}{0.497048\gamma + 0.0030803} \right| \quad (9)$$

Equation 9 was solved using experimental data for q and γ represented in Figure 2 and the calculated $\Delta\phi$ are in Figure 8, showing that the potential difference between the electrified drop and the surrounding atmosphere is much smaller than the voltage applied to the water drop. For instance, the potential drop at the water–air interface amounts to -14 ± 1 V only, when the needle bias voltage is -4 kV. The small potential difference across the interface is explained considering that the gas phase adjacent to the interface also contains a significant concentration of ions producing a large negative potential relative to the ground.

As for the water charging mechanisms, we suggest the following (Figure 9):

- (1) Water acquires charge when it is in direct contact with a positive needle because negative ions (OH^- , HCO_3^- , and others) are attracted to the metal surface, where they are discharged (eq 10).



Thus, 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 9a).

- (2) On the other hand, when a neutral water drop formed in a grounded needle passes through the center of a positive biased metal ring, the electrochemical potential of H^+ ions increases and these ions leave the drop, associated to water molecule clusters. The falling drop then acquires excess negative charge (Figure 9b). This is a direct proof

of ion evaporation that is one of the competing models for charged droplet formation in electrospray.^{43,44}

The mechanism described in Figure 9a 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.

Since surface tension is strongly connected to cohesion of solids and liquids, the phenomena described in this work should have a strong effect on water dispersion colloidal properties and on water solvency and phase transitions, including atmospheric phenomena.³

CONCLUSION

Nonelectroneutral water is reproducibly obtained using simple but well-defined experimental setups. Under low electric fields and slow water flow, charge acquired by static water drops and bulk water is well in excess of the Rayleigh limit. Electrified water γ 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.

ASSOCIATED CONTENT

S Supporting Information. Plot of surface tension vs charge per drop volume. This material is available free of charge via the Internet at <http://pubs.acs.org>.

W Web Enhanced Feature. A video showing water dropping from a biased needle is available.

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