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Ion and Liquid Dependent Dielectric Failure in Electrowetting Systems

Balaji Raj,† Manjeet Dhindsa,† Neil R. Smith, Robert Laughlin, and Jason Heikenfeld*

Novel Devices Laboratory, Department of Electrical and Computer Engineering, University of Cincinnati, Cincinnati, Ohio 45221. † These authors contributed equally to this work and should both be considered first authors.

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Electrowetting devices often utilize aqueous solutions with ionic surfactants and inorganic salts to modify the electrowetting response. It has been observed in low-voltage electrowetting devices (thin dielectric, < 12 V) that a frequent onset of dielectric failure (electrolysis) occurs with use of ionic solutes such as potassium chloride (KCl) or sodium dodecyl sulfate. More detailed current−voltage investigations reveal less dielectric failure for the larger size ions. Specifically, improved resistance to failure is seen for surfactant ions carrying a long alkane chain. Therefore, a catanionic surfactant (in which both ions are amphiphilic) was custom synthesized, and elimination of dielectric failure was observed in both negative and positive voltage. Because water is a small molecule that easily penetrates dielectrics, further experiments were performed to show that dielectric failure can also be eliminated by use of larger size polar molecules such as propylene glycol. In addition to these results, important parameters such as conductivity and interfacial tensions are reported.

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Introduction

Electrowetting[1] is the common term used to describe the electromechanical[2] reduction of a liquid contact angle on a hydrophobic dielectric/electrode substrate. In an oil ambient, this basic effect can provide >100° of reversible contact angle change with fast contact line velocities (>10 cm/s) and low electrical energy (~1's to 10's mJ/m^2 per switch). As a result, there has been an intense global effort using electrowetting for applications such as lab-on-chip,[3−5] optics,[6,7] and displays,[8,9] to name a few. For all these applications it is generally desirable to use low voltages (V) to switch from Young's angle (θ_Y) to the electrowetted contact angle (θ_V). According to the electrowetting equation[1]

$$\cos\theta_V = \cos\theta_Y + CV^2/2\gamma_{ao} \quad (1)$$

low voltage can be achieved by reducing the interfacial surface tension between the aqueous and oil phases (γ_{ao}). This is typically achieved through use of ionic surfactants.[10] However, ionic content can exacerbate electrolysis at dielectric defects and cause electrochemical corrosion of electrodes. Alternately, low voltage can be achieved by decreasing the hydrophobic dielectric thickness (d) and therefore increasing the capacitance (C). However, even though the reduced dielectric thickness reduces the required operating voltage, the required electric field across the dielectric actually increases. This again increases the occurrence of device failure through dielectric failure. Therefore, it should not be surprising that the first commercial electrowetting products are higher voltage ~60 VAC liquid lenses (Varioptic SA) where a thicker (~3−5 μm) Parylene dielectric is utilized. If reliable low-voltage electrowetting devices are to be eventually achieved, a better understanding is needed on the nature of dielectric failure in electrowetting systems. Dielectric failure modes for electrowetting should be distinct from failure in purely solid-state systems. Liquid electrodes are unique in their ability to propagate through even complex networks of dielectric defects. Reported herein are consistent trends showing that the larger the physical size of ionic content in the polar liquid, the less likely the onset of dielectric failure. To investigate, ionic species were utilized where the cation and anion were of distinct size, and then positive and negative voltage sweeping was implemented to reveal clear trends in dielectric failure. It is further shown that dielectric failure is strongly dependent on the size of the polar liquid molecules themselves. Although the materials tested herein are not comprehensive, this work provides initial guidance on how careful selection and synthesis of liquid and ionic content might lead to improved electrowetting reliability.

Background and Experimental Results

Before continuing further, background and assumptions will be reviewed to provide meaning to the choice of materials and experiments. First, it should be noted that use of a polar liquid such as deionized water is often not a practical option for electrowetting because (1) for bioapplications like lab-on-chip ionic content is crucial to the health of proteins, cells, DNA, etc., and (2) for electrowetting optics, an ac voltage (conducting liquid) is preferred to reduce contact angle hysteresis.[11] Furthermore, it will be shown that even the dc electrowetting response is poor for a low-conductivity liquid like propylene glycol, and ionic content must be added to properly accumulate charge near the contact line (electromechanical force). Therefore, it can be assumed that many, if not most, real-world electrowetting applications require ionic content. It will also be assumed that low-voltage electrowetting devices require a two-layer dielectric stack (Figure 1a) because of the inherently porous nature of fluoropolymer films. In

*Corresponding author: Tel 513-556-4763; Fax 513-556-7326; e-mail heikenjc@ucmail.uc.edu.

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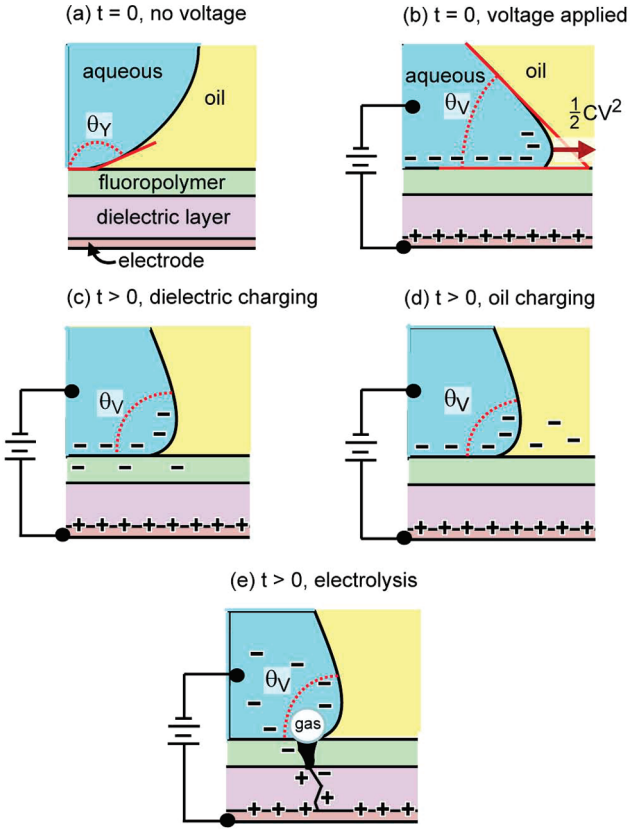


Figure 1. (a) Initial state of a sessile droplet in an oil ambient. (b) Proper charge buildup and electromechanical alteration of the wetting response. (c, d, e) Nonideal behavior due to dielectric charging, oil charging, or electrolysis at dielectric defects.

a two-layer approach, the conductive pathways (pores) that can severely plague a stand-alone thin fluoropolymer instead terminate against the superior insulation properties of an inorganic dielectric. However, it will be seen that even with a high-quality inorganic oxide or nitride dielectric, prevention of dielectric failure is only marginally improved. Furthermore, the possibility of self-healing failure[12] is precluded for a system using a liquid electrode. Therefore, for low-voltage and reliable electrowetting operation, it is postulated that one must pay close attention to selection of ionic content.

The electrowetting effect can degrade due to dielectric failure, but also for several other reasons. For ideal electrowetting behavior, it is assumed that all ions or charge remains in the liquid and solid electrodes. As diagrammed in Figure 1, ions that appear anywhere else but the solid or liquid electrodes cause degradation of the electrowetting response. For example, as observed in Figure 1c, fluoropolymer charging[13] can cause contact angle saturation (sometimes also called contact angle relaxation). Similarly, as seen in Figure 1d, the oil can be inadequately insulating[14] and a degraded response observed (the oil molecules should also have weak dipole moment[14]). The onset of electrolysis (Figure 1e) can certainly degrade the electrowetting response, by progressively destroying the electrowetting surface or by causing a voltage drop across the liquid electrode. For all these degradation methods, it is postulated that larger size ions will generally be less able to penetrate the insulating materials such as the dielectric or oil phase. Therefore, both dielectric failure and dewetting (saturation) tests will be presented herein for a variety of ionic solutions. Only dc voltages will be tested. For systems that show reliable dc operation, one can further use bipolar or ac voltage to reduce the net propagation of ions through the dielectric layer. Therefore, dc voltage represents the most challenging test case.

Table 1. Table of Surfactants Utilized Herein

Surfactant	Structure
SDS	C_{12} SO_4^- Na^+
SOS	C_8 SO_3^- Na^+
DTAC	C_{12} NH_3^+ Cl^-
DTA-OS	C_8 SO_3^- NH_3^+ C_{12}

Choice, Preparation, and Synthesis of Test Liquids. Two polar liquids were tested, deionized (DI) water and propylene glycol. H_2O partially dissociates into H_3O^+ (hydronium) and OH^- (hydroxide) at 300 K and under applied electric field even further dissociation occurs.[15] Therefore, deionized water can be marginally conductive enough for dc electrowetting experimentation but as described in the previous section is often impractical in many devices or devices biased with ac voltage. In addition to water, propylene glycol (PG) was also tested as an alternate polar liquid with larger size molecules. Commonly used inorganic salts (NaCl or KCl) were explored as a source of small inorganic ions (hydrodynamic radii of ~1−2 Å). As shown in Table 1, the effect of large ions was explored by using an anionic surfactant sodium dodecyl sulfate (SDS) and a cationic surfactant dodecyltrimethylammonium chloride (DTAC). Nonionic surfactants were not tested, as they would not likely impact dielectric failure in a primary manner.

Critical to confirming ion-size-dependent failure is ionic content that has a large molecule for both the anion and the cation. Therefore, using the following process, we custom-synthesized a catanionic surfactant, dodecyltrimethylammonium octanesulfonate (DTA-OS). First, 1 g of DTAC and 1 g of sodium octanesulfonate (SOS) were each separately dissolved in methanol (≥99.8%, M-Tedia Corp.) to make two clear solutions containing 0.867 g (3.787×10^{-3} mol) of the dodecyltrimethylammonium cation and 0.894 g (4.6296×10^{-3} mol) of the octanesulfonate anion, respectively. The two solutions were then combined at room temperature, and a final clear solution was obtained. The ion-exchange reaction is essentially instantaneous and goes to completion. The solvent was then evaporated leaving behind ~2 g of a solid residue consisting of a mixture of inorganic salt (NaCl) and catanionic surfactant (DTA-OS). The residue was then dissolved in ~75 mL of DI water and placed in a dialysis tube (Fisherbrand) having a porosity of 12 000−14 000 Da and a dry cylinder diameter of 28.6 mm. This porosity should allow the diffusion of organic ions to a lesser degree than individual inorganic ions in solution and to an even lesser degree the micelles or other multimolecule phases. The electrode of a conductivity meter (OAKTON CON6/TDS6 measured in μS/cm, ±0.5%) was placed in the dialysis tube for conductivity measurements. The tube was sealed and submerged in a continuous flow of DI water. Conductivity was measured at 30 min intervals until a time of

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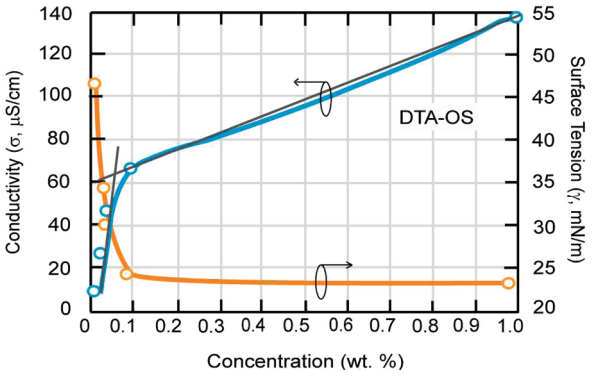


Figure 2. Conductivity (μS/cm) and interfacial surface tension (IFT, mN/m) of aqueous DTA-OS catanionic surfactant solution vs concentration (wt %). The cmc value for DTA-OS was determined to be ~0.065 wt %.

6 hrs, at which point the conductivity became constant indicating that most of the inorganic salt had diffused out of the tube. The remaining solution containing DTA-OS was removed from the dialysis tube and heated to evaporation, and ~0.968 g of a solid residue was recovered. Earlier tests have shown that NaCl and SOS fail to dissolve in chloroform (≥99.9%, M-Tedia Corp.). Therefore, to test the complete removal of NaCl and identify any excess unreacted SOS, ~0.2 g of the residue was redissolved in chloroform. This resulted in a cloudy mixture signaling the presence of NaCl salt and/or SOS. This cloudy precipitate was removed using a filter paper. The remaining filtrate was heated to evaporate the chloroform and obtain ~0.135 g of solid DTA-OS surfactant. For further confirmation, a 0.05 wt % aqueous DTA-OS solution was tested for Cl^- by adding ~5 drops of 0.1 M silver nitrate ($AgNO_3$) in ~20 mL of the DTA-OS solution. The test was negative (no precipitate of AgCl was observed).

Critical micelle concentration (cmc) for DTA-OS was not available, and therefore it was experimentally determined by measuring conductivity vs concentration (wt %) of the DTA-OS solution. Plotted in Figure 2 are conductivity (σ, μS/cm) and surface tension (γ in air, mN/m) vs concentration (wt %) of the DTA-OS solution. Conductivity increases more slowly above the cmc point because of the reduced electrophoretic mobility for larger micelles, lamellar sheets, and precipitates.[16−18] The cmc was found to be ~0.065 wt % (1.54 mM). This value is much lower than the cmc for SDS (~0.24 wt %, 8.32 mM), which is expected since both the component ions (DTA- and -OS) are amphiphilic. The cmc point for DTA-OS was further confirmed by measuring surface tension vs concentration (wt %) of the DTA-OS solution (Figure 2). The pendant drop function of a VCA Optima contact angle measurement system was utilized to measure surface tension of the DTA-OS solution.

Electrowetting Dieletric Preparation. Generally, thick dielectrics (~3−5 μm) such as those constructed of Parylene C exhibit excellent resistance to dielectric failure but at the cost of high operating voltage (~50−100 V). Explored herein is a high-capacitance, low-voltage (<10 V) dielectric stack used in many electrowetting devices developed at the University of Cincinnati.[7] To begin fabrication, commercial aluminosilicate glass substrates coated with a transparent conducting electrode, indium tin oxide (SnO_2:In_2O_3, 100 Ω/sq, ~50 nm thickness, display grade), were purchased from PG & O Inc. This transparent electrode was then coated with 100 nm of Al_2O_3 (ε_r ~9.1) via atomic layer deposition at 250 °C (Cambridge Nanotech Savannah 100 ALD System). The precursors used were trimethylaluminum (Sigma-Aldrich) and DI water. The precursor pulse time and N_2 purge time used

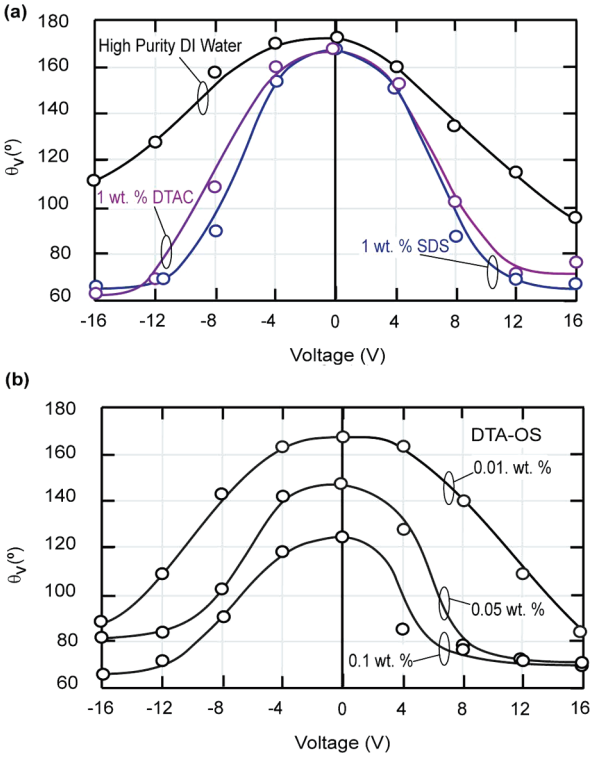


Figure 3. (a) Plot of contact angle vs electrowetting voltage for conventional surfactant solutions; the wt % used are above the cmc points. (b) Electrowetting (EW) contact angle response for several wt % of catanionic surfactant (DTA-OS) solution.

were 0.015 s and 8 s, respectively. The Al_2O_3 film was then spin-coated with 1 wt % solution of Asahi CYTOP 809 M in fluorosolvent Ct. Solv. 180. The spin cycle involved a 500 rpm spread for 15 s and 1000 rpm spin for 45 s. The sample was then annealed at 180 °C for 30 min, resulting in a fluoropolymer of ~50 nm thickness. DuPont Teflon AF was not investigated because in thin film (< 0.5 μm) form it has been observed to suffer from severe charge injection. The final substrate was stored in a N_2 drybox until testing was performed.

Experimental Setup for Electrowetting and Dielectric Failure Tests. For all electrowetting tests, a VCA Optima contact angle measurement system was used. These tests were performed in a dodecane (Fisher, Lab grade) ambient because most practical electrowetting devices use oil to reduce hysteresis and the influence of gravity. A clear acrylic box was used to contain the dodecane immersed substrate. A sample polar liquid droplet (~1 μL) was placed on the substrate and viewed through the transparent acrylic sidewalls. To provide electrical bias to the polar liquid solution, a tungsten cat whisker probe tip (0.5 μm in diameter) was inserted into the polar droplet. The other end of this probe was connected to a Trek linear amplifier (model 603A) coupled to a Tektronix AFG 310 function generator. A LabVIEW program was written to allow a repeatable 1 V/s step of voltage and synchronized video capture of the droplet profile. The SnO_2:In_2O_3 was held at electrical ground.

Dielectric failure tests were done in air (not in oil) because Young's contact angle (θ_Y) of the polar droplet is generally <115° in air, as compared to >160° in oil. A lower Young's angle reduces the electrical influence of increasing capacitor area with voltage (droplet/dielectric/SnO_2:In_2O_3). The alternate approach of using a completely fixed area capacitor[19] was not explored because it eliminates high-field generation near the sharp contour of the contact line, an effect that must be included if the dielectric failure

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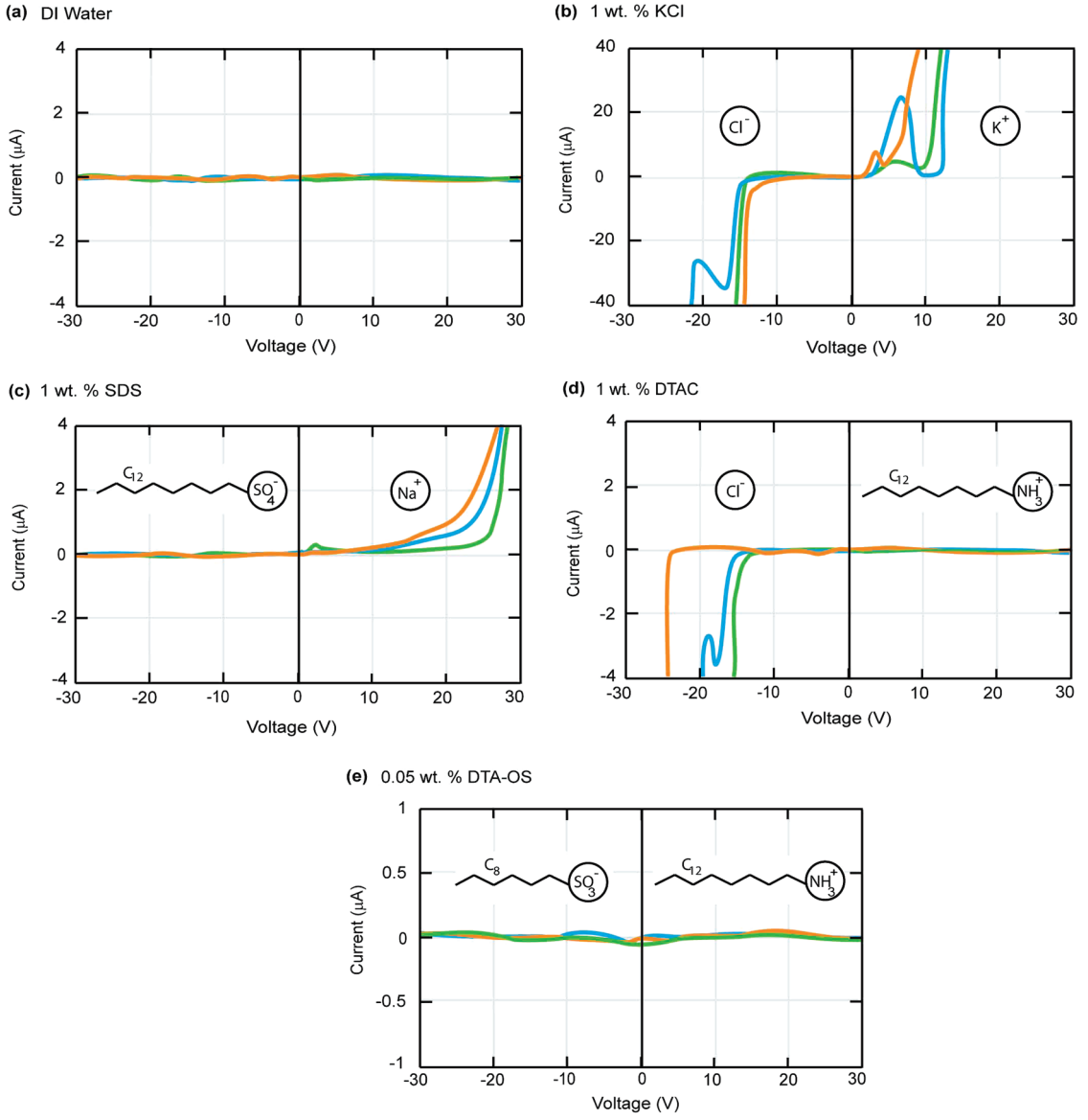


Figure 4. Dielectric failure current vs voltage for various aqueous solutions on a fluoropolymer/Al_2O_3 dielectric stack. Every test, and individual positive and negative polarity voltage sweeps, were measured at independent dielectric sites. The data are presented without any averaging, allowing one to appreciate that the data are fairly repeatable even for dielectric failure tests.

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measurements are to be practically meaningful. For each failure test the voltage was swept from 0 to ±30 at 1 V/s. The positive and negative polarity voltage sweeps were independently measured at fresh sample locations (otherwise failure in one polarity could damage the dielectric and influence failure in the other polarity). The diameter of the contacting droplet was ~2 mm for each experiment. Three current−voltage plots were taken for each solution tested and plotted independently in order to show any variation in the voltage for dielectric failure.

Results

The electrowetting results for DI water and several surfactant solutions are shown in Figure 3. The plotted results confirm the expected ability of surfactants to lower γ_{ao} and therefore the required electrowetting voltage. The values for γ_{ao} as measured by the pendant drop method in oil ambient are ~53 mN/m for DI water and ~5.7 mN/m for 1 wt % SDS solution. From the plot in Figure 3b for DTA-OS, it can also be observed that a higher wt % of the DTA-OS reduces the initial contact angle (θ_Y). This is likely due to lower interfacial surface tensions at the aqueous solution−fluoropolymer interface and the aqueous solution−oil interface.

Next, Figure 4 shows results of a series of dielectric failure tests performed on the various solutions. As shown in Figure 4a, no failure was observed for both positive and negative polarities of applied voltage on a DI water droplet. Even if a dielectric defect did exist, the low conductivity of the DI water (Table 2) could preclude any measurable electrolysis. Therefore, a more meaningful measurement is one in which small inorganic ions (salt) are added to the DI water. As shown in Figure 4b, an aqueous 1 wt % KCl solution causes dielectric failure repeatedly. It is well-known that atomic layer deposition produces high-density, pinhole-free Al_2O_3 films. Thus, the observed failure could not be a result of ionic conduction through large defects such as pinholes. Also, with standard metal electrodes the electric field for dielectric failure (E_{bd}) of Al_2O_3 dielectric is > 30 V/100 nm. Therefore, with a liquid electrode it is clear that the small inorganic ions and water are able to propagate through even the smallest of pathways in the dielectric. The polarity dependence of failure in Figure 4b is

Table 2. Conductivity Measurements for Various Liquids Tested

solution	conductivity (μS/cm)
1 wt % KCl in water	1002
1 wt % SDS in water	877
1 wt % DTAC in water	1330
0.05 wt % DTA-OS in water	46.5
0.1 wt % DTA-OS in water	67.0
1 wt % DTA-OS in water	138.3
propylene glycol	*a*
1 wt % SDS in propylene glycol	31.1

[a] Not measurable.

worthy of brief discussion. It is generally accepted that monovalent anions such as Cl^- and OH^- typically adsorb at a neutral polymer surface. Preferential anion adsorption has even been experimentally validated for electrowetting on fluoropolymers.[20] These adsorbed ions do not easily move unless under very high electric field, and even when they do move they are not as mobile as ions positioned further away from the surface. The surface adsorbed anions locally deplete additional anions via Debye screening. This could explain why a stand-alone thin fluoropolymer film often exhibits water electrolysis at lower voltage for positive bias (because only the positive ions comprise the mobile Debye sheath inside a small pore). Such thinking might explain the polarity dependence of failure in Figure 4b, where it is clear that K^+ ions are more easily driven into a pathway for dielectric failure. However, in our experiments a fluoropolymer/Al_2O_3 stack was used and Al_2O_3 favors surface adsorption of cations instead of the anions,[21] which could alter the above conclusions. Additional exploration of this possible polarity dependency was not performed herein and could be a lengthy future investigation in itself. However, as will be seen in the next set of data, the size of ions has a much stronger effect on dielectric failure than ion polarity. Concluding on ion-size dependence of failure is the primary goal of this present work.

Next, the commonly used anionic electrowetting surfactant SDS was tested. For all low-voltage electrowetting devices fabricated at Cincinnati,[7] it has been consistently seen that electrolysis occurs rapidly for positive bias with SDS, but not with negative bias. A desire to better understand this phenomenon triggered the more thorough investigation that is presented herein. As shown in Figure 4c, the small inorganic Na^+ ion must easily penetrate the dielectric, whereas the larger dodecyl sulfate ion is clearly less able to penetrate the dielectric. However, one might ask if this is simply a manifestation of the Stern layer and Debye screening effect postulated for the polarity dependence of failure for the KCl solution (Figure 4b). To further confirm that the failure is dominated by ion size, cationic DTAC surfactant was next tested. As shown in Figure 4d, the failure trend is the opposite of Figure 4c, where in positive bias the large dodecyltrimethylammonium group is unable to measurably penetrate through the dielectric. In negative bias the smaller inorganic Cl^- ion far more easily penetrates the dielectric. Comparison of the current−voltage results for SDS and DTAC, both at 1 wt % and similar conductivity (~1000 μS·cm, Table 2), supports the argument that ion size can be a dominant factor for dielectric failure in electrowetting devices.

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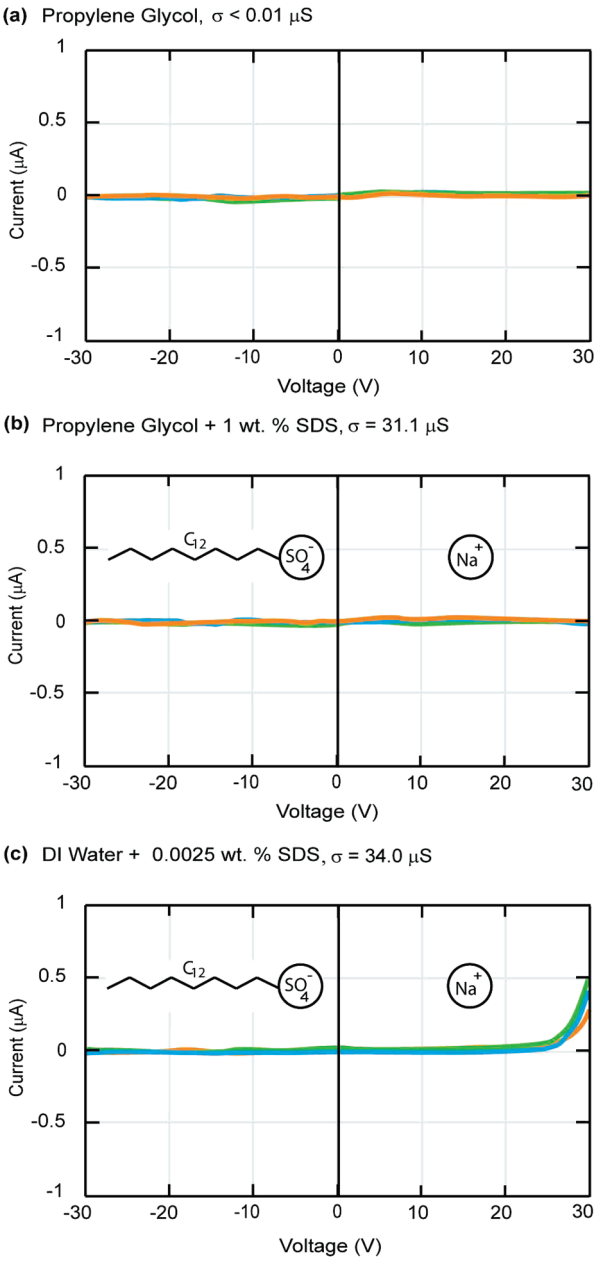


Figure 5. Dielectric failure current vs voltage for (a) pure propylene glycol (PG) and (b) PG with 1 wt % SDS. For comparison with (b) a water:SDS solution of similar conductivity is plotted in (c).

The catanionic DTA-OS surfactant was next explored. The motivation was as follows. DTA-OS might provide the requisite electrical conductivity needed for ac bias of electrowetting devices, but with greatly reduced dielectric failure due to the following factors: (1) both the cation and anion are large due to an attached alkane chain; (2) the cmc point is lower and thus the solution more electrically resistive. As shown in Figure 4e, the dielectric failure results confirm that DTA-OS is free from failure in both the positive and negative polarities. It is concluded for the DTA-OS that ion size is the dominant factor, not the lower conductivity (~46 μS·cm, Table 2), because it will be shown in Figure 5c that small ions like Na^+ still cause dielectric failure even for a solution with lower conductivity than that of the DTA-OS solution.

After gaining an understanding of the dielectric failure dependence on ion size, we next explored the effect of molecular size for

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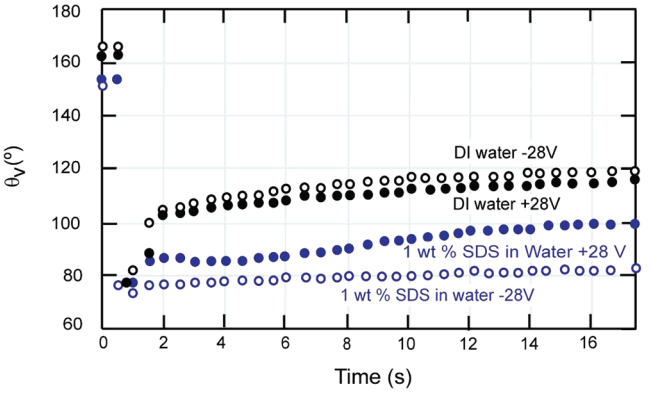


Figure 6. Measured contact angle relaxation (charge injection) vs time for several aqueous solutions biased at ±28 V. Voltage was applied at ~0.5 s, and the contact angles captured with a VCA Optima system.

the polar liquid. For the time scales and electric fields tested herein, the ions obviously will not traverse the dielectric without the presence of a water wire (a conductive pore, network, or pathway) through the dielectric. Water easily penetrates even the smallest of hydrophobic pores; for example, consider recent demonstrations of water penetration into single-wall carbon nanotubes.[22] In fact, smooth and hydrophobic pores often exhibit the least drag for ion flow. Therefore, it is likely difficult to design a material that would completely preclude water penetration and an alternate approach must be taken. It was next postulated that an alternate solvent of propylene glycol (PG, ≥99.5%, Fisher Chemical) with a larger liquid molecule size would reduce liquid penetration into the dielectric. In first tests with pure PG it was found that the PG was far too electrically resistive to allow electrowetting with even dc voltage. It is therefore not surprising that dielectric failure could not be observed for pure PG (Figure 5a). When 1 wt % SDS was added to the PG, the conductivity improved to ~31 μS·cm, and robust dc electrowetting was achieved (143° to 57° for 0 to 16 V bias). For the PG:SDS solution no dielectric failure was observed in positive bias (Figure 5b), which is unlike the failure observed for water:SDS (Figure 4c). However, the lack of failure may be attributable to the lower conductivity of the PG:SDS solution. Therefore, a similar conductivity water:SDS solution was tested (Figure 5c), and dielectric failure was observed in positive bias. Therefore, it is likely that PG is indeed less able than water to form a liquid wire through the dielectric. As a result, PG may be a useful liquid for increased reliability of some electrowetting devices (nonaqueous), but an additional cosolvent (medium size molecule) is needed to reduce the liquid viscosity for fast fluid motion.[23] Other possible factors affecting liquid wire formation, such as surface adsorption along the walls of a pore, might also differ for propylene glycol as compared to water. These factors were not explored and may be of interest in a detailed future study.

The results presented thus far primarily deal with dielectric failure of electrowetting dielectrics. Toward the end of the experiments, it was decided to briefly explore ion-size relationship to the onset of electrowetting saturation (charge injection).[12] Saturation due to charge injection is measurable in several ways, one of which is to look at the time-dependent contact angle relaxation. Time-dependent contact angle relaxation for DI water and SDS solution are plotted in Figure 6. The applied voltages are well beyond saturation (±28 V). The data show an ion dependence on the contact angle relaxation. The case for driving the largest ion (dodecyl sulfate, $C_{12}SO_4^-$ at −28 V) into the dielectric exhibits the least relaxation. This is a preliminary study that support previous conclusions made, but other factors need to be considered. The effects of interfacial tension and time-dependent interfacial tension[24] can affect relaxation behavior. Furthermore, OH^- ions in the SDS solution should also be able to inject into the dielectric unless the dodecyl sulfate somehow screens similarly charged ions at the pore entrances. Relating the data in Figure 5c with Figure 6 suggests that ion-dependent dielectric failure may have similar implications on understanding contact angle relaxation due to charge injection. Such similarity between the failure and saturation (charge injection) is not surprising.

Discussion and Conclusion

All presented data support an electrowetting failure mode that is highly dependent on ion size. Although the materials tested herein are far from comprehensive, this work provides initial guidance to electrowetting practitioners. Many of the dielectric failure voltages reported here were greater than the required electrowetting voltage. However, this does not imply that reliable and long-lived electrowetting operation is guaranteed if failure is not observed. In fact, it is nearly always the case for solid or liquid electrodes that the further one operates away from the dielectric failure voltage of a dielectric, the less the electrical degradation of the dielectric or electrodes. Therefore, use of large size ions in electrowetting liquids is generally suggested for improved reliability as they attempt to eliminate the root cause (charge penetration) rather than simply delaying the visible charging effects. However, numerous other factors must be considered such as the electrochemical reactivity of the dielectric and electrode. Although no such degradation was observed as a result of the small electrical currents measured herein, prior aging studies have shown radially propagating electrochemical degradation that starts at points of electrical failure. Future investigations may also take a closer look at the surface adsorption and Debye screening inside dielectric pores. The work reported herein, and such future work, may prove beneficial to the commercialization prospects of low-voltage (< 10 V) and long-lifetime electrowetting devices.

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