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J. Adhesion Sci. Technol. (2011) DOI:10.1163/156856111X599580

Journal of ADHESION SCIENCE and TECHNOLOGY
brill.nl/jast

Experimental Validation of the Invariance of Electrowetting Contact Angle Saturation

Stéphanie Chevalliot [a,b], **Stein Kuiper** [c] **and Jason Heikenfeld** [a,*]

[a] Novel Devices Laboratory, School of Electronic and Computing Systems, University of Cincinnati, Cincinnati, OH 45221, USA

[b] School of Energy, Environmental, Biological and Medical Engineering, University of Cincinnati, Cincinnati, OH 45221, USA

[c] Philips Research Eindhoven, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands

Abstract

Basic electrowetting theory predicts that a continued increase in applied voltage will allow contact angle modulation to zero degrees. In practice, the effect of contact angle saturation has always been observed to limit the contact angle modulation, often only down to a contact angle of 60 to 70°. The physical origins of contact angle saturation have not yet been explained successfully and unequivocally. At best, scientists have produced multiple disconnected hypotheses (droplet ejection, charge injection, a thermodynamic limit, etc.) that do not satisfactorily hold for the large body of electrowetting experimental results. Herein we experimentally demonstrate that when using DC voltage, electrowetting contact angle saturation is invariant with electric field, contact line profile, interfacial tension, choice of non-polar insulating fluid, and type of polar conductive fluid or ionic content. The selected experiments were performed and designed using conventional electrowetting materials, without bias toward supporting a particular theory. Because the experimental results show such a strong invariance of saturation angle to multiple parameters, electrowetting saturation parallels many of the trends for Taylor cone formation. However, the contact line geometry is distinct from a Taylor cone, suggesting that some other (though related) form of electrohydrodynamic instability might cause saturation. Although this work does not unequivocally prove what causes contact angle saturation, it reveals what factors play a very limited or no role, and how dominant factors causing saturation may change with time of voltage application. This study thereby provides additional direction to the continued pursuit of a universal theory for electrowetting saturation.

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Keywords

Electrowetting, contact angle, saturation, dielectric

1. Introduction

Electrowetting research continues to increase in both academia and industry, largely due to potential application for lab-on-chip devices [1–3], adaptive optical systems

* To whom correspondence should be addressed. Tel.: 513-556-4763; e-mail: heikenjc@email.uc.edu

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[4–6], and electronic displays [7, 8]. In the case of partial wetting, the contact angle as a function of the applied voltage (θ_V) is given by the electrowetting equation [9]:

$$\cos\theta_V = \cos\theta_Y + \frac{CV^2}{2\gamma_{ci}} \quad \text{and} \quad C = \frac{\varepsilon_0\varepsilon_r}{d}, \quad \cos\theta_Y = \frac{\gamma_{id} - \gamma_{cd}}{\gamma_{ci}} \tag{1}$$

which includes the interfacial tensions (γ) between the conducting fluid (c) insulating fluid (i) and solid dielectric surface (d), θ_Y is the Young's contact angle, C is the capacitance per unit area of the dielectric of thickness d, V is the applied DC voltage or AC RMS voltage, ε_0 is the permittivity of vacuum, and ε_r is the relative permittivity of the dielectric. Although this equation (equation (1)) is widely accepted, different hypotheses have been advanced to derive it. In the thermodynamic and electrochemical approaches, electrowetting phenomenon is explained by the reduction of the interfacial tension between the dielectric and the conducting liquid, resulting from the induced electric charges at the interface [9]. Another method based on energy minimization considers that the free energy of a droplet contains both interfacial and electrostatic components [10]. Finally, in the electromechanical approach proposed by Jones [11, 12], the reduction of contact angle is viewed as a result of the forces exerted on the liquid by the electric field near the contact line. This last explanation is currently the most widely accepted, especially so after Mugele and Buehrle [13] observed that the microscopic contact angle remains at Young's angle and interfacial tensions do not actually change with voltage. According to the electrowetting equation (equation (1)), it should be possible to obtain complete wetting (zero contact angle) by continuing to increase the applied voltage. However, complete wetting has never been observed experimentally. Instead, experimental evidence shows that above a certain voltage the electrowetting contact angle starts to deviate from equation (1), after which it plateaus or in some cases even reverses with further increase in voltage. The exact mechanism of the contact angle saturation has not yet been elucidated and is the object of numerous debates [14]. Herein we experimentally validate that when using DC voltage, electrowetting contact angle saturation is invariant with electric field, contact line profile, interfacial tension, choice of non-polar insulating fluid, and type of polar conductive fluid or ionic content. Our experimental investigation was performed without bias toward supporting or disproving a particular saturation theory. Rather, the selected experiments were performed and designed using conventional electrowetting materials and test conditions. Importantly, all the experiments were carried out in oil as the insulating fluid (not air), which generally is the most commercially relevant approach. It will be seen that experimental data refute many previous hypotheses on contact angle saturation, parallel in several ways the physics of Taylor cone formation, and might further support that contact angle saturation is due to electrohydrodynamic instability at the contact line. The observed time dependence of contact angle will also suggest that the dominant factor in saturation could change with the duration of voltage application. This work does not solve the debate over contact angle saturation. However, it reveals what factors play a very limited or no

role, thereby helping give direction to the continued pursuit of a universal theory for electrowetting saturation.

2. Brief Review of Existing Saturation Theories

Several of the most widely referenced and debated theories on contact angle saturation are briefly reviewed in this section. It should be noted that saturation can be experimentally interpreted in two ways. First, the onset of saturation is commonly agreed upon as the point where the cosine of the electrowetting contact angle deviates from the parabolic behavior predicted by equation (1). Second, complete saturation can be seen when the contact angle ceases to respond to voltage (plateaus) or even begins to reverse. In some experiments, the onset of saturation can be more difficult to extract from the experimental data (requires some interpretation). As will be seen in the experimental results from this investigation, complete saturation is far more easily visualized in the specific experiments performed herein. Therefore in analysis of the data, the discussion will mainly focus on complete saturation.

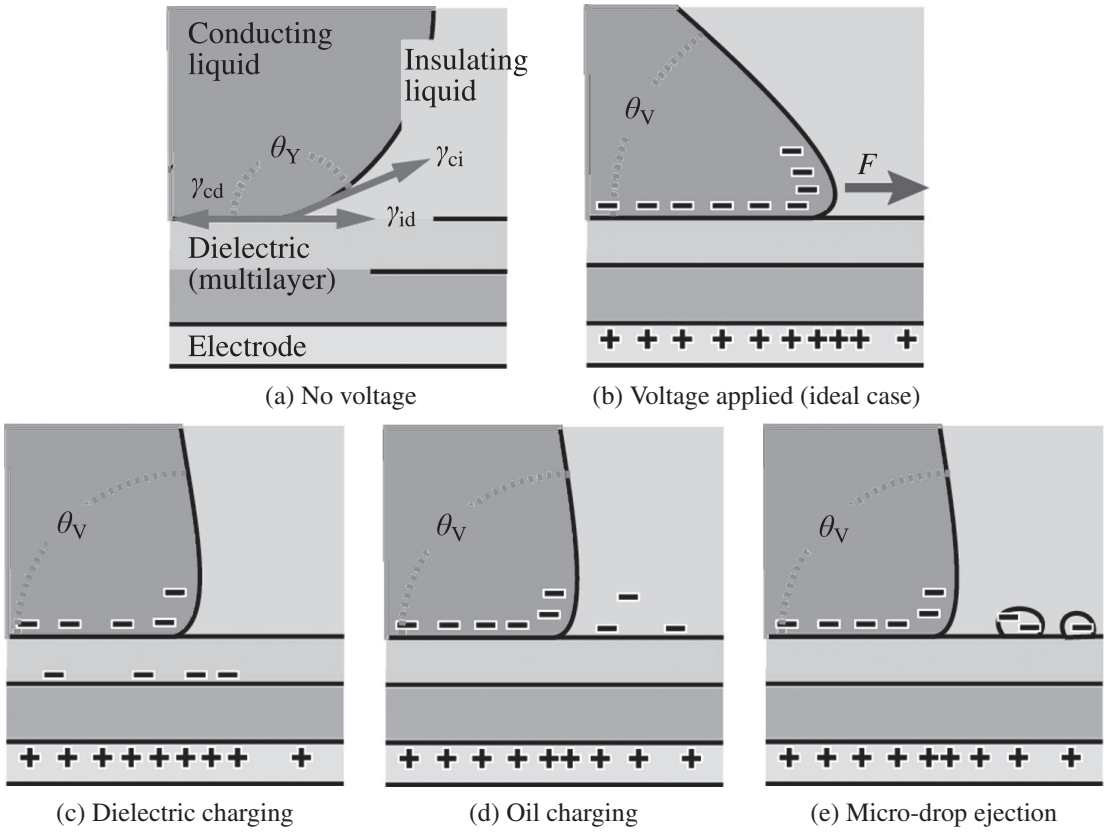
We now discuss several existing theories for saturation. Each of these theories can be used to describe complete saturation, or just the onset of saturation. It should be noted that in the discussion section, one new hypothesis will be discussed: microdroplet ejection similar to that observed from Taylor cones [15].

2.1. Hypothesis 1: "Dielectric Charging"

In the vicinity of the triple contact line (TCL), the electric field diverges and its strength reaches significantly high values. The TCL takes on a geometry similar to a wedge conductor, which can be used to predict the localized electric field enhancement. It has been proposed that this field enhancement can exceed the electrical insulation ability of the dielectric and charges are then trapped in or on the dielectric [16]. This trapped charge in the dielectric does not contribute to the electrowetting effect, and reduces the available electromechanical force by screening the electric field (Fig. 1(c)). The diverging field was thought by some researchers to lead to saturation through not charge injection, but through local breakdown (self-ionization) of the dielectric [17]. Regardless, either interpretation can be thought of as 'dielectric charging', and it is well known that charge injection into dielectrics or partial ionization and space charge generation [18] can occur at electric fields well below the electrical breakdown field.

2.2. Hypothesis 2: "Insulating Fluid Charging"

Although no articles have yet been published regarding the connection between charging of the insulating fluid (the oil) and saturation, it is also a fully possible theory. The insulating fluid is an organic material just like many of the dielectrics used, and in some cases is exposed to similar electric fields at which electrical insulation fails. A strong 'relaxation' of the contact angle is often observed in electrowetting displays [19] and optics [20] when using insulating fluids that consist of



(a) No voltage (b) Voltage applied (ideal case)

(c) Dielectric charging (d) Oil charging (e) Micro-drop ejection

Figure 1. Diagrams of (a), (b) ideal electrowetting from Young's angle (θ_Y) to the electrowetting contact angle (θ_V) as a result of the electromechanical force (F) with no contact angle saturation, and (c), (d), (e) several hypotheses for the cause of electrowetting saturation.

molecules with a non-zero dipole moment such as chloronaphthalene, or that contain a polar additive in the fluid such as a dye or surfactant. In patent literature it has been suggested that polar molecules in the insulating fluid facilitate charge injection into the oil [21], because they show increased affinity for ions from the conductive fluid. Charge injection from the conducting liquid into the oil may also occur under influence of the high local electric field according to the Iribarne-Thompson ion evaporation effect [22]. Iribarne and Thompson found that high electric fields may directly release ions from the bulk liquid before droplet ejection occurs. Their experiments were done in air, but the results might well be translated to an oil ambient.

The dissolved or injected ions will drift towards the electrode and accumulate on the insulator surface, where they screen the electric field and cause contact angle relaxation (Fig. 1(d)). Nearly all insulating fluids used in electrowetting can be classified as oils, hence this effect will be referred to as 'oil charging'. The effect can be compared to the relaxation that occurs in liquid crystal displays under DC driving. Liquid crystals are insulating liquids that could, in principle, be driven under DC conditions. However, charged impurities dissolved in the liquid crystals will mi-

grate towards the electrodes, thus shielding the field. For that reason liquid crystal displays are driven under (low frequency) AC conditions.

2.3. Hypothesis 3: "Instabilities, Micro-droplet Ejection and Gas Ionization"

Early experiments with conducting droplets on thick dielectrics surrounded by air led to the observation of spontaneous micro-droplet ejection from the contact line around the saturation (AC) voltage [23, 24]. It was suggested that the diverging charge density at the TCL causes surface instabilities beyond a certain voltage. The electromechanical force and self-repulsion of like ions might be increased to the extent that micro-droplets can be ejected spontaneously from the electrowetting droplet. These ejected charged droplets are driven to the insulator surface, where they accumulate and screen the electric field (Fig. 1(e)). This effect could very well contribute to saturation. However, Vallet *et al*. [23] found that adding salt to the pure water suppressed micro-droplet ejection. Instead, they observed air ionization and formation of a hydrophilic ring just outside the TLC. What they may have observed is the transition from drop ejection to ion evaporation due to the earlier mentioned Iribarne–Thompson effect, which depends on conductivity of the liquid [25]. Recently, the micro-droplet ejection hypothesis was theoretically supported by a publication [26] in which it was mathematically shown that electrowetting drops cannot spread indefinitely by introducing a sufficient amount of electric charges, but only can reach a limiting (saturation) size. After that, the axial symmetry would be lost and finger-like shapes would be electrically preferred. It was mentioned by Mugele that the effect has some, but limited, similarities to the well-known Taylor cone instability of electrified liquid jets [14]. It has not been investigated whether or not this effect can occur in an insulating fluid like oil. For a conducting fluid like water surrounded by oil, as surfactants are added interfacial tensions are reduced, sometimes by an order of magnitude in comparison to water in air. Therefore, micro-droplet ejection into the oil is a possibility. This idea is supported by the observation that AC voltage as well as DC voltage can be used for water/oil emulsification [27, 28]. One might expect to see micro-drops build up over time, but this may not occur due to electric field screening. Only little charge (few drops) may be needed to screen the electric field and stop the ejection process. The authors at Cincinnati have observed AC emulsification in electrofluidic displays. 'Micro-droplet ejection' should then also be considered in the analysis presented herein.

2.4. Hypothesis 4: "Zero Interfacial Tension"

Finally, some researchers attribute saturation to a thermodynamic limit of stability [29, 30]. They suggest that the interfacial tension between the conducting fluid and dielectric (γ_{cd}) has to remain positive for the interface to be stable. Thus, saturation occurs when this interfacial tension reaches zero. However, this hypothesis is in conflict with the accepted theory that electrowetting is an electromechanical effect [11, 12] and with experimental observation that Young's angle never actually changes microscopically [13]. In our investigation, we will revisit the 'zero inter-

facial tension' theory once more to verify whether it fits the observed experimental results.

3. Experimental

Test substrates consisted of aluminosilicate glass coated with a transparent indium tin oxide (ITO) conducting electrode (SnO_2:In_2O_3, 100Ω/sq, ∼50 nm thickness, from PG & O, Santa Ana, CA, USA). The ITO was coated with a two-layer stack of an insulating dielectric and hydrophobic fluoropolymer (Fig. 1(a)). Parylene C (chlorinated) and Parylene HT (fluorinated) were the two options used for the dielectric. Parylene C was vapor deposited with a Specialty Coating Systems 2010 lab coater, whereas for Parylene HT ITO-coated glass slides were sent to Specialty Coating Systems (Indianapolis, IN, USA) for coating [31]. Fluoropel 1601V (from Cytonix, Beltsville, MD, USA) and Cytop 809M (1 wt% solution in fluorosolvent Ct. Solv. 180, from Asahi, Tokyo, Japan) were spin-coated onto the dielectric and baked as candidate fluoropolymers in this investigation. Fluoropel was baked at 120°C and Cytop at 180°C for 30 min to yield hydrophobic fluoropolymer layers that were 50 nm thick.

For electrowetting tests, the complete substrates were then placed in a clear acrylic box and immersed in an oil bath (insulating fluid). Unless otherwise stated, the oil consisted of a blend of Dow Corning OS silicone oils (80 wt% OS-20, 10 wt% OS-10, 10 wt% OS-30). The conducting liquid to be tested was subsequently deposited with a pipette (drop of 1 μl) and electrically biased through the insertion of a platinum probe tip (0.5 μm in diameter) connected to a Trek linear amplifier (model 603A) coupled to a Tektronix AFG 310 function generator. The ITO was held at electrical ground. The data were then recorded with a VCA Optima contact angle measurement system. DC or AC (1 kHz square wave) voltages were applied in 2 V/2 s step increments from 0 V to as high as ±90 V. The experiments were repeated 3 times at fresh sample locations for each of the solutions studied. The average curves and their associated errors are reported.

It is fully feasible that alternate materials systems and test configurations could be tested and show a greater variation of contact angle saturation with materials or test parameters. However, as stated in the Introduction, this study chose conventional materials and test conditions that are known to perform well in a variety of electrowetting applications. Exploration of alternate materials to support a particular saturation theory was not performed, rather the experiments performed and materials used herein were chosen with minimum bias toward supporting or refuting any particular theory.

4. Results and Discussion

In this section we will systematically discuss the effect of the most relevant variables in our experiments. We explore dielectric thickness, interfacial tension, pH,

ion type and size, solute-solvent interaction, AC/DC driving, oil surface tension, and type of dielectric.

4.1. Influence of the Dielectric Thickness on Saturation

The dielectric thickness was the first parameter varied in this set of experiments. Dielectric thickness was measured with a Dektak 3030 profilometer. As dielectric thickness decreases, the electric field strength increases for a given contact angle (equation (1), required voltage is proportional to the square root of dielectric thickness). Also, as the dielectric becomes thinner, the contact line profile sharpens (microscopic Young's angle evolves to the macroscopically observed electrowetting angle over a distance similar to the dielectric thickness [13]). This sharper profile leads to larger local peak values in the electric field. Therefore based on both factors discussed above, the electric field near the contact line, where the electromechanical electrowetting force originates, should significantly increase as dielectric thickness is decreased. There are several saturation hypotheses that should be dependent on electric field: dielectric charging, oil charging, and micro-droplet ejection (hypotheses 1, 2 and 3). Therefore, based on these theories the contact angle should saturate at larger angles for thinner dielectrics.

For the experiments, an aqueous solution of NaCl (0.02 wt%) with the non-ionic surfactant Triton X102 (0.028 wt%, $\gamma_{ci} = 10$ mN/m) was chosen as the conducting fluid, while the insulating fluid consisted of the OS oils blend. For the tests, Parylene C layers of 0.43, 1.3 and 5.5 μm were deposited on ITO-coated glass slides, and were covered with a 50 nm layer of Fluoropel hydrophobic coating. Even without contact line profile sharpening and related electric field enhancement, this translates to an increase in the applied electric field by more than a factor of 3 (equation (1), assuming constant θ_V). The experimental results are plotted in Fig. 2.

The contact angle reaches a complete saturation just below 60° regardless of the dielectric thickness. Thus, it appears that neither the electric field nor the TCL sharpness has an effect on saturation. Using first-order theoretical consideration, Fig. 2 suggests that dielectric charging, oil charging, or micro-droplet ejection are not dominant factors in the observed electrowetting saturation.

4.2. Effect of the Interfacial Tension (γ_{ci}) on Saturation

The next experiment was designed to vary the electric field strength, while trying to keep the contact line profile constant. It could be possible that changing multiple variables (bulk electric field and contact line profile) could cancel each other out in some unforeseen manner. For testing, different amounts of Triton X102 were dissolved in a 0.02 wt% NaCl aqueous solution. A non-ionic surfactant was chosen to minimize the number of changing parameters, such as ion concentration. These solutions were electrowetted under DC voltage on the same substrate (glass/ITO/1.3 μm Parylene C/50 nm Fluoropel) in the OS oils blend. The electrowetting results are shown in Fig. 3.

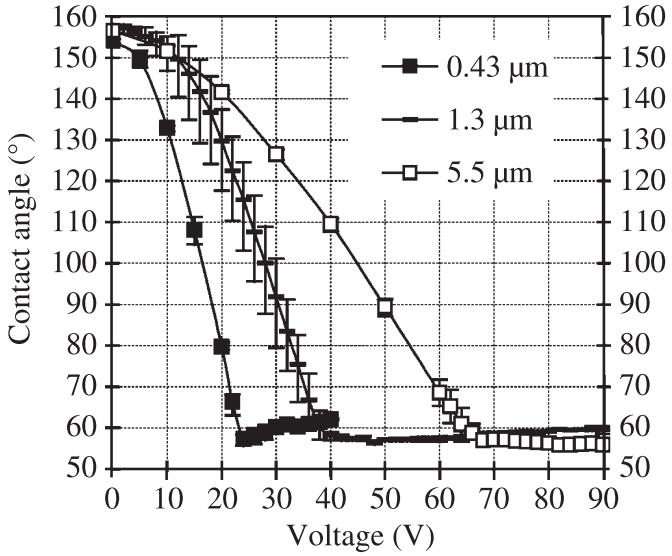


Figure 2. Influence of dielectric thickness on saturation for: glass/ITO/Parylene C/50 nm Fluoropel; test fluid 0.02 wt% NaCl aqueous solution with 0.028 wt% Triton X102; OS oils blend; DC voltage, steps of 2 V/2 s.

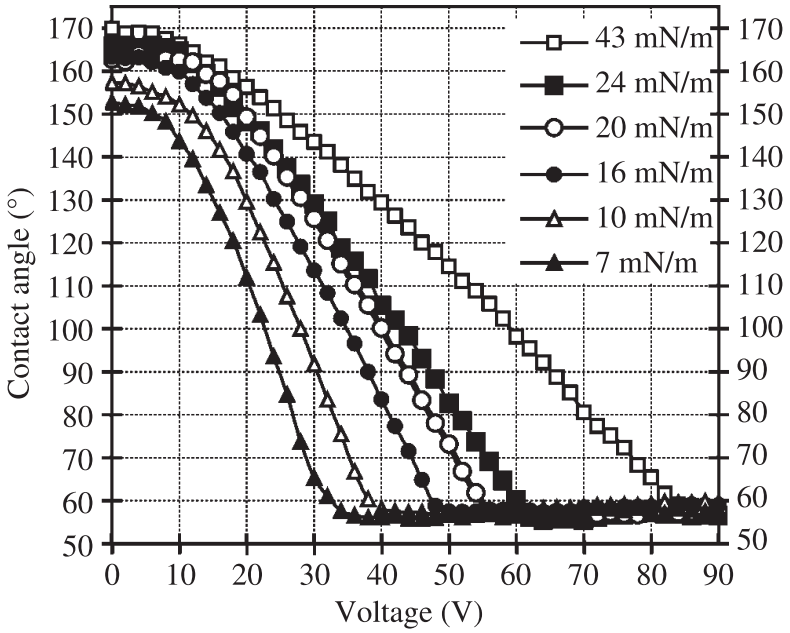


Figure 3. Effect of interfacial tension on saturation for: glass/ITO/1.3 µm Parylene C/50 nm Fluoropel; test fluid 0.02 wt% NaCl aqueous solution with Triton X102 from 0 to 0.055 wt%; OS oils blend; DC voltage, steps of 2 V/2 s.

No significant difference is observed in the contact angles at complete saturation for the various solutions. Like the experiment illustrated in Fig. 2, the data in Fig. 3 have a variation in the applied electric field by approximately a factor of 3, but unlike Fig. 2 the contact line profile is fairly constant since the dielectric thickness is unchanged (there is a small change in θ_Y for the droplet with the lowest interfacial

Table 1.
Fitting of electrowetting results of solutions containing different amounts of Triton X102. γ_{id} was derived from the experimental results and the "zero γ_{cd}" theory

Sample	Triton conc. (wt%)	Fitted γ_{ci} (mN/m)	Exp. θ_s (°)	Exp. V_s (V)	Est. γ_{id} (mN/m)
A1	0	43	77	72	10
A2	0.004	24	64	58	11
A3	0.007	20	67	52	8
A4	0.014	16	71	44	5
A5	0.028	10	68	36	4
A6	0.055	7	65	30	3

tension, but not enough to dramatically alter the TCL contour). The results again suggest that the observed contact angle saturation is independent of electric field. One further observation can be made. If dominated by process similar to AC emulsification [27, 28], micro-droplet ejection might increase with a decrease in γ_{ci} from 43 mN/m to 7 mN/m. Therefore, it could be argued that micro-droplet ejection is not a cause for the observed saturation. However, as will be reviewed later in the discussion section, other mechanisms may be possible for ejecting micro-droplets.

The data for Fig. 3 were also used to briefly explore the zero interfacial tension theory for saturation (hypothesis 4). The curves were fitted according to the electrowetting equation (equation (1)) to determine the different values for γ_{ci} (Table 1). The voltage and contact angle at which the experimental data did not follow the electrowetting equation (considered as the saturation values) are also listed in Table 1. These values were used to validate the "zero γ_{cd}" theory, as described by Quinn *et al*. [32]:

$$\cos\theta_s = \frac{\gamma_{id}}{\gamma_{ci}}, \tag{2}$$

$$V_s = \sqrt{\frac{2(\gamma_{id} - \gamma_{ci}\cos\theta_Y)}{C}}. \tag{3}$$

Validation was done as follows: equations (2) and (3) were applied to estimate γ_{id}, based on the observed contact angles at the onset of saturation (θ_s) and the liquid/oil interfacial tensions (from curve fitting). If the "zero γ_{cd}" theory is correct, identical values should be obtained for the different samples, since the dielectric and oil used are exactly the same for these experiments (Triton X-102 is insoluble in oil).

As can be seen in Table 1, significant variations are obtained for the estimated values of γ_{id} from one sample to the other. Therefore, it seems reasonable to conclude that saturation is not the result of a thermodynamic limit of stability. This conclusion is in agreement with the recent results of Paneru *et al*. [33, 34] for ionic liquids solutions which also fail to follow the "zero γ_{cd}" theory.

4.3. Influence of pH on Saturation

The previous experiments (Fig. 2 and Fig. 3) did not show signs of electric field dependence on saturation. Next, an attempt was made to determine what kind of charges, if any, could be trapped in (or on) the dielectric and oil, and to what extent this would influence saturation. It is known that adsorption of protons (H^+) and hydroxide ions (HO^-) on surfaces gives rise to a surface potential. The magnitude of this potential is determined by the pH of the solution. In order to investigate the influence of this potential on electrowetting performance, aqueous solutions of pH ranging from 0 to over 13 were prepared by dissolving different amounts of HCl (for acidic solutions) and NaOH (for basic solutions). The pH of the different solutions was measured with a Mettler-Toledo S47BIO Biopharm pH-meter. The basic and acidic test solutions were electrowetted under DC voltage on the same substrate (glass/ITO/1.3 μm Parylene C/50 nm Fluoropel) in the OS oils blend. Figure 4 plots the contact angle as a function of applied voltage for solutions of different pH.

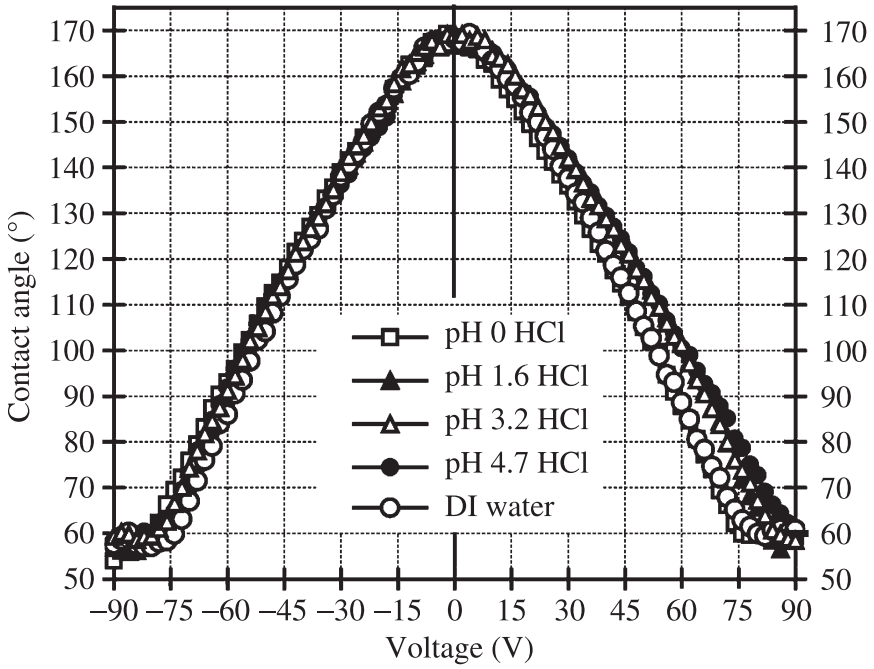
For the acidic solutions, the same contact angle at saturation is obtained regardless of the pH. A slight positive/negative asymmetry in the curves can be noticed and is likely due to double layer potential changing with pH [30]. Clearly, for the acidic solutions the concentration of protons (H^+) in the conducting fluid does not seem to play a role in saturation, and therefore also does not seem to lead to strong dielectric or oil charging.

For the basic solutions, under positive voltages, the same contact angle at saturation was observed regardless of pH. A slightly different electrowetting response with a large amount of NaOH is apparently due to a decreasing θ_Y and γ_{ci}. The only distinct feature of the experiment is for negative voltage and pH $>$ 13 where the contact angle relaxes from $\sim$60° at -60 V to $\sim$80° beyond -70 V. This observation may lead to the suggestion that HO^- is injected into the dielectric or into the oil, but also degradation of the oil in this harsh electrochemical environment should not be excluded.

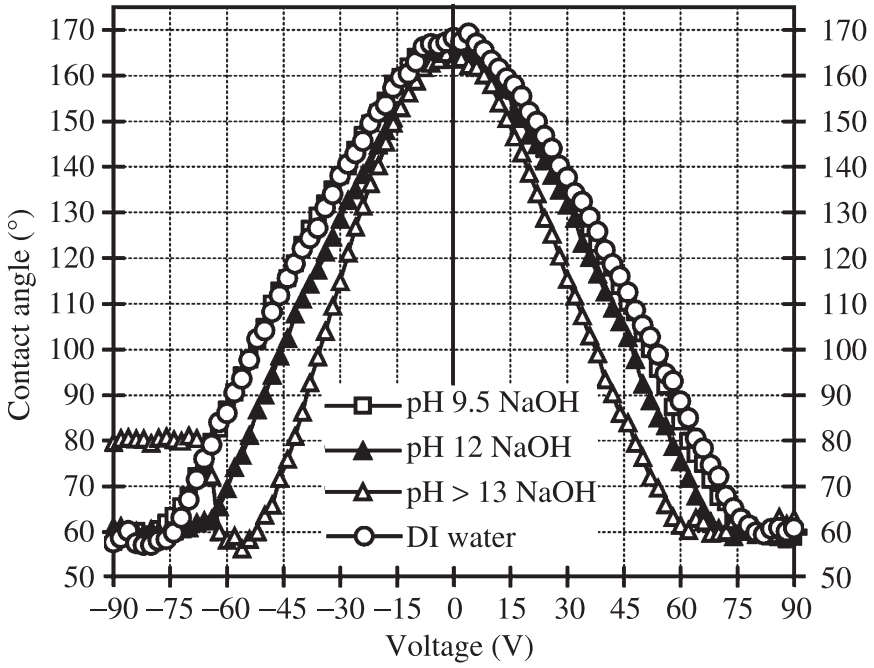
Except in the case of extremely high pH (which has so far never been encountered in any practical electrowetting based device), injection of H^+ and HO^- into the dielectric or oil, if occurring, does not seem to significantly affect the saturation. This invariance of saturation with pH occurs even though the ion concentration is varied over 13 orders of magnitude.

4.4. Effect of Ion Type/Size on Saturation

Without a strong saturation dependence on the ions associated with pH, ions other than H^+ and HO^- were identified as the next step toward assessing whether saturation was dependent on ion size [35] or ion type (more or less hydrophobic). Aqueous solutions of acetic acid (CH_3COOH, pH = 4.4) and ammonium hydroxide (NH_4OH, pH = 9.6) were prepared along with comparative test solutions with HCl and NaOH at similar pH. These solutions were tested on the same substrate (glass/ITO/1.3 μm Parylene C/50 nm Fluoropel) in the OS oils blend. The electrowetting results are presented in Fig. 5.



(a)



(b)

Figure 4. Influence on saturation of concentration of (a) HCl, and (b) NaOH for: glass/ITO/1.3 μm Parylene C/50 nm Fluoropel; test fluids: aqueous solutions of HCl and NaOH with pH ranging from 0 to over 13; OS oils blend; DC voltage, steps of 2 V/2 s.

The data in Fig. 5 show that contact angle saturation is invariant, regardless of the ion nature. If ions were being injected into the oil (oil charging), one might expect some dependence on the hydrophobicity or size of the ions. Regarding dielectric charging, a clear dependence on dielectric failure (current flow through the

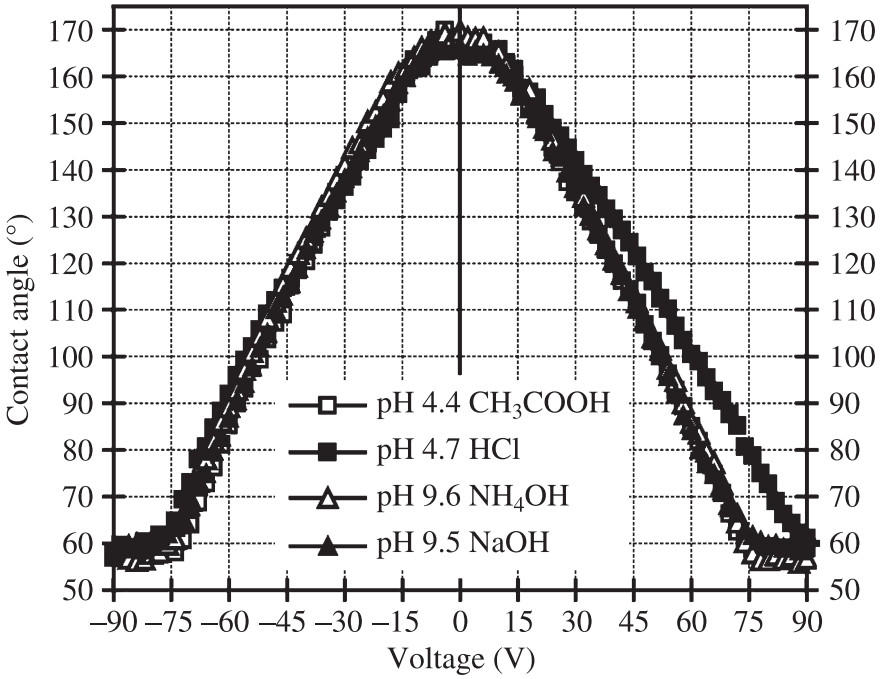


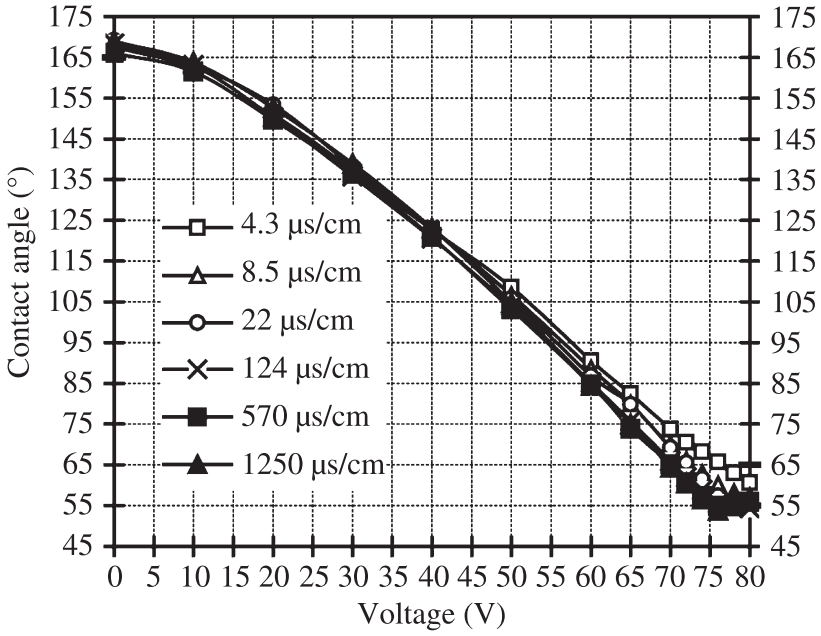
Figure 5. Influence of ions type/size on saturation for: glass/ITO/1.3 μm Parylene C/50 nm Fluoropel; test fluids: aqueous solutions with CH_3COOH (pH = 4.4), HCl (pH = 4.7), NH_4OH (pH = 9.6), and NaOH (pH = 9.5); OS oils blend; DC voltage, steps of 2 V/2 s.

dielectric) and ion size has been previously reported [35]. If dielectric failure (ion penetration through a dielectric) is dependent on ion size, then charging of a dielectric by ions might also be dependent on ion size. Therefore, the observed results in Fig. 5 could be interpreted to suggest that neither oil charging nor dielectric charging impacts the observed saturation angle. It should be noted, however, that Fig. 5 does not disprove dielectric or oil charging theory because of the possibility of self-ionization (breakdown) of a material [17, 18]. It may well be possible that such charging becomes a major limiting factor for the contact angle on a long time scale. However, on a short time scale, the angle at complete saturation does not seem to be affected.

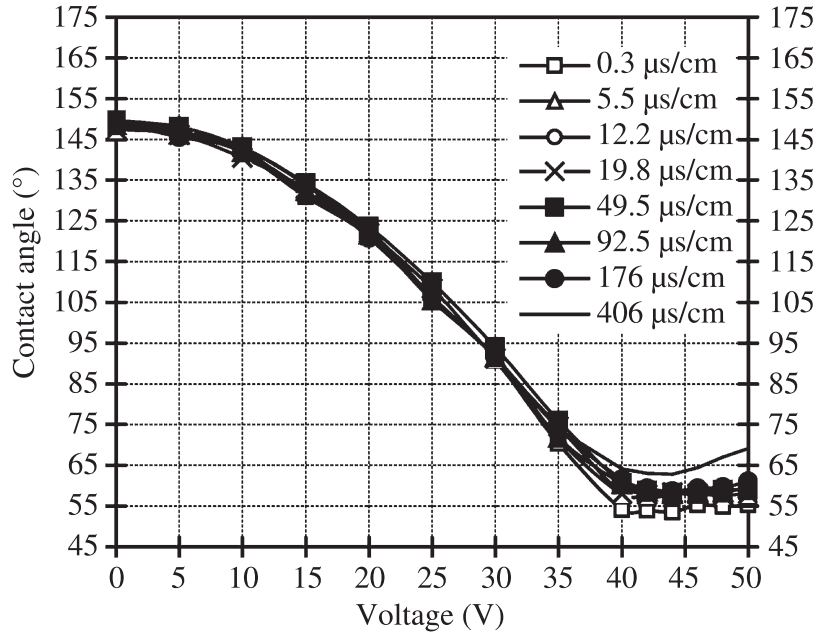
4.5. Influence of the Solute/Solvent Interaction on Saturation

The influence of the solute/solvent interaction was next investigated. It is well known for electrical insulation with polymers that dielectric breakdown can be strongly dependent on the weight % (swelling) of an ionizing solvent like water. Similar results are seen for electrical breakdown of air with various humidities. Also, for other unforeseen reasons, it could be that saturation is dependent on the choice of conducting fluid. In order to investigate the effect of the solvent on saturation, tetrabutylammonium acetate (TBA-Ac) was dissolved in both deionized water (surface tension of 73 mN/m) and propylene carbonate (surface tension of 42 mN/m) to yield solutions of similar conductivities. The conductivities of the different solutions were measured with an OAKTON CON6/TDS conductivity meter

(in µs/cm, ±0.5%). TBA-Ac was chosen because it could be dissolved in both solvents at high concentrations, and because it would enable a simultaneous study of the effect of concentration for large ions. The solutions were tested on the same substrate (glass/ITO/1.3 µm Parylene C/50 nm Fluoropel) in the OS oils blend. Their electrowetting behavior is shown in Fig. 6. The low θ_Y obtained with propylene



(a)



(b)

Figure 6. Electrowetting behavior of conducting fluid solutions containing different amounts of TBA-Ac in (a) deionized water, and (b) propylene carbonate for: glass/ITO/1.3 µm Parylene C/50 nm Fluoropel; OS oils blend; DC voltage, steps of 2 V/2 s.

carbonate is likely not real and is due to gravity, since propylene carbonate is quite dense (1.21 g/cm^3), and because the propylene carbonate/oil interfacial tension is lower which increases the influence of gravity.

Saturation was observed at lower voltages for propylene carbonate based solutions than for aqueous ones (because of lower γ_{ci}) but the contact angles at complete saturation were similar. The most interesting feature of the data in Fig. 6 is for propylene carbonate. As the conductivity (TBA-Ac concentration) is increased, the saturation angle also increases by as much as 10°. Therefore, the ions do play a slight role in the observed saturation effect. A liquid with higher ion concentration will have a shorter Debye length and might support a higher concentration of ions causing charging in a dielectric defect or pore. Electrowetting relaxation is easily observable for the propylene carbonate based solution with conductivity of 406 μs/cm, which is similar to the results obtained with extremely basic aqueous solution (Fig. 4(b), pH > 13). Whether or not dielectric charging is actually occurring and causing saturation cannot be concluded from the data, and the observed electrowetting saturation is at best weakly dependent on ion concentration and Debye length.

If any charge injection is taking place, it should exhibit an observable time constant (similar to RC charging) or other temporal behavior. Additional experiments were performed to investigate the contact angle relaxation as a function of time for the 406 μs/cm conductivity propylene carbonate solution. A 40 V DC voltage was applied abruptly (no voltage ramp) to 3 different drops of the solution and maintained for 1 min. The contact angle as a function of time was measured. The results are presented in Fig. 7 and are not unlike previous observations of relaxation with time [35].

Contact angles of about 60° were obtained after direct application of the voltage and increased as the voltage was maintained (up to 75°–80°). In almost all experiments (Fig. 1 to Fig. 7), if a DC voltage was held long enough relaxation would slowly occur. Based on most electrowetting experiments performed by our group and others, long term DC voltage followed by removal of voltage results in a reduced Young's angle θ_Y, which is a strong indicator of charging (charge injection and/or adsorption). Relaxation and charging seems to occur even with the highest performance dielectric materials [31]. *This raises an important question as to whether the dominant factor in saturation changes with time.* It could be that over a long time scale (s to min) charge injection may dominate the saturation effect. This would be in agreement with dielectric charging theory based on dielectric breakdown [17].

In Fig. 7, at higher voltages the droplet escaped from the electrical probe. This is direct evidence of inhomogeneous charge injection or localized dielectric failure, either of which results in a force imbalance on the droplet, moving the droplet slightly onto virgin (non-wetted) dielectric, and therefore further accelerating the droplet motion. This observation further supports that some dielectric charging is occurring. However, for the experiments performed herein, the invariance of this

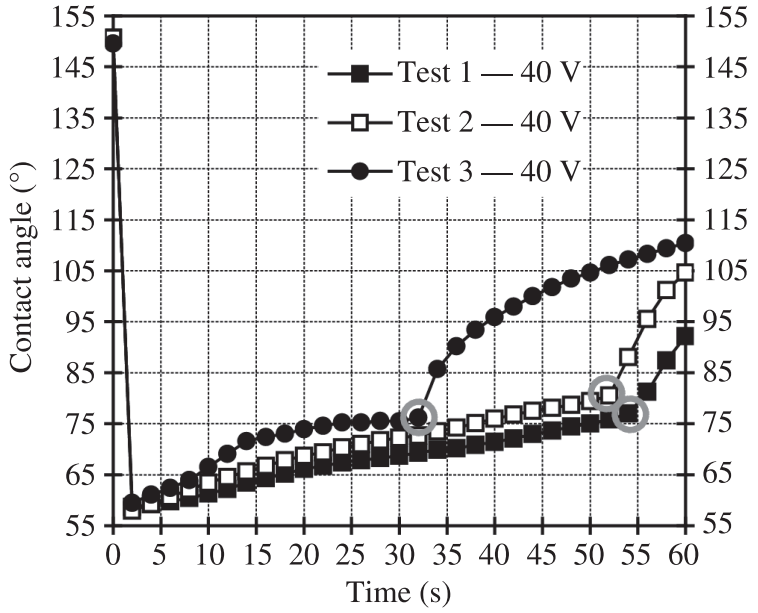


Figure 7. Relaxation of a drop of 406 μs TBA-Ac in propylene carbonate solution as a function of time under abrupt application of 40 V DC voltage for: glass/ITO/1.3 μm Parylene C/50 nm Fluoropel; OS oils blend; DC voltage. The gray circles indicate when the drop escaped from the probe.

effect with electric field (Fig. 2 and Fig. 3) is unexpected, and strongly suggests that saturation is not due to dielectric charging on a shorter time scale. To summarize, dielectric or oil charging could be the dominant saturation effect over a longer period of voltage application, or over shorter periods of time when using dielectrics or oils that are poor electrical insulators to a conducting fluid. It is, however, questionable whether we should call this relaxation effect saturation, as the low angle of 60° can be obtained immediately after applying the saturation voltage. It seems as if there is a fundamental contact angle limit at saturation of just below 60° that is not dependent on variables that influence charge injection.

4.6. Effect of DC vs. *AC Voltage Saturation*

To further investigate the effect of time scale on contact angles and saturation, the type of voltage applied was varied. A 0.02 wt% NaCl aqueous solution with 0.028 wt% Triton X102 was electrowetted on the same substrate (glass/ITO/800 nm Parylene HT/50 nm Fluoropel) in the OS silicone oils blend under DC and AC 1 kHz square wave voltages, at an increase of 2 V every 2 s. The experimental results are plotted in Fig. 8. This experiment is the first in which we see a clear effect on the angle at complete saturation. The seemingly unbreakable limit of just below 60° is lowered to about 45° for the AC case. It may be that the quickly changing polarity removes injected or adsorbed charges, but the observed results could also be due to less sticking/pinning of the contact line when using AC voltage [14]. Kinetic aspects of saturation need to be further explored to provide further insight into time scale effects. However, in Section 5 of this article, we will show that the saturation difference between AC and DC may be explained in a totally different way.

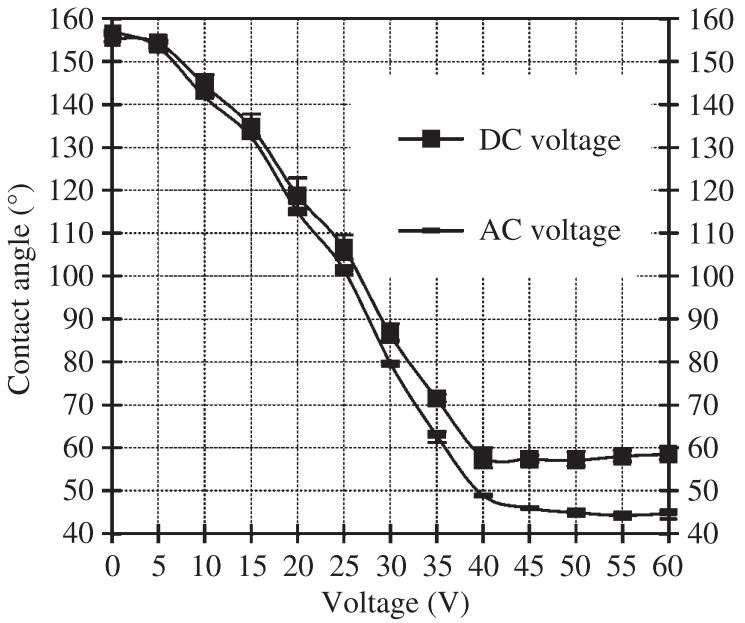


Figure 8. Influence of the voltage type (AC *vs*. DC) on the saturation for: glass/ITO/800 nm Parylene HT/50 nm Fluoropel; test fluid 0.02 wt% NaCl aqueous solution with 0.028 wt% Triton X102; OS oils blend; voltage: either DC or 1 kHz AC, steps of 2 V/2 s.

4.7. Influence of Oil Surface Tension on Saturation

Next, we tested the influence of the oil surface tension on saturation. A 0.02 wt% NaCl aqueous solution was used as the test fluid. The following oils were chosen for the test: OS-10 silicone oil ($\gamma_i = 15.2$ mN/m), OS-30 silicone oil ($\gamma_i = 17.3$ mN/m), tetradecane ($\gamma_i = 26.6$ mN/m), and decahydronaphthalene (known as Decalin, $\gamma_i = 30$ mN/m). In addition, Triton X15 (oil soluble non-ionic surfactant) was dissolved in tetradecane (1 wt%) in another sample, to decrease the interfacial tension with water. Electrowetting experiments were carried out on a new substrate (glass/ITO/1.3 μm Parylene C/50 nm Fluoropel) for each oil tested. The results are plotted in Fig. 9. As expected, the influence of gravity causes a lower observed θ_Y when Triton X15 is added to the oil phase (lower interfacial tension).

Almost identical electrowetting curves were obtained for the tests carried out in OS-10, OS-30, tetradecane, and Decalin with a contact angle at complete saturation of around 55°. Therefore, oil surface tension does not seem to dictate the saturation contact angle.

Like polymers, oils can exhibit slight uptake of water, and typically higher surface tension oils will have a greater uptake of water. Even only 10's of ppm changes in the amount of water in an oil can significantly affect the breakdown voltage [36]. Therefore, these results (through the assessment of oils of different surface tensions) might suggest that oil charging does not have an influence on electrowetting response and saturation. However, this proposition has to be considered with care, since actual water uptake in ppm was not directly measured. Lastly, and interestingly, the breakdown trend for an oil with increasing water content is highly

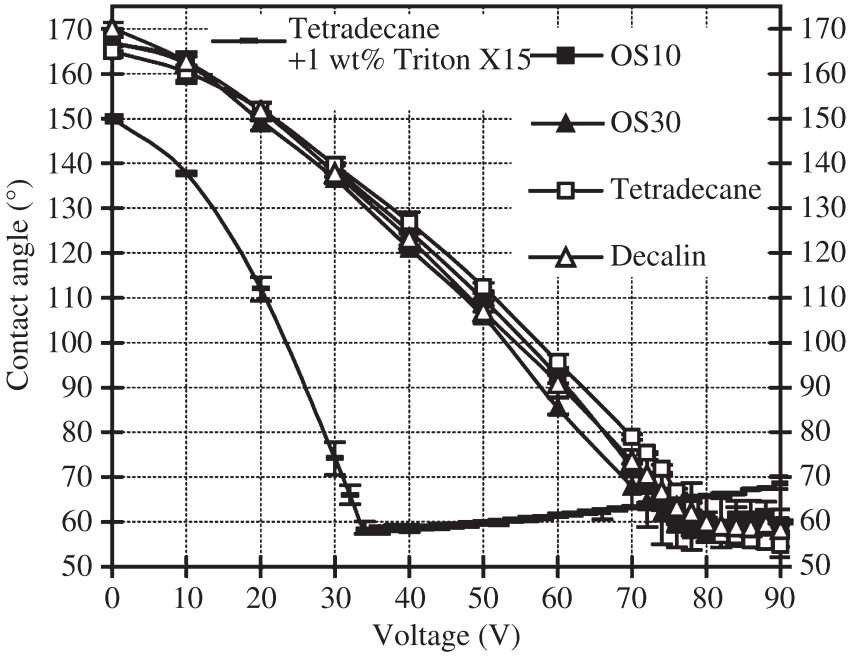


Figure 9. Effect of oil surface tension on the saturation for: glass/ITO/1.3 μm Parylene C/50 nm Fluoropel; test fluid 0.02 wt% NaCl aqueous solution; oil phase OS-10 ($\gamma_i = 15.2$ mN/m), OS-30 ($\gamma_i = 17.3$ mN/m), tetradecane ($\gamma_i = 26.6$ mN/m), Decalin ($\gamma_i = 30$ mN/m) and tetradecane with 1 wt% Triton X15; DC voltage, steps of 2 V/2 s.

dependent on whether AC or DC voltage is used, and is still not fully understood at this time [36].

4.8. Effect of Dielectric Type on Saturation

In a last attempt to obtain further insights into the influence of dielectric charging/breakdown on saturation, the type of dielectric and hydrophobic coating used were varied. A 0.02 wt% NaCl aqueous solution with 0.028 wt% Triton X102 was used as test fluid in the OS oils blend. It was electrowetted on the following substrates: glass/ITO with 1.3 μm Parylene C/50 nm Fluoropel, 800 nm Parylene HT/50 nm Fluoropel and 800 nm Parylene HT/50 nm Cytop. The resulting electrowetting curves are shown in Fig. 10.

The test fluid displayed the same electrowetting behavior, regardless of the dielectric type (Parylene C or HT) on substrates coated with a hydrophobic layer of Fluoropel. However, when Cytop was used in place of Fluoropel, a strong difference in the contact angle at saturation was noticed (10° higher). Therefore the fluoropolymer top-coat has a strong influence on the final saturation angle. It may be that dielectric charging dominates the saturation in Fig. 10 with the Cytop top-coat, as no other explanation seems plausible. However, as noted in previous sections, using dielectric systems with poor performance will always likely lead to strong dielectric charging, and does not necessarily mean that dielectric charging dominates when using the highest quality materials systems.

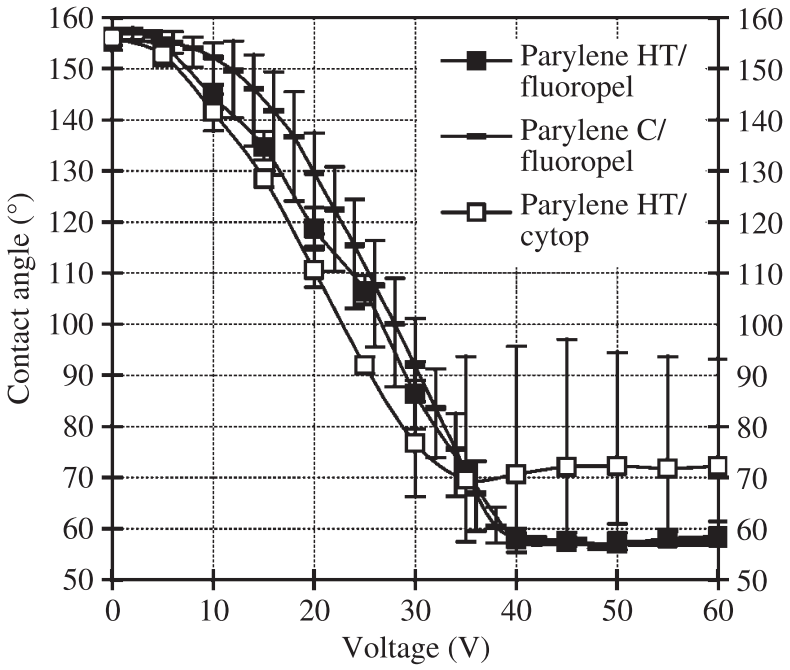


Figure 10. Influence of the dielectric type on saturation for: ITO-coated glass slide with 800 nm/50 nm Parylene HT/Fluoropel, 1.3 μm/50 nm Parylene C/Fluoropel and 800 nm/50 nm Parylene HT/Cytop; test fluid: 0.02 wt% NaCl aqueous solution with 0.028 wt% Triton X10; 2 OS oils blend; DC voltage, steps of 2 V/2 s.

5. Discussion, Parallels to Taylor Cone Formation and Electrohydrodynamic Instability

The results show that for DC conditions it is not possible to obtain electrowetting contact angles smaller than approximately 55°. We call this complete saturation. It was, however, observed that this angle at complete saturation was not always reached when changing various electrowetting variables and materials. We will call this incomplete saturation.

The experimental findings of this investigation can be briefly summarized in relation to existing saturation theory as follows. This work and other works [13, 33, 34] continue to reveal that zero interfacial tension theory (hypothesis 4) cannot explain complete or incomplete saturation (Fig. 3). It is clear from this work and prior work [16] that dielectric charging, oil charging, or localized dielectric breakdown [17] (hypotheses 1 and 2) can dominate saturation effects on a longer time scale and therefore can be a cause for not reaching or maintaining complete saturation. However, invariance of the contact angle at complete saturation with electric field on a short time scale for much of the data, suggests that with high quality insulating materials dielectric charging is not the cause for complete saturation.

At first sight, micro-droplet ejection (hypothesis 3) does not seem to explain complete saturation, because one would expect micro-droplet ejection to be dependent on surface tension and electric field. Our results show that the angle at complete saturation is clearly not dependent on these variables. However, there is

a reason to assume that micro-droplet ejection is not dependent on these variables. This reason is the fact that micro-drop ejection originating from a Taylor cone [15] is also highly invariant to many of the parameters explored herein.

Taylor cones refer to the conical shape taken by the interface formed by a conducting fluid in an insulating medium (oil or air) under application of a high electric field. When the voltage overcomes a threshold value, a jet of micro-droplets of the fluid are ejected. This is the fundamental basis for electrospinning and electrospraying [37]. Taylor cones exhibit invariant behavior that from a first principles viewpoint may seem unusual or highly unexpected. Taylor cones uniquely include all of the following traits of invariance:

- Taylor cones invariably display the same conical (half) angle, around 45–50° [15, 38]. Although some theories show that the angle is smaller, it is still invariant to fluid parameters [39];
- The Taylor cone angle is the same, irrespective of surface tension, as shown for glycerine/air, water/oil and soap solution [15];
- Electric field, or threshold voltage for forming a Taylor cone can vary widely based on the materials used and experimental setup, but still the reported cone angles remain fairly constant [40];
- The Taylor cone angle does not change as the applied voltage is further increased [15].

Furthermore, several other trends for Taylor cones behave similar to some of the unique trends observed for the electrowetting saturation experiments performed herein:

- AC voltage reduces the Taylor cone angle, for example the cone angle for ethanol is approximately 9° for the AC case as compared to 47° for the DC case [38];
- The observed Taylor cone angle is independent of ionic content or conductivity for non-insulating fluids [39].

More speculative parallels between electrowetting saturation and Taylor cones include the following hypotheses:

- Electrowetting saturation in air tends to ∼70° [30] and this work shows that in oil saturation tends to ∼60°, which shows a strong independence on θ_Y (θ_Y in air is ∼120° and in oil can be much greater, up to 180°). Electrowetting saturation and Taylor cone formation are geometrically independent of the insulating fluid (liquid or gas) and the original shape of the conducting fluid before cone formation or saturation. A larger saturation angle in air could be due to contact angle hysteresis that is usually present in the absence of oil.

If micro- or nano-droplet ejection did occur, similar to droplet ejection from Taylor cones, it could place droplets in a position where they could screen electric field (Fig. 1(e)). If voltage were increased, more and more micro-droplets could be ejected to further screen the electric field. The parallels between Taylor cones and electrowetting saturation are striking. However, unlike Taylor cones the contact line is dominantly a 2D (not 3D) system. Mathematically, Taylor theory does not directly apply to electrowetting saturation, where electrohydrodynamic instability is likely to occur across the contact line. Still, the parallels between saturation and Taylor cones might support the cause of saturation as some similar form of electrohydrodynamic instability and fluid ejection. If electrowetting saturation is due to electrohydrodynamic instability, then saturation is likely to occur at the same value for electrowetting number (CV^2/γ) [41], which compares electrostatic energy with surface energy. Analysis of the data in Fig. 3 (interfacial surface tension) shows saturation at a fairly constant electrowetting number of $\sim$1.50, but saturation in Fig. 2 (thickness of dielectric) is not as closely matched to constant electrowetting number. Comparison between saturation in air and in oil differs even more in electrowetting number: a water drop on a fluorinated polymer in air has an initial angle of about 120°, but it does not spread further than the limit of complete saturation that we observed for an oil ambient, thus leading to an electrowetting number of about 1. However, other electrowetting saturation effects such as charge injection could play secondary roles which would distort a relation between saturation and constant electrowetting number. Therefore, based on the present data and analysis technique, the validity of the electrohydrodynamic instability theory cannot be proven or disproven.

Lastly, we touch upon two very recent papers that are appropriate for further discussion. First, there is a modeling paper [42] which claims that at a sufficiently high electric field a thin liquid layer can be extruded from the edge of an electrowetting droplet. This film then breaks into small droplets, which certainly would screen the electromechanical force driving the electrowetting process. This is consistent with saturation arguments made for droplet ejection, the key question being whether or not this recent model predicts the same level of invariance as the experimental results we report herein. Secondly, there is a recent report on electrowetting on structured surfaces [43] where certain geometries could promote formation of downward facing Taylor cones. Such Taylor cones could potentially form and dominate depinning from structured surfaces [44]. This case is, however, unique from our analysis performed on smooth surfaces. Regardless, it is clear that electrohydrodynamic instabilities can dominate other limiting wetting effects.

6. Conclusions

It has been experimentally shown that for DC driving there exists a contact angle at complete saturation that is invariant with numerous variables. These experimental data refute several hypotheses including dielectric charging, oil charging, and zero

interfacial tension theories. Charging may, however, prevent the system from reaching the angle at complete saturation. Because the angle at complete saturation is so invariant to multiple parameters, experimental results suggest further exploration and discussion of micro-droplet ejection similar to Taylor cones (electrohydrodynamic instabilities). Although this work does not unequivocally prove what causes contact angle saturation, it reveals what factors play a very limited or no role. Furthermore, the experimental data clearly show that saturation is a time-dependent phenomenon, with different physical mechanisms dominating saturation behavior over different time scales. The pursuit continues for a universal theory on electrowetting saturation.

Acknowledgements

The University of Cincinnati authors acknowledge partial supports from NSF CAREER Award #0640964 (University of Cincinnati), NSF IHCS Award #1001141, AFRL contract # 5408-25-SC-0003 (Rajesh Naik, John Busbee) and an ARL grant #W9111NF-09-2-0034 (Dave Morton and Eric Forsythe).

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