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A Fundamental Study on Electrowetting by Traditional and Multifunctional Ionic Liquids: Possible Use in Electrowetting on Dielectric-Based Microfluidic Applications

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Water or aqueous electrolytes are the dominant components in electrowetting on dielectric (EWOD)-based microfluidic devices. Low thermal stability, evaporation, and a propensity to facilitate corrosion of the metal parts of integrated circuits or electronics are drawbacks of aqueous solutions. The alternative use of ionic liquids (ILs) as electrowetting agents in EWOD-based applications or devices could overcome these limitations. Efficient EWOD devices could be developed using task-specific ILs. In this regard, a fundamental study on the electrowetting properties of ILs is essential. Therefore electrowetting properties of 19 different ionic liquids, including mono-, di-, and tricationic, plus mono- and dianionic ILs were examined. All tested ILs showed electrowetting of various magnitudes on an amorphous fluoropolymer layer. The effects of IL structure, functionality, and charge density on the electrowetting properties were studied. The enhanced stability of ILs in electrowetting on dielectric at higher voltages was studied in comparison with water. Deviations from classical electrowetting theory were confirmed. The physical properties of ILs and their electrowetting properties were tabulated. These data can be used as references to engineer task-specific electrowetting agents (ILs) for future electrowetting-based applications.

Electrowetting is the decrease in contact angle achieved by applying an external voltage across a solid/liquid interface. The control of wettability by using external electric fields has opened new opportunities in microfluidics. The motion of small volumes of liquid segments can be controlled by programmed electric fields. Recently, interest in electrowetting on dielectric (EWOD) has increased substantially compared to interest in simple electrowetting. In EWOD, when the voltage is removed, a droplet returns to its original shape, while a droplet stays at its wetting shape in simple electrowetting.¹ Reversibility is critical for wettability control to be useful in microfluid applications. EWOD has been successfully applied to develop digital (digitized droplet

based) microfluidics.^{2,3} Digital EWOD microfluidic devices have provided successful laboratory-on-a-chip platforms for various biological sample preparation and analysis processes.^{4–10} Besides bioanalytical applications, electrowetting has also been found to be very useful in many other applications such as fluid lens systems,¹¹ electrowetting displays,¹² programmable optical filters,¹³ paint drying,¹³ micromotors,¹⁴ electronic microreactors,¹⁵ and to control fluids in multichannel structures.¹⁶

Traditionally, water or aqueous electrolyte solutions are used in most EWOD experiments and applications. Although water has useful solvent properties, its low thermal stability, evaporation, and propensity to facilitate corrosion of the metal parts of integrated circuits or electronics still can cause problems in various applications. Another drawback in most microfluidic devices is fouling, which occurs in many ways.¹⁷ For example, in microfluidic devices, fouling can occur via precipitation of salts from aqueous electrolytes due to evaporation and from degasification of the electrowetting solvents. Clearly the use of aqueous electrolytes as electrowetting agents in a variety of devices can have significant limitations. Unfortunately, few substances have been proposed or successfully tested as viable substitutes for

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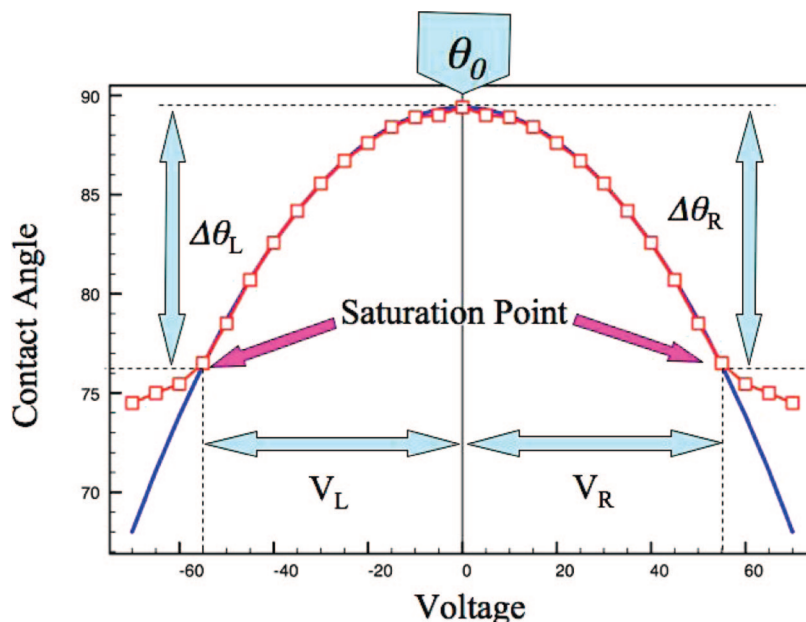


Figure 1. Characteristic parameters that can be measured from an electrowetting curve.

water.¹⁸ In this regard, we believe that ionic liquids (ILs) may have advantages over water and other aqueous electrolytes. For example, they are liquid over a wider range of temperatures,^{19,20} they have negligible or very low vapor pressures, most ILs have high thermal stability,²⁰ most ILs are nonflammable,²¹ and they have “tunable” solvent properties that can be selected and optimized for specific tasks.²² Consequently, ILs may be ideal replacements for, or complementary to, traditional aqueous electrolytes in many electrowetting applications. Specifically, fouling can be effectively controlled in electrowetting-based microfluidic devices by using ILs due to their nonvolatility and favorable solvent properties for diverse compounds. A previously published communication about electrowetting of ILs²³ demonstrated electrowetting of ILs on an amorphous fluoropolymer surface, but their experiment was limited to three simple and less stable ILs. Dubois et al. reported the use of IL droplets as electronic microreactor on an open digital microfluidic chip.¹⁵ Also, Chatterjee et al. demonstrated the successful use of two ILs in digital microfluidic devices.²⁴ However, a systematic study of the effect of IL structure on their electrowetting behaviors has not been done to our knowledge. With the emergence of new types of ILs, including dicationic,^{20,25} tricationic,^{26,27} and even dianionic²⁸ types, the electrowetting properties are expected to be more

diverse and potentially can be tailored for variety of EWOD applications. In this study, the electrowetting behaviors of 19 different ILs, including mono-, di-, and tricationic, plus mono- and dianionic ILs were examined. The effects of structure, functionality, and charge density on the electrowetting properties were examined. The relevant physical properties of these ILs were determined. Finally, some ILs are suggested as potential replacements for traditional electrowetting solvents for specific applications. By examining physical properties and electrowetting properties of a broad range of ILs one can identify suitable agents for particular applications.

Theoretical Background. An equation that relates the contact angle (θ) of a liquid drop on a dielectric surface to the external applied voltage (V) can be derived from a combination of Young's equation and Lippmann's equation (eq 1).^{1,23}

$$\cos \theta = \cos \theta_0 + \frac{c}{2\gamma} V^2 = \cos \theta_0 + \frac{\epsilon \epsilon_0}{2\gamma t} V^2 \quad (1)$$

Where c is the capacitance per unit area (specific capacitance), ϵ is the relative permittivity of the dielectric layer (dielectric constant), ϵ_0 is the permittivity of a vacuum, γ is the surface tension of the liquid, t is the thickness of the dielectric layer, θ is the contact angle at the designated voltage across a dielectric layer, and θ_0 is the contact angle at zero voltage. At some point (saturation point) the contact angle does not continue to change in a regular factor with increasing voltage. The voltage and corresponding contact angle where this occurs is referred to as the saturation voltage and saturation angle, respectively. According to eq 1, a plot of contact angle versus applied voltage should be a parabola as shown in Figure 1.

Five quantities can be extracted from such plots and used to characterize the electrowetting of different solvents (Figure 1). They are as follows: θ_0 is the contact angle at zero voltage, $\Delta\theta_L$ is

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the change in contact angle at negative voltages, and $\Delta\theta_R$ is the analogous contact angle change at positive voltages. V_L is the saturation voltage in the negative voltage realm, and V_R is the analogous saturation voltage in the positive voltage realm. In this work, we demonstrate that a wide variety of ionic liquids follow typical electrowetting behaviors and that this behavior can vary with the nature of the IL. Although we focused on the electrowetting properties of ILs, with a view toward their use in EWOD-based microfluidic devices, it should be noted that droplets can be moved or actuated by various other forces along with electrowetting forces.^{29–32} The physics of these forces are still being investigated for common liquids such as water. Thus, the study and understanding of even more complex and diverse solvents such as ionic liquids are likely to be important future endeavors.

EXPERIMENTAL SECTION

The structures of the studied ionic liquids are shown in Figure 2 and some of their physical properties are listed in Table 1. IL17 and IL18 were provided from CYTEC (www.cyttec.com, West Paterson, NJ). All of the other ILs were synthesized in our laboratory as reported previously.^{20,25,27,28}

The experimental setup for the electrowetting determinations is shown in Figure 3. The electrowetting experiments were performed somewhat differently from those reported by Millefiorini et al.²³ First, indium tin oxide (ITO, 30-nm thickness) precoated unpolished float glass slides (www.delta-technologies.com, Stillwater, MN) were dip-coated with an amorphous fluoropolymer layer (Teflon). The Teflon solution was prepared by dissolving 4% (w/v) of Teflon AF1600 (www2.dupont.com, Wilmington, DE) in Fluoroinert FC75 solvent (www.fishersci.com, Barrington, IL). The dipping speed was set to 750 $\mu\text{m/s}$ in a custom-made dip coater. Once 3/4 of the slide was dipped in the solution, dipping was stopped for 5 s, and then the slide was raised at the same speed. The coated slides were then heat treated for 6 min at 112 °C, 5 min at 165 °C and 15 min at 328 °C in an oven. Teflon-coated glass slides were then allowed to cool to room temperature, washed thoroughly with acetone and deionized water, and air-dried. The resulted Teflon thickness was 260 ± 10 nm. The thickness was measured using a Tencor Alphastep 200 Profilometer. The electrowetting experiment was conducted using a contact angle goniometer CAM 101 system (Figure 3a; www.ksvltd.com, Monroe, CT).

Typically, a drop of ionic liquid was placed on top of the Teflon layer using a capillary tube. The volume of the drop was calculated by using CAM 200 software (www.ksvltd.com, Monroe, CT); the drop volume was between 3 and 8 μL for all experiments. The voltage was applied in 5 V increments starting from 0 to +70 V, using a Keithley 2400 SourceMeter (www.keithley.com, Cleveland, OH). The positive probe was attached to the Pt wire (36 gauge), and negative probe was attached to the ITO layer (Figure 3b). Afterward, a fresh drop of IL was placed at a different position on the surface and the above procedure was repeated for 0 to −70 V. Only for IL19 the experiment was conducted from 0 to +200 V and from 0 to −160 V. After each experiment with one IL, the

platinum wire was thoroughly washed with acetone and DI water, respectively, and air-dried. At each voltage increment, a picture was taken and contact angles were measured using CAM 200 software. Finally, the contact angle versus voltage curves were plotted. For some selected ILs, the above procedure was repeated applying voltage from 0 to +100 V in 5 V increments, from 100 to 150 V in 10 V increments, from 150 to 500 V in 50 V increments, and from 500 to 1000 V in 100 V increments, followed by the same procedure for negative voltages. However, when applying higher voltages, some ILs tended to decompose or to burn; at that point applying voltage was stopped. The purpose of applying higher voltages is to determine the stability of ILs upon higher voltages. The effect of water on electrowetting of ILs was studied by using both a water-miscible (i.e., IL1) and a water-immiscible IL (IL4). A series of IL1 + water solutions (w/w) were prepared, and the θ_0 values were measured for each solution. Then electrowetting experiments were conducted for solutions of 5, 10, and 20% (w/w) water containing IL1. Exactly 0.5 mL of the water-immiscible IL4 was mixed with 5 mL of water, shaken for 2 min, and then allowed to settle. After 1 h, two layers were clearly observed. Water layer was decanted, and the electrowetting experiment was conducted for the IL4 layer. All experiments were conducted in ambient atmosphere at 23 ± 1 °C unless otherwise noted.

In regard to their safety, all the tested ILs are nonflammable; however, IL3 may produce HF upon decomposition.

RESULTS AND DISCUSSION

Table 1 summarizes some physical properties of the studied ILs, and Table 2 summarizes the five electrowetting parameters obtained for 19 different ILs.

Anion Effects. Ionic liquids IL1–IL4 have same cation, BMIM⁺. The size of the anion and the delocalization of its charge increases from IL1 to IL4. The reported diameters of the anions are IL1 = 3.62 Å, IL2 = 3.90 Å, IL3 = 5.10 Å, and IL4 = 7.57 Å.³³

Anion Effect on the θ_0 Value. Figure 4a shows the electrowetting curves of IL1–IL4. It is observed that an increase in the size of the anion and charge delocalization leads to a decrease in the θ_0 value. The θ_0 value obtained for IL1 is similar to that of IL2 even though the diameter of Cl[−] is slightly smaller than that of Br[−]. θ_0 is the contact angle at zero external voltage, which can be described by Young's equation (eq 2) as the equilibrium contact angle.³⁴

$$\theta_0 = \cos^{-1}[(\gamma_{\text{SV}} - \gamma_{\text{SL}})/\gamma] \quad (2)$$

Here, γ , γ_{SV} , and γ_{SL} are the interfacial tensions associated with the liquid/vapor, solid/vapor, and solid/liquid interfaces, which are the only three parameters that govern the θ_0 value (Figure 3b). Increasing the size and charge delocalization leads to a decrease of the surface tension (γ); this is due to a combination of entropic contribution and enthalpic contributions. An increase in the size of anions will increase the entropy, which lowers the ordering of ions within the liquid and accordingly on the surface.³⁵ Delocalization of charge will decrease the ability to form hydrogen bonds. Both contributions ultimately reduce the surface tension

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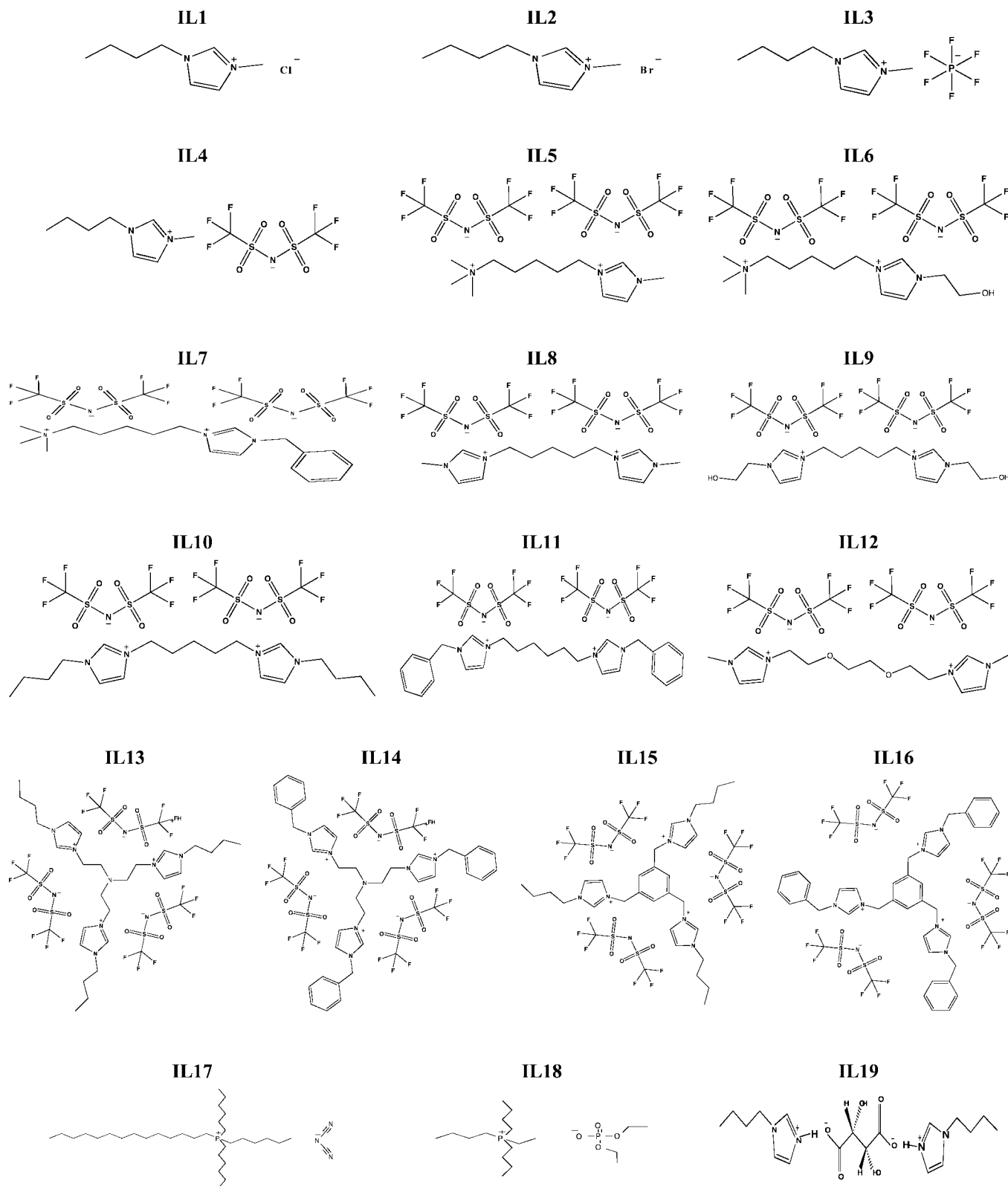


Figure 2. Structures and numbering system for the ILs tested.

of IL.³⁵ From IL1 to IL4, the size of the anion and charge delocalization increase; as a consequence, the surface tension of these ILs decreases in a logical fashion. According to eq 2 and considering the $(\gamma_{SV} - \gamma_{SL})$ values are approximately same for the four ILs, a decrease in γ will result decrease in the θ_0 value. Thus, it can be concluded that size of the anion and charge delocalization have a direct relationship with the θ_0 value.

Effect of the Anion on $\Delta\theta_L$, $\Delta\theta_R$, V_L , and V_R . In Figure 4b, the electrowetting plots of IL–IL4 were overlaid normal to the maximum θ_0 value. The negative branch of the curves was similar for all four ILs, while the positive branch shows some differences. It is clearly observed that $\Delta\theta_L$ and V_L values are comparable for all four ILs, whereas the $\Delta\theta_R$ and V_R values are all different. $\Delta\theta_R$ and V_R values tend to decrease IL2 > IL1 > IL3 > IL4, which

Table 1. Physical Properties of the Studied ILs

| ionic liquid | MW (g/mol) | melting point (°C) | density ρ^a (g/cm ³) | refractive index | viscosity ^b at 30 °C (cSt) | approximate thermal stability (°C) | surface tension ^c (dyne/cm) | work of adhesion (dyne/cm) | miscibility with water |
|-------------------|---------------------|--------------------------|---------------------------------------|--------------------|---------------------------------------|------------------------------------|--|----------------------------|------------------------|
| IL1 ^d | 174.7 ^e | 65 ^e | 1.10 ^e | 1.523 | 1701 | 145 ^e | 60.7 | 53.3 | M |
| IL2 ^d | 219.1 ^e | 70 ^e | 1.30 ^e | 1.538 | 804 | | 54.3 | 47.7 | M |
| IL3 | 284.2 | -8 ^g | 1.36 ^g | 1.411 ^g | 170 | | 44.8 | 45.6 | I ^g |
| IL4 | 419.4 | -4 ^f | 1.43 ^f | 1.427 ^f | 36 ^f | 185 ^f | 32.8 | 41.3 | I |
| IL5 ^h | 771.7 | -51.5 | 1.54 | 1.431 | 357 | 302 | | | I |
| IL6 ^h | 801.2 | -54.2 | 1.54 | 1.435 | 398 | 133 | | | I |
| IL7 ^h | 847.1 | -36.2 | 1.50 | 1.458 | 1217 | 328 | | | I |
| IL8 ^h | 794.2 | -61.0 | 1.57 | 1.441 | 251 | 365 | | | I |
| IL9 ^h | 854.2 | -65.0 | 1.58 | 1.456 | 241 | 257 | | | I |
| IL10 | 878.3 ^h | -62.0 ^h | 1.44 ^h | 1.433 ^h | 355 ^h | 376 ^h | 41.5 | 51.8 | I ^h |
| IL11 | 960.9 | | 1.08 | 1.511 | 6021 | | | | I |
| IL12 | 840.7 | | 1.36 | 1.444 | 350 | | 43.4 | 47.9 | I |
| IL13 | 1311.2 ⁱ | -47.5 ⁱ | 1.41 ⁱ | 1.451 ⁱ | 1580 ⁱ | 308 ⁱ | 43.2 | 52.9 | I ⁱ |
| IL14 ⁱ | 1413.2 | -6.7 | 1.51 | 1.493 | 25000–30000 | 348 | | | I |
| IL15 ⁱ | 1330.2 ⁱ | -24.6 ⁱ | 1.53 ⁱ | 1.467 ⁱ | 2320 ⁱ | 344 ⁱ | | | I ⁱ |
| IL16 | 1432.2 ⁱ | -87.4 ⁱ | 1.55 ⁱ | 1.588 ⁱ | 20000–25000 ⁱ | 262 ⁱ | 52.9 | 60.3 | I ⁱ |
| IL17 | 493.8 | > -76 < -22 ^f | 0.90 ^f | 1.484 ^f | 269 ^f | 360 ^f | 40.8 | 49.3 | I |
| IL18 | 384.5 | > -76 < -22 ^f | 1.01 ^f | 1.470 ^f | 360.6 ^f | 350 ^f | 38.5 | 47.2 | M |
| IL19 | 314.3 | | 1.080 | 1.500 | 2104 | | 55.3 | 52.4 | M |

^a Measured using a pycnometer. ^b Measured using a capillary viscometer. ^c Measured using a Fisher surface tensiometer (model 20), due to limited availability, surface tension of all ILs were not determined. ^d Measured at a supercooled state. I = immiscible; M = miscible. ^e Data taken from Reference 33. ^f Reference 44. ^g Reference 45. ^h Reference 25. ⁱ Reference 27.

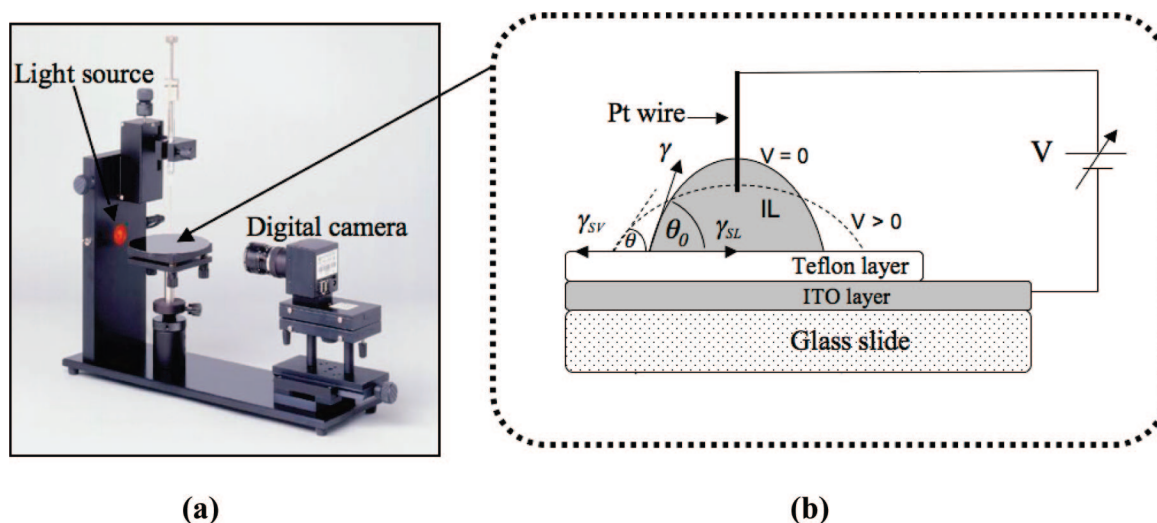


Figure 3. Electrowetting experimental setup: (a) CAM 101 system; (b) schematic diagram of glass slide and IL drop. Solid line of the drop represents the drop shape without any external voltage. Dashed line of the drop represents the drop shape with external voltage applied.

also appears to be related to size and charge delocalization of the anion although IL2 seems to have a relatively high V_R .

Effect of the Anion on Curve Asymmetry. The liquid–solid interfacial free energy can be described by the work of adhesion between a liquid and a substrate (W_a). A stronger interaction between a liquid and a substrate will provide a higher work of adhesion value. The value of W_a is given by the Young–Dupré equation (3).³⁶

$$W_a = \gamma(1 + \theta_0) \quad (3)$$

W_a values were calculated for the ILs for which surface tension values were available (Table 1). Teflon AF 1600 is a random copolymer of 4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole (PDD)

and tetrafluoroethylene.³⁴ The previous work of Quinn et al.³⁴ demonstrated that, as the PDD content increases, deviations from theory at positive voltages is significant due to the adsorption of hydroxide and halide ions to the Teflon layer. Although they reported a relatively small effect caused by halide anions, in our case, this effect appears to be more substantial. According to Table 1 W_a values decrease in the order of IL1 > IL2 > IL3 > IL4. The size of the anion increases in a similar order. It appears that smaller anions have stronger interactions with Teflon layer than larger anions. This can be clearly observed in Figure 4c, where the contributions of Cl^- , Br^- , and PF_6^- to the asymmetry of the electrowetting curves are higher than those of NTf_2^- .

Effects of the Cationic Moieties. IL5–IL12 are dicationic ILs, which have same NTf_2^- anion. IL5–IL7 contain two different

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Table 2. Electrowetting Properties of Studied ILs

| ionic liquid | θ_0 | $\Delta\theta_L$ | $\Delta\theta_R$ | V_L | V_R |
|--------------|------------|------------------|------------------|-------|-------|
| IL1 | 97 | 13 | 17 | -60 | 50 |
| IL2 | 97 | 15 | 27 | -60 | 65 |
| IL3 | 89 | 16 | 11 | -60 | 35 |
| IL4 | 75 | 10 | 7 | -40 | 25 |
| IL5 | 86 | 19 | 19 | -50 | 55 |
| IL6 | 88 | 15 | 14 | -55 | 45 |
| IL7 | 84 | 17 | 16 | -50 | 40 |
| IL8 | 83 | 14 | 11 | -45 | 40 |
| IL9 | 85 | 18 | 12 | -55 | 35 |
| IL10 | 76 | 17 | 14 | -45 | 50 |
| IL11 | 84 | 14 | 16 | -50 | 40 |
| IL12 | 84 | 14 | 16 | -48 | 40 |
| IL13 | 77 | >25 | >20 | <-70 | >70 |
| IL14 | 88 | 15 | 18 | -55 | 60 |
| IL15 | 77 | 20 | 25 | -55 | 60 |
| IL16 | 82 | >15 | >14 | <-70 | >70 |
| IL17 | 78 | 10 | 16 | -30 | 40 |
| IL18 | 77 | 7 | 13 | -25 | 35 |
| IL19 | 93 | 29 | 28 | -160 | 190 |

cationic moieties (unsymmetrical) while all other dications are symmetrical (i.e., the linked cationic moieties are the same). Figure 5 shows the electrowetting curves of IL5–IL12.

Cation Effect on the θ_0 Value. Among these ILs, IL10 has a considerably lower θ_0 value whereas the others have similar θ_0 values. According to eq 2, $(\gamma_{SV} - \gamma_{SL})$ and γ govern the θ_0 value. There is limited availability of IL surface tension data. However, there were sufficient amounts of IL10 and IL12 to determine their surface tensions and the values of the others can be predicted.^{20,35} IL10 contains two butyl chains in its structure. Flexibility of these butyl chains can increase the molecular disorder or entropy of the system. This leads to an increase in the irregularity within the liquid and ultimately on the surface, consequently giving a lower surface tension value for IL10 than its related ILs.³⁵ According to eq 1, this relatively lower surface tension value translates directly into a lower θ_0 value for IL10. An analogous trend can be observed for the tricationic ionic liquids IL13–IL16. IL13, and IL15, with *N*-butyl substituents, have considerably lower θ_0 values than the benzyl-substituted analogues IL14 and IL16 (Table 2).

Cationic Effect on $\Delta\theta_L$, $\Delta\theta_R$, V_L , and V_R values. IL11 had considerably lower $\Delta\theta_L$, $\Delta\theta_R$, V_L , and V_R values than the other

dicationic ILs, all of which had similar $\Delta\theta_L$, $\Delta\theta_R$, V_L , and V_R values (Table 2). IL11 contains two benzyl groups in its structure. Introduction of these two benzyl groups provides additional π – π interactions for this ionic liquid, and these may lead to the lower values. It appears that effect of these benzyl groups can be found in the tricationic ionic liquids as well; $\Delta\theta_L$, $\Delta\theta_R$ values of IL14 and IL16 are much lower than those of IL13 and IL15 (Table 2).

Cationic Effect on Asymmetry of Electrowetting Curves. The asymmetry of the electrowetting curves for IL5–IL12 is generally less than that for IL1–IL4. IL 5–IL12 are dicationic ILs, which have same NTf_2^- anion; hence, interactions with PDD in the Teflon layer are about same and lower than that for the anions of IL1–IL3, as was discussed previously. This leads to lower adsorption, ultimately resulting in lower asymmetry for all of the dicationic ILs that share same NTf_2^- anion. Analogous behavior is observed for tricationic ILs IL13–IL16.

Effect of the Number of Cationic Groups. Figure 6 shows the electrowetting curves of IL4, IL10, and IL13. These three ILs have a common anion (NTf_2^-) and the same butyl imidazolium cationic moiety. The difference between them is that IL4 is monocationic, IL10 is dicationic, and IL13 is tricationic.

Regardless of the cationic charge, the θ_0 values of IL4, IL10, and IL13 are approximately same. This is due to their comparable surface tension values (Table 1). The $\Delta\theta_L$, $\Delta\theta_R$, V_L , and V_R values of this series of ILs decrease in the order of IL13 > IL10 > IL4. Hence, it can be concluded that the number of charged cationic groups directly affects the $\Delta\theta_L$, $\Delta\theta_R$, V_L , and V_R values.

Other Relevant Observations. IL19 is the only dianionic IL studied. It has the largest $\Delta\theta_L$, $\Delta\theta_R$, V_L , and V_R values among all ILs studied (Table 2). IL17 and IL18 are phosphonium-based ILs. There does not seem to be significant differences in the electrowetting properties between phosphonium ILs and imidazolium ILs. It was observed that ILs were decomposed or burned, when experiments were conducted at much higher voltages. However, some ILs were stable even at 1000 V. Some of the ILs had different decomposition voltages at positive and negative voltages. Table 3 shows the maximum voltage values of selected ILs that can be obtained without any decomposition of the IL itself or breakdown of the Teflon layer. Comparison data for water were

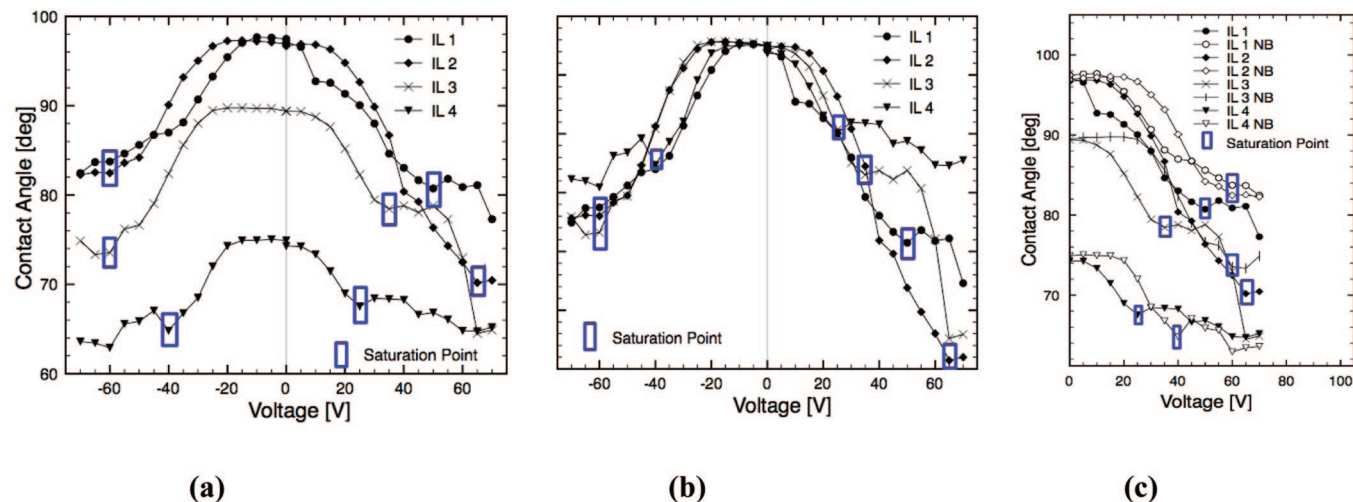


Figure 4. (a) Electrowetting curves of IL1–IL4. (b) Electrowetting curves of IL1–IL4 were overlaid normal to the maximum θ_0 value. (c) Folded curves showing the asymmetry in the electrowetting curves.

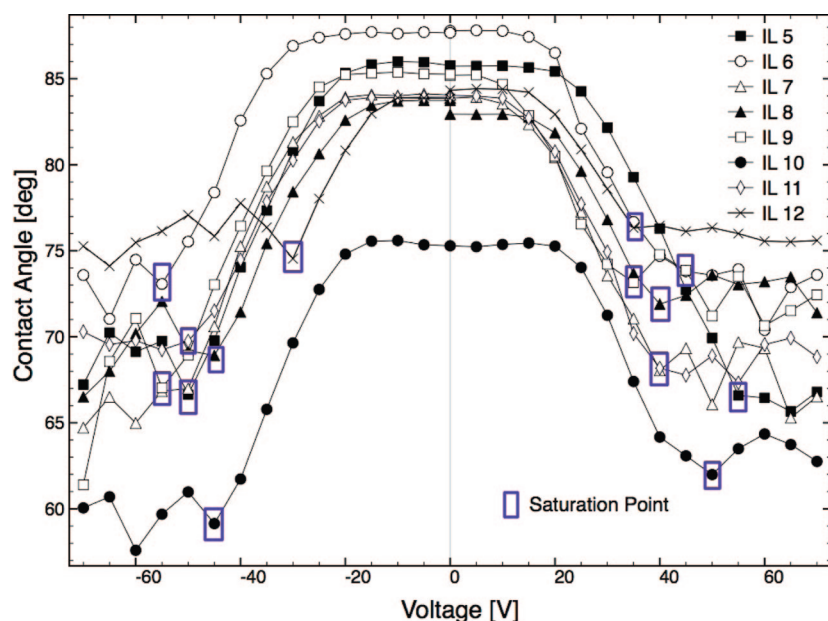


Figure 5. Electrowetting curves of dicationic ILs IL5–IL12.

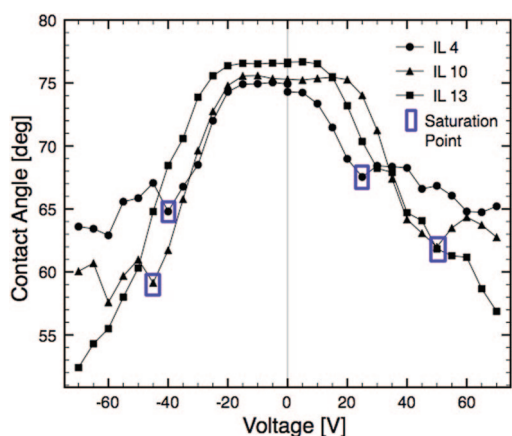


Figure 6. Electrowetting curves of IL4, IL10, and IL13.

Table 3. Stability of Selected ILs in Higher Voltages

| ionic liquid | Teflon layer thickness (nm) | maximum voltage at which liquid remains stable | |
|--------------------|-----------------------------|--|--------------|
| | | positive (V) | negative (V) |
| IL5 | ~260 | 350 | >1000 |
| IL6 | ~260 | >1000 | >1000 |
| IL8 | ~260 | >1000 | >1000 |
| IL9 | ~260 | >1000 | 800 |
| IL11 | ~260 | 150 | >1000 |
| IL12 | ~260 | >1000 | 900 |
| IL13 | ~260 | 200 | 200 |
| IL17 | ~260 | 200 | 150 |
| IL18 | ~260 | 90 | 500 |
| water ^a | ~250 | 100 ^b | |
| water ^a | ~550 | 120 ^b | |

^a Data taken from ref 46. ^b Reported as breakdown voltage with no voltage polarity indication.

also tabulated in Table 3. Clearly, ionic liquids are stable at much higher voltages than water when they are used in electrowetting applications. Furthermore, it appears that the imidazoloim-based ILs (IL5–IL12) are more stable at high voltages than phosphonium-based ILs (IL17 and IL18).

Deviation from the Theoretical Curve. It is observed that, unlike water and other aqueous electrolytes, ILs show deviations from eq 1. A previous study by Millefiorini et al.²³ and Dubois et al.¹⁵ also observed such deviations. According to eq 1, a plot of $2\gamma(\cos\theta - \cos\theta_0)$ versus V^2 should give the same c value (specific capacitance) for all ILs. However, the calculated c values for the ILs (Table 4) are different for each IL showing deviations from the theoretical c value. Note that the $2\gamma(\cos\theta - \cos\theta_0)$ versus V^2 were plotted separately for the positive and negative voltages. The individual c values were then extracted from the plots (see Supporting Information). The theoretical c value in eq 1 can be calculated by $1/c = 1/c_d + 1/c_{H(aq)}$, where c_d is the capacitance of dielectric layer (Teflon) and $c_{H(aq)}$ is the capacitance of liquid double layer at the dielectric layer/aqueous electrolyte interface. However, due to the fact that $c_d \ll c_{H(aq)}$,³⁷ $c_{H(aq)}$ has less of an effect on the theoretical c value in eq 1. Therefore, the approximation $c \approx c_d$ is generally valid for water and other aqueous electrolytes [$c_d = \epsilon\epsilon_0/t$, ϵ , and t are dielectric constant (1.93) and thickness of the dielectric layer, respectively].³⁷ However, according to Table 4, the c values obtained for ILs are all significantly lower than the theoretical c value. There may be several reasons for this. First, a finite leakage current across the dielectric layer (0–21 μ A depending on the applied voltage value) was observed during the EWOD measurement and it may be an evidence of some imperfections in thin (260 ± 10 nm) Teflon layer (See Supporting Information). The Teflon layer is not a perfect dielectric (capacitor) layer. Rather it can be modeled as a parallel connection of a resistor and a capacitor, which can cause smaller c . Similar deviations from electrowetting theory were reported elsewhere.^{1,38} Moon et al. also pointed ion adsorption to the Teflon layer as a possible reason for the deviation.¹ Second, $c_{H(aq)}$ is calculated by modeling ions in aqueous electrolytes or water as charged spheres. However, Kornyshev³⁹ indicated that ILs should not be modeled as charged spheres due to the asymmetry of their

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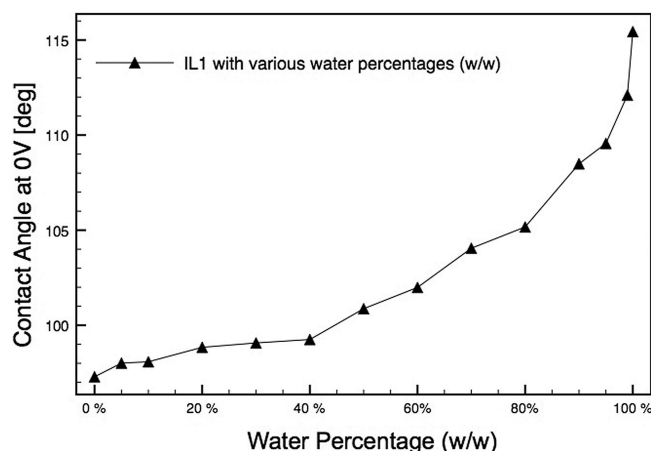
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Table 4. Comparison of c Values of ILs with the Theoretical c Value^a

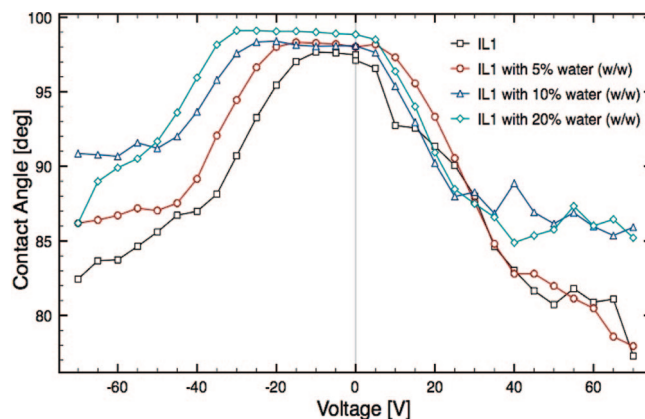
| IL | specific capacitance (c) ($\mu\text{F}/\text{m}^2$) | | specific capacitance of double layer of IL ($c_{\text{H(IL)}}$) at Teflon layer-IL interface ($\mu\text{F}/\text{m}^2$) ^b | | double layer thickness of IL (t_{IL}) at Teflon layer-IL interface (nm) ^c | | specific capacitance of double layer of IL ($c_{\text{H(IL)}}$) at Pt electrode ($\mu\text{F}/\text{m}^2$) ⁴¹ | double layer thickness of IL (t_{IL}) at Pt electrode (nm) ⁴¹ |
|---------------------------------|---|------------|--|------------|---|------------------|--|---|
| | positive V | negative V | positive V | positive V | positive V | negative V | | |
| theor value ($c \approx c_d$) | 66 | 66 | | | | | | |
| IL1 | 16 | 17 | 21 | 23 | 29×10^2 | 27×10^2 | | |
| IL2 | 12 | 9 | 15 | 10 | 42×10^2 | 59×10^2 | | |
| IL3 | 15 | 7 | 19 | 8 | 32×10^2 | 79×10^2 | 19×10^4 | 30 |
| IL4 | 12 | 8 | 15 | 9 | 42×10^2 | 68×10^2 | 15×10^4 | 40 |
| IL10 | 8 | 12 | 9 | 15 | 68×10^2 | 42×10^2 | | |
| IL12 | 10 | 16 | 12 | 21 | 53×10^2 | 29×10^2 | | |
| IL13 | 9 | 8 | 10 | 9 | 59×10^2 | 68×10^2 | | |
| IL16 | 5 | 6 | 5 | 7 | 115×10^2 | 94×10^2 | | |
| IL17 | 16 | 13 | 21 | 16 | | | | |
| IL18 | 12 | 16 | 15 | 21 | | | | |
| IL19 | 4 | 4 | 4 | 4 | | | | |

^a c values extracted only for the ILs for which surface tensions data is available. ^b Calculated using the equation, $1/c = 1/c_d + 1/c_{\text{H(IL)}}$. ^c Calculated using the equation, $c_{\text{H(IL)}} = \epsilon\epsilon_0/t$ ($\epsilon = 7$ for imidazolium based ILs).⁴¹

**Figure 7.** Contact angle at zero voltage vs water percentage in IL1.

structures. Hence, the capacitance of the liquid double layer at the dielectric layer/ionic liquid interface ($c_{\text{H(IL)}}$) may not be calculated in classical ways.³⁹ Therefore, the approximation $c \approx c_d$ in eq 1 may not be valid for ILs. Lastly, different functional groups and structural differences in ILs may influence $c_{\text{H(IL)}}$. Lazzari and co-workers⁴⁰ showed that ILs with the same anion and different cations, with approximately same size, have different capacitance responses due to different polarizabilities and differences in the structures of the two cations. Hence, again, the approximation $c \approx c_d$ is doubtful for ILs in eq 1.

Conversely, it was recently reported⁴¹ that the double layer thickness of imidazolium-based monocationic ILs at the Pt electrode have thickness values comparatively similar to those of aqueous electrolytes. In these calculations, the dielectric constants (ϵ) of imidazolium-based ILs were taken as 7.^{41,42} Table 4 shows the calculated double layer thickness values at Teflon surface and a comparison to the values for the Pt surface.

**Figure 8.** Electrowetting curves of IL 1 and its diluted solutions.

Effect of Water. All ILs contain water to a certain extent as do all other liquids. Water and other solvents were removed using a rotary evaporator in the final synthesis step of the ILs as indicated in the Experimental Section. Approximately 0.5 mL of each IL was stored in a vacuum oven for 12–18 h with phosphorus pentoxide (P_2O_5) at room temperature before the test to minimize the water content. There are water-miscible ILs and water-immiscible ILs. The effect of water in the ILs on their electrowetting was studied using IL1 (a water-miscible IL) and IL4 (a water-immiscible IL).

Figure 7 shows the θ_0 values of IL1 with different percentages of water. According to Figure 7, the higher the water percentage in IL1, the higher the θ_0 values obtained. Also, the surface tension values are proportional to the percentage of water in water-miscible ILs.⁴³ According to Figure , it can be concluded that a increase of water content will result an increase in the θ_0 value for water-

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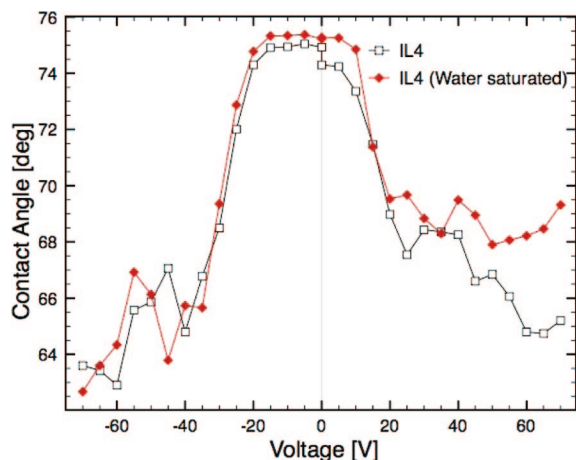


Figure 9. Electrowetting curves of IL4 and water saturated IL4.

miscible ILs. Figure 8 shows the electrowetting curves of IL1 and its diluted solutions. It can be observed that the positive branch of the curve for IL1 was not affected by water content of IL 1. However, the negative branch of the curve was affected by water content. According to Figure , it can be concluded that the higher the percentage of water, the higher the asymmetry of the obtained curves. IL4 is a water-immiscible IL. Figure 9 shows the electrowetting curves of IL4 and that of water-saturated IL4. It can be observed that both electrowetting curves are approximately same for the IL4 and water-saturated IL4. Therefore, it can be concluded that water has less or no effect on the electrowetting of water-immiscible ILs in this study. Also, absorption of water into the IL drops during the experiment can be considered to have a smaller or negligible effect.

CONCLUSION

The successful electrowetting of nonpolar, dielectric surface by 19 different ILs was demonstrated. The electrowetting properties of these ILs depend on their ion size, number of functional groups, and overall structure. The electrowetting plots of ILs have larger deviation from eq 1; this may be due to leakage current, large size of ions, functional groups, and structure of ILs. ILs with 20° or more $\Delta\theta_L$ or $\Delta\theta_R$ values may be used in microfluidic devices. ILs with high $\Delta\theta_L$ and $\Delta\theta_R$ values plus low V_L and V_R values can be used in low-voltage electrowetting applications. Physical properties and electrowetting properties data of these ILs can be used as references to engineer task-specific electrowetting agents (ILs) for future electrowetting-based microfluidic applications. ILs are generally more resistant to decomposition at high voltages than water or aqueous solutions in electrowetting scenarios.

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SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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