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Electrowetting: a recent outbreak

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Abstract

This paper deals with recent developments of electrowetting, i.e. the facility of modifying the spreading of a liquid on a substrate by bringing electrostatic charges on the latter. This field of research is currently seeing a revival, particularly since the interspersing of an insulator to prevent charge leaking from the substrate interface, greatly improves this phenomenon. Such electrowetting on an insulator coated electrode (EICE) concerns the majority of recent work. Some of the present studies concern the limitations of this phenomenon, whose physics is not yet fully understood, whilst others exploit EICE, either for various academic purposes or in practical situations. These are presented in the last paragraph, as well as applications of classical electrowetting.

Keywords: Electrowetting; Contact angle; Electrocapillarity; Insulator

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1. Major recent advances (1998–2000)

Electrowetting on insulator coated electrodes (EICE), using an electrode covered by an insulating film as the substrate for a conducting water drop, enables production of large and reversible contact angle variations, opening a wide field of applications in the areas of biology and microphysics. Recent progress in understanding the fundamental limitations of this phenomenon, like saturation, highlights the special role of the three-phase contact line.

2. Introduction

Lippmann recognized that externally added electrostatic charge can significantly modify the capillary forces at an interface [1]. Already at this time, electrocapillarity was used both in applications (Lippmann constructed an electrometer based on the capillary rise of a polarized mercury-electrolyte interface) and to obtain first-grade microscopic information about liquid interfaces. In the 1930s, Froumkine and co-workers referred directly to the same principle to investigate situations where an electrolyte wets a polarized metallic surface against air [2]. More recently, the effect could be made sharper by grafting electroactive-terminated alkane-thiol molecules to the metallic surface [3]. Meanwhile, another configuration was investigated; instead of a simple metallic substrate, a layered structure made of a conductor covered by an insulating film of macroscopic thickness produces large wettability changes [4]. We call this effect electrowetting on insulator coated electrodes (EICE). The robustness, reversibility, simplicity and low-cost of this new process facilitates various applications and the development of new devices. Nevertheless, the large separation of charges on both sides of the insulator means that electrostatic interactions are much less screened, introducing new physics. The

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basic limitations of electrowetting, like saturation phenomena or instabilities, still need to be understood.

Several text books present excellent descriptions of classical electrowetting studies [5,6]. As presented in Fig. 1a, the charges at the interface form a parallel plate capacitor in which the gap thickness is of the order of the Debye-Hückel length. It is possible to polarize the interface without creating any crossing current as long as the potential difference is maintained between the thresholds for oxidizing and reducing the surface. Lippmann understood how the metal–electrolyte interfacial tension evolves in the case of a solid metal, as:

$$\frac{d\gamma_{\mathrm{SL}}}{dV} = -\sigma \qquad (1)$$

where γ_{SL} is the solid–liquid interfacial tension, V the voltage difference applied across the interface and σ the surface charge density. For partial wetting, the Young equation combined with the derivative of Eq. (1) gives:

$$\frac{d^2\cos(\theta)}{dV} = \frac{c}{\gamma} \qquad (2)$$

where θ is the contact angle of the liquid, γ its surface tension and c the easily measured solid–liquid capacitance (capacity per unit surface) [7•].

In EICE (Fig. 1b), an insulating film of macroscopic thickness, ranging typically from micrometers to hundreds of micrometers, is deposited on a conducting solid and an electrostatic potential, a.c. or d.c., is applied between this electrode and a droplet lying on the insulator. We suppose the liquid to be a much better conductor than both the insulating film and the surrounding fluid (gas, oil etc.). This situation was first analyzed in 1993, although experiments existed before this [8–11]. We can deduce the evolution of the contact angle from Eq. (2) [4]:

$$\cos\theta = \cos\theta_0 + \frac{c}{2\gamma}V^2 \qquad (3)$$

where θ_0 is the contact angle in the absence of a field. Here the presence of a macroscopic insulating film changes the orders of magnitude of the voltage V necessary to affect the contact angles significantly. From Eq. (3) V equals:

$$V \approx \sqrt{\frac{\gamma}{c}} \approx \sqrt{\frac{e\gamma}{\varepsilon\varepsilon_0}} \qquad (4)$$

with the capacitance c being ~ 100 pF/cm^2 for EICE, while in conventional studies on bare metal surfaces, c is at least 10^4 times larger (e and ε are the insulator thickness and permittivity, respectively.). Thus, instead of the 100 mV necessary to drive a bare metal–electrolyte interface, the EICE currently needs hundreds of volts, which is not prohibitive as long as

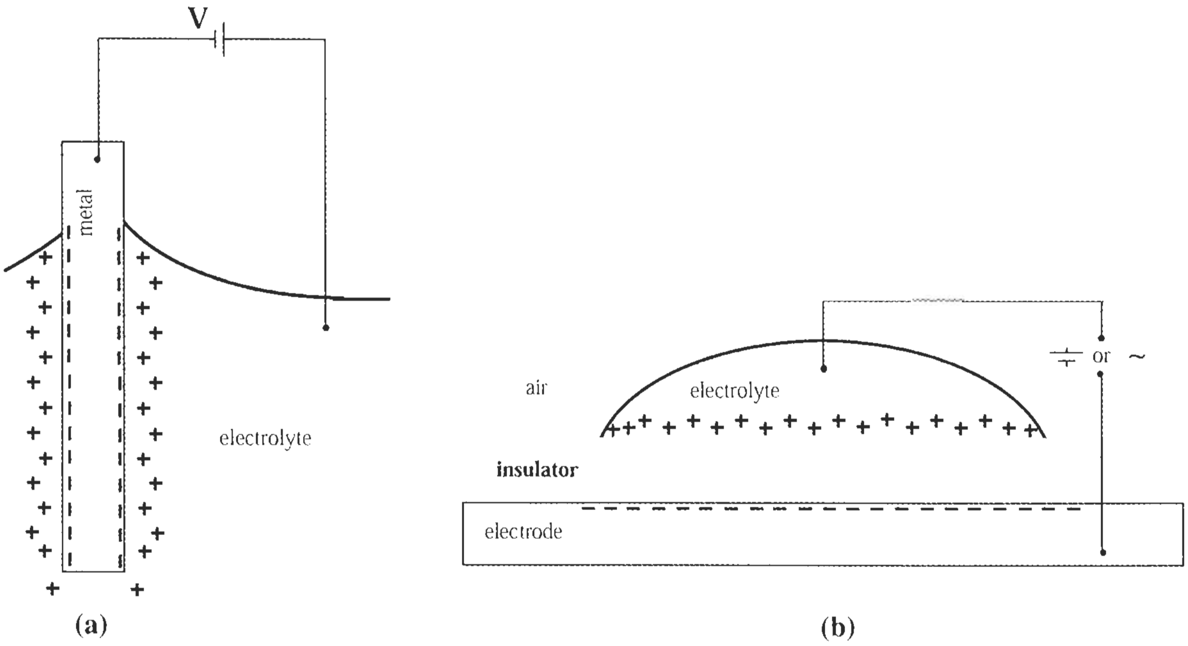

Fig. 1. (a) Classical electrocapillarity set-up; in the absence of charge exchange between metal and electrolyte, the configuration energetically favours an increase of the metal-electrolyte surface contact. Charge separation ~ 1 nm. (b) Intercalation of an insulator between the aqueous phase and the electrode increases charge separation (1–100 μm). The so-called electrowetting on insulator coated electrodes (EICE) allows large changes of contact angle with robustness, reversibility and flexibility.

the electric field remains under the breakdown threshold in the insulator. If we feed into Eq. (4) typical orders of magnitude, we find that the driving voltage for a commercial plastic film ($e \sim 12$ μm, $\varepsilon \sim 3$ for polyethylene, $\gamma \sim 70$ mN/m for a water solution containing no surfactant) is approximately 170 V. Since this voltage is far below the dielectric breakdown, the insulator is likely to undergo little degradation due to the applied voltage, which is good for practical applications. This is the main benefit of using an insulator, where Froumkine and others have experienced contact angle variations of a few tens of degrees, similar to what EICE can do (up to 80° [12•,13••]). Other advantages include numerous possibilities of control, with proper design of the electrodes or of the insulator.

In this review, we first present recent progress on fundamental problems: what happens at the wetting line, and how experiments sometimes depart from the theory. Then we detail briefly some new applications of electrowetting.

3. Understanding the wetting line

Far from the wetting line, the charge density in EICE is constant and small compared to usual electrocapillarity; for an insulator of 12 μm subject to a voltage of 200 V, one gets $\sigma \sim 4.5 \times 10^{-4}$ C/m^2. Near the wetting line, the parallel plate approximation may lose validity since the edge of the drop is likely to behave like a sharp-edged conductor. Verheijen and Prins [14••] calculated that the resulting stray capacitance modifies the parallel plate calculation of the global capacity by a few percent only. On the other hand, excess charge accumulated at the edge of the conducting droplet (Fig. 2a), although representing a few percent, gives rise to several new phenomena:

1. Reduced coalescence of neighboring droplets due to repulsion by edge charges (see Fig. 2b).
2. When the voltage is sufficiently high, small droplets form which are expelled from the main drop [15,16]. A simple theory dealing with electrostatic phenomena at the line perimeter accounts for the order of magnitude of the voltage where this instability occurs; it explains the experimentally-observed size-dependence of the expelled droplets with the insulator thickness [13••]. A hand-waving argument equates the size of the emitted droplets to the only length scale in the problem (the dielectric coating thickness *e*) — close to the imprecise experimental observations. A remaining difficulty is to understand why this electrostatically driven instability is apparently suppressed when salt is added to the water solution.
3. For a given liquid–gas interface shape we can, in principle, calculate the charge profile along the solid–liquid interface and along the liquid–gas interface. If, as assumed in Fig. 2a, the radius of curvature of the interface at the edge is small compared to the dielectric coating thickness *e*, then the excess charges are expected to be significant in a region of size *e* close to the edge. Those charges at the liquid–gas interface should increase the curvature of the meniscus, which Vallet attempted to observe without much success [15].

It is now clear that many important phenomena happen at or near the wetting line. For instance it is difficult to understand how the Debye–Hückel length

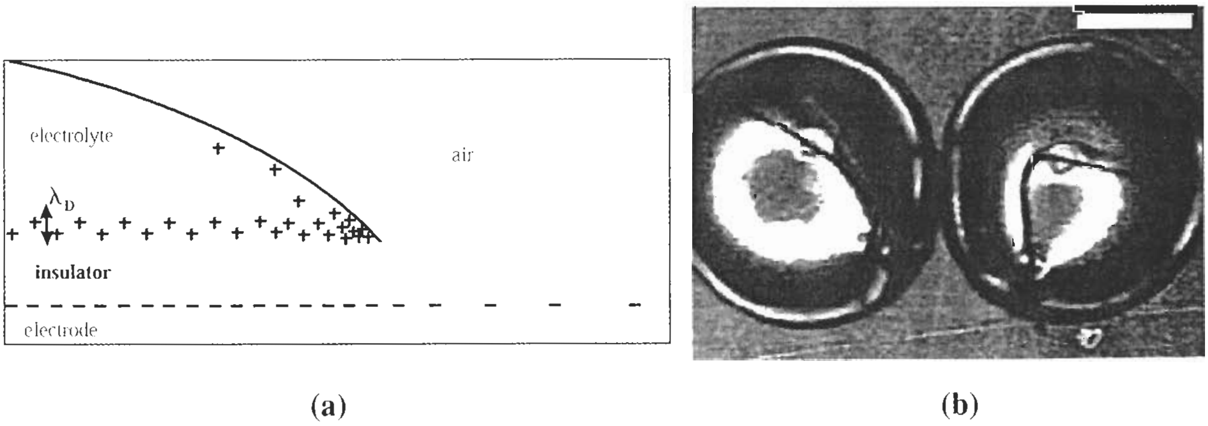

Fig. 2. (a) Schematic representation of the situation found in EICE; surface charge at the solid-liquid interface is constant, except near the contact line where charge accumulates due to the electrostatic edge effect. (b) Experimental evidence for charges at the border of the drop; the borders of two sessile drops experience repulsion. As they spread by electrowetting, they do not coalesce since a small dry gap remains between the drops. Bar = 1 mm.

enters in the problem, apart from being a natural cut-off length at small length scales. Experimental studies as well as theoretical analyses would certainly be helpful.

4. Mechanisms of saturation and deviations from thermodynamics

Almost all publications that display the quantitative evolution of the contact angle with electric field [4,12•,13••,14••,16–19•,20•], show at some point discrepancies with Eq. (3). To our knowledge, saturation is present in all situations (EICE stops working at some high voltage [12•,13••,16,18,19•]). But even at low voltages some experiments show a quadratic dependence of the cosine of the contact angle on the voltage, with a smaller coefficient than predicted by the thermodynamic relation Eq. (3) [12•,19•].

4.1. Saturation effects

At high fields, the contact angle variation slows down more or less gradually, saturating before reaching total wetting. This happens in a different way for a.c. and d.c. experiments. For a.c., saturation occurs concomitantly with air ionization in the vicinity of the sharp droplet edge [13••]. The resulting charge which crosses through the ionized air, from the edge to the insulator surface surrounding the droplet, reduces then stops the electrowetting effect. An hydrophilic ring which marks the insulator at the outside of the droplets suggests that the charges damaged the hydrophobic surface. In d.c. experiments, charge trapping in the insulator is invoked [18], which is likely to cause the hydrophilic disk observed a posteriori at the exact location of the droplet; but there is no predictive model for this at the moment. As this process is expected to be weaker in a.c. experiments, d.c. electrowetting efficiency may differ from that of a.c. Similarly, we may notice that saturation in published d.c. experiments occurs 'sooner', i.e. for higher contact angles (60 to 100°) [12•,18] than for a.c. experiments (~ 30°) [13••,16]. Experiments performed with both a.c. and d.c. voltages on the same system [19•], seem to confirm this tendency of better spreading through a.c., but it is hard to estimate the extent since contact angle values are not provided. Of course, both effects can overlap; Blake et al. [19•] report a tentative increasing field far beyond saturation in a d.c. experiment, that created an exterior hydrophilic ring as in a.c.: air ionisation may occur for a high enough voltage if the electrical breakdown due to charge injection is not sufficient. There is, in any case, a lack of systematic studies of this phenomenon.

4.2. Deviations from thermodynamics

Reference [19•] presents an experiment performed in direct current (d.c.) where the wetting evolution with the electrostatic field follows Eq. (3) between 0 and 450 V (before saturation), just as in references [14••,17,18,20•] except that the V^2 coefficient is approximately $c/4\gamma$ instead of $c/2\gamma$. A thermodynamic analysis was done in this special case, with which we do not agree, but this is out of the scope here. Let us simply remark that a.c. experiments exposed in the same publication do fit Eq. (3). In-situ charge and current measurements and experiments using different waveforms (square, sinusoidal, triangle) should clarify the situation.

In another 'exception to the rule', decane (insulating) droplets with constant volume were surrounded by (conducting) water, and a d.c. voltage was applied to the latter [12•]. Many substrates were tested: the more hydrophilic ones saturated at once; one was consistent with Eq. (3) for increasing field but very hysteretic; and some others had a nearly quadratic behaviour with a different coefficient (a factor of 0.15 to 0.25 instead of 0.5 for Eq. (3)). The authors invoke the surface roughness of the polymer, which is, in our opinion, not typical of the presented experiments, and probably insufficient to explain such a large discrepancy.

4.3. Reversibility

Some references present reverse electrowetting data (with decreasing potential) [12•,16,18,19•,20•,21•]. The most recent ones show much improved reversibility [12•,14••,21•]. It has to be noticed that EICE allows the use of a multi-dielectric layered structure for the insulator film. The Philips group, for instance, used substrates where a 10-μm first layer of Parylene (a polymer known for its insulating properties) is covered with a thin Teflon-like coating (sometimes oil-impregnated) [14••,17,18], to obtain a remarkably low-hysteresis surface.

5. Applications

Besides its importance to industrial coatings (reference [19•] gives a recent example), other striking applications of electrowetting have emerged recently.

5.1. Wetting dynamics

Thanks to its ability to change a droplet's shape from its equilibrium configuration with a fast control parameter (the electrostatic field), electrowetting is suitable for studying dynamic aspects of wetting. Ref-

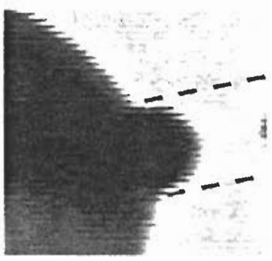

Fig. 3. Creation of a hydrophobic defect through inverse electrowetting. In black; detail of a sessile oil droplet in a salt water environment, viewed from above. The authors designed the experiment to produce a smaller field between the two dashed lines (1.6×10^6 V/m) than outside them (3.8×10^6 V/m). As the field is directly proportional to the surface charge, electrowetting should induce a less hydrophilic zone (here a strip of width 0.9 mm), which then wets oil, in a uniform background.

erence [14••] shows that capacitive measurements provide contact angle values in a much more rapid and automatable way than direct image methods, making a performant tool for dynamic measurements. In reference [22], unsteady wetting is generated through Froumkine-like electrocapillarity. The other publications check the validity of the molecular-kinetic theory in EICE, with diverging results for the constancy of pertinent parameters [19•,20•].

5.2. Oil-in-water electrowetting

Wetting of oil droplets in a water environment is a very promising system as it presents weak hysteresis [21•], allowing creation of flat wetting defects controlled by a local field to study additional hysteresis (Fig. 3). It should also allow de-wetting transitions controlled by the electric field, for initial total wetting. Experiments by Janocha et al. [12•] show, nevertheless, that the choice of substrate material is crucial to obtain good reversibility.

5.3. Microelectromechanical devices

Microactuation provides a golden opportunity for the application of electrowetting, which has just been realised. We are aware of three examples; in the first, a mercury droplet follows a potential drop ('continuous electrowetting') in an electrolyte solution, its movement dragging a micromotor [23,24]. The second [25] presents microlabs in which aqueous solution droplets move and possibly mix in an oil environment on paths made from electrically-isolated electrodes. In the third example, electrowetting in high density microcell devices [26•] drives the contact angle above and below 90°, reversibly; it is thus possible to build a device which is at will filling and emptying a capillary or porous medium. A possible application is a spatially programmable filter, consisting of multiplexed channel structures filled with absorbing liquid (e.g. X-ray absorbers) [17,26•].

5.4. Electrical engineering

Recent works noticed that flashover performances of insulators depend strongly on atmospheric humidity and the wetting properties of the insulator surface [27,28], a phenomenon that obviously derives from electrowetting.

5.5. Optics

A recent paper exploits EICE to create gradients of wettability, by simply producing an insulating layer of inhomogeneous thickness [21•], to precisely center an oil drop inside a transparent water compartment. 'Classical' electrowetting could not achieve such precise control [29]. Reference [21•] thus presents a focusing lens, whose optical power can be electrically controlled. As for other studies, the reversibility is surprisingly good, producing cheap, practical devices that work very well.

6. Conclusion

During the past few years, EICE (electrowetting on insulator coated electrodes) has been studied more and more. Its versatility, robustness and reversibility made possible emerging applications like microlabs, adaptative optics or microactuation. Nevertheless, EICE involves new physics which is still only partially understood. For instance, the partial screening of excess charges present at the contact line demands detailed experiments. EICE should also be considered as a new and precise tool for studying other problems in classical colloid and interface physics (wetting transitions, hysteresis, porous media etc.) or in other fields like biology.

References and recommended reading

- • of special interest
- •• of outstanding interest

[1] Lippmann G. Relation entre les phénomènes électriques et capillaires. Ann. Chim. Phys. 1875;5:494–549.

[2] Froumkine A. Couche double. Electrocapillarité. Surtension. Actualités Scientifiques 1936;373:5–36.

[3] Sondag-Huethorst JAM, Fokkink LGJ. Potential-dependent wetting of electroactive ferricene-terminated alkanethiolate monolayers on gold. Langmuir 1994;10:4380–4387.

[4] Berge B. Electrocapillarité et mouillage de films isolants par l'eau. C.R.A.S. III 1993;317:157–163.

[5] Adamson AW. Physical chemistry of surfaces. 5th edn New York: John Wiley and Sons Incorporated, 1990.

[6] Antropov L. Electrochimie théorique. Mir eds Moscou, 1975.

[7]
•
A paper about the theory of electrowetting (Digilov R. Charge-induced modification of contact angle: the secondary electrocapillary effect. Langmuir 2000;16:6719–6723.) claims that the spreading of an electrified water drop is not a surface tension, but rather a line tension effect. If true, this effect would lead to a dependence of the contact angle on the size of the droplet, observed in none of the experiments presented in this review. In addition a detailed discussion of the distribution of charges at the three-phase contact line can be found in Refs. [13••,18], but the author does not make any reference or comparison to them. Finally no convincing arguments against the classical Lippmann treatment are presented.

[8] Minnema L, Barneveld HA, Rinkel PD. An investigation into the mechanism of water treeing in polyethylene high-voltage cables. IEEE. Trans. Electr. Insul. 1980;EI-15:461–472.

[9] Sheridon NK. Electrocapillary imaging devices for display and data storage. Xerox. Disclos. J. 1979;4:385–386.

[10] Sheridon NK. Electrocapillary color display sheet. U.S. Pat. 1997;No. 5659330.

[11] Hato M. Electrically-induced wettability change of polyaniline. Potential controlled tensiometric study. Chem. Lett. 1988;1:1959–1962.

[12] Janocha B, Bauser H, Oehr C, Brunner H, Göpel W. Com-
• petitive electrowetting of polymer surfaces by water and decane. Langmuir 2000;16:3349–3354.

Many polymer substrates are investigated in inverse (water in decane) electrowetting.

[13] Vallet M, Vallade M, Berge B. Limiting phenomena for the
•• spreading of water on polymer films by electrowetting. Eur. Phys. J. (B) 1999;11:583–591.

Detailed analysis of saturation and electrostatic instability for ac driven systems.

[14] Verheijen HJJ, Prins MWJ. Contact angle and wetting veloc-
•• ity measured electrically. Rev. Sci. Instrum. 1999;70: 3668–3673.

Highly reversible system plus fast capacitive measurement of contact angle.

[15] Vallet M. Etude des phenomènes limitant l'étalement de solutions aqueuses sur des films de polymères par électromouillage. Thesis Univ. J. Fourier, Grenoble, 1997.

[16] Vallet M, Berge B, Vovelle L. Electrowetting of water and aqueous solutions on poly(ethylene terephthalate) insulating films. Polymer 1996;37:2465–2470.

[17] Welters WJJ, Fokkink LGJ. Fast electrical switchable capillary effects. Langmuir 1998;14:1535–1538.

[18] Verheijen HJJ, Prins MWJ. Reversible electrowetting and trapping of charge: model and experiments. Langmuir 1999;15:6616–6620.

[19] Blake TD, Clarke A, Stattersfield EH. An investigation of
• electrostatic assist in dynamic wetting. Langmuir 2000; 16:2928–2935.

In this paper and the following, EICE is used to investigate the molecular–kinetic theory of dynamic wetting.

[20] Schneemilch M, Welters WJJ, Hayes RA, Ralston J. Electri-
• cally-induced changes in dynamic wettability. Langmuir 2000;16:2924–2927.

Cf. previous reference.

[21] Peseux J, Berge B. Variable focal lens controlled by an
• external voltage: an application of electrowetting. Eur. Phys. J. (E) 2000;3:159–163.

EICE allows the miniaturization of a focusing optical device without moving parts.

[22] Perng Y-Y, Lichter S. Unsteady wetting on a rough surface due to electrically altered surface tension. J. Colloid. Interface. Sci. 1999;217:119–127.

[23] Kim CJ, Lee J. Liquid micromotor driven by continuous electrowetting. Heidelberg, Germany: IEEE Micro Electro Mechanical Systems Workshop, 1998:538–543.

[24] Lee J, Kim C-J. Surface tension-driven microactuation based on continuous electrowetting (CEW). J. Microelectromechanical Syst. (to be published).

[25] Pollack MG, Fair RB, Shenderov A. Electrowetting-based actuation of liquid microdroplets for microfluidic applications. Applied. Phys. Lett. 2000;77:1725–1726.

[26] Prins MWJ. Multichannel structures made from micrometer-
• thick plastic foils. J. Micromech. Microeng. 1999;9:1–2.

Smart microchannel realization for electrocapillary liquid actuation.

[27] Moreno-Villa VM, Ponce-Velez MA, Valle-Jaime E, Fierro-Chavez JL. Effect of surface charge on hydrophobicity levels of insulating materials. IEEE. Proc. Gener. Transmiss. Distribution 1998;145:675–681.

[28] El-Kishky H, Gorur RS. Electric field computation on an insulating surface with discrete water droplets. IEEE. Trans. Dielectr. Electr. Insul. 1996;3:450–456.

[29] Gorman CB, Biebuck HA, Whitesides GM. Control the shape of liquid lenses on a modified gold surface using an applied electrical potential across a self-assembled monolayer. Langmuir 1995;11:2242–2246.