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Electrowetting of Ionic Liquids

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Abstract: We have successfully demonstrated that imidazolium- and pyrrolidinium-based commercial room-temperature ionic liquids can electrowet (with a dc voltage) a smooth fluoropolymer (Teflon AF1600) surface. Qualitatively, the process is analogous to the electrowetting of aqueous electrolyte solutions: the contact angle versus voltage curve has a parabolic shape which saturates at larger voltages (positive or negative). On the other hand we observed several peculiarities: (i) the efficiency is significantly lower (by about an order of magnitude); (ii) the influence of the bulky cation is larger and the importance of the smaller anion is lesser, especially with respect to electrowetting saturation; (iii) there is an asymmetry in the saturation contact angles found for positive and negative voltages. The asymmetry may be correlated with the cation−anion asymmetry of the ionic liquids. The low efficiency may be caused by the presence of water and other impurities in these commercial materials.

Introduction

We consider the potential of ionic liquids (IL) as a novel class of electrowetting agents. Room-temperature ionic liquids (RTIL), an increasingly important set of electrolytes, are organic salts that are liquid at room temperature[1] (often below 100 °C). These liquids have unique physicochemical characteristics:[1−5] no significant vapor pressure, nonflammability, good thermal stability, and a wide useable temperature range.[2] There is growing interest in their use as clean solvents in various processes, e.g., pharmaceutical synthesis, catalysis, and extraction.[3−5] They are nonvolatile with high ionic conductivity and therefore very promising in various electrochemical and industrial applications,[2] including lithium ion batteries.[2,5,6]

Electrowetting (EW) is the decrease in contact angle (i.e., enhanced wettability) achieved by applying an external voltage across the solid/liquid interface. The effect has been known for some time but has recently attracted a lot of interest in relation to directed and switchable fluid movement. EW is essentially an electrocapillary effect on a solid electrode insulated with a thin hydrophobic layer.[7,8] The external voltage creates an electric field which drives oppositely charged species (ions or particles) to the insulator/liquid interface. The surface tension of this interface is effectively reduced in accordance with Lippmann's equation (the relation between charge density and applied potential[9]). In the popular case of a flat electrode covered with an insulating polymer (thickness, t) the Young equation describing the contact angle can be combined with Lippmann's equation and the result is[7,8]

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

where θ is the contact angle, θ_0 is the contact angle at zero external voltage, C is the capacitance, V is the external voltage, γ is the surface tension of the liquid, ϵ is the relative permittivity of the layer, and ϵ_0 is the electric constant.

As ionic liquids gain industrial significance, the manipulation of these fluids becomes increasingly important. Electrowetting is a prime candidate for the actuation of these fluids since it is reversible, has no moving parts, and is conducive to computerized triggering.[10−12] The usefulness of EW in reversibly switching a two-phase flow configuration has been clearly demonstrated.[13] To implement the EW effect for the manipula-

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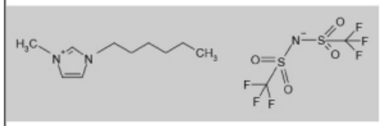
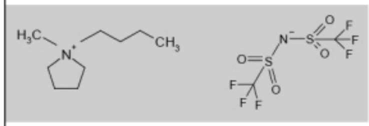
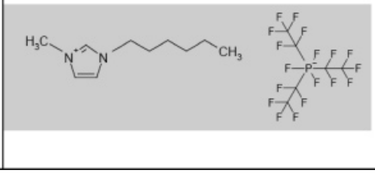
Table 1. Ionic Liquids and Their Properties: *M*, Molecular Mass; ρ, Density; η, Viscosity (Data from the Manufacturer[14])

Abbr.	Name	Structure	M [g/mol]	ρ [g/cm³]	η [Pa.s]	Water Miscibility
IL31	1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide		447.42	1.37	60	No
IL46	1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide		422.41	1.40	100	No
IL78	1-Hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate		612.28	1.56	116	No

tion of ionic liquids, it is crucial to examine their wettability under an external voltage. Successful EW-based manipulation of RTILs for reaction control would enhance their role as more environmentally sustainable industrial solvents and allow for enhanced small-scale reactions. To the best of our knowledge this is the first demonstration of electrowetting of ionic liquids.

Materials and Methods

The ionic liquids studied in this report and some of their properties are listed in Table 1.

Indium−tin-oxide (ITO) coated glass slides (unpolished float glass slides, 30 nm ITO coating, Delta Technologies Ltd., Stillwater, MN) were dip coated with an amorphous fluoropolymer layer. The dip coating was performed on a Sartorius Analytic A200S balance with controlled immersion of the glass slide into a 4% (w/v) of Teflon AF1600 (DuPont Fluoroproducts, Wilmington, DE) dissolved in a Fluorinert FC75 solvent (www.fluorochem.net, Derbyshire, U.K.). The slides were lowered at 750 μm/s, allowed to settle for a few seconds, and then raised at the same speed. The Teflon-covered ITO glass slides were then heat-treated for 6 min at 112 °C, 5 min at 165 °C, and 15 min at 328 °C in order to remove residual solvent and improve the adhesion of the Teflon layer to the substrate. This procedure resulted in AF1600 film thicknesses of 410 ± 10 nm, as measured by a Filmetrics F20 spectral refractance thin film analyzer (Filmetrics, San Diego, CA).

The coated slides were then loaded into a custom-made sessile drop apparatus, where drops of ionic liquids were formed with a vertical syringe on top of the AF1600 coating. Side-view images of the drops were obtained using a digital camera with zoom lens (the needle of the syringe was kept in contact with the droplet, 20 to 50 μL in size). A potential difference was applied across the insulated ITO electrode (in increments of 2, 5, and 10 V) with a power supply (Trek Model 610D high-voltage amplifier/controller, Medina, NY). The high-voltage source was connected to the ITO substrate while the needle, i.e., the liquid droplet, was grounded. For each drop of ionic liquid, the voltage was increased from zero to the maximum achievable value (positive or negative). Various spots on the same sample or different samples were used to obtain the positive and the negative branches of the full electrowetting curve. The potential was no longer increased once the ionic liquid became compromised (e.g., by gas evolution).

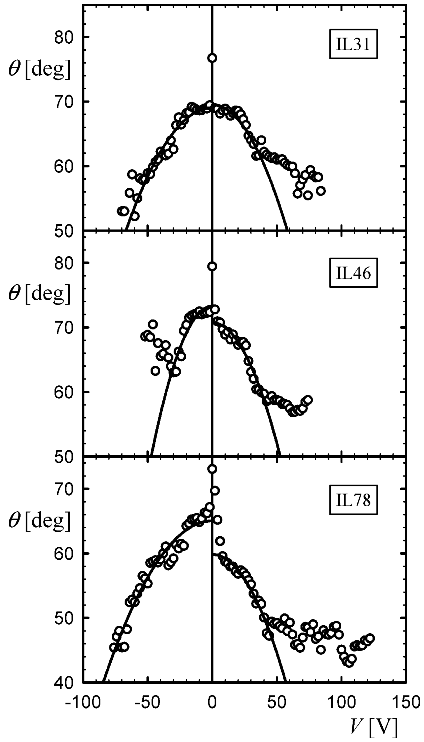


Figure 1. Electrowetting curves for three ionic liquids (see Table 1 for structure and properties). The dc voltage is applied to the insulated electrode, and the liquid droplet is grounded. The solid lines are fits of the equation $\cos\theta = \cos\theta_0 + bV^2$ (θ_0 and b are free parameters; see Table 2 for values).

All experiments were conducted in ambient atmosphere (humidity approximately 45%) in a class 100 clean room at 23 ± 1 °C.

Results

The electrowetting curves for the three ionic liquids studied here are shown in Figure 1.

The experimentally determined contact angles are shown with open circles. A Young−Lippmann type of equation ($\cos\theta = a + bV^2$, a and b are free parameters) was used to fit the data−

Table 2. Comparison of the Curvature of the Fitted Parabolas (Shown with Solid Lines in Figure 1) with Theoretical Estimates from the Young−Lippmann Equation (the Wilhelmy Plate Technique Was Used for Surface Tension Measurements)

			$C/2\gamma [V^{-2}]$		
RTIL	γ [mJ/m^2]	θ_0 [deg]	negative branch	positive branch	estimated
IL31	27.2	69/69	$6.6(3) \times 10^{-5}$	$9.2(8) \times 10^{-5}$	7.9×10^{-4}
IL46	32.4	73/71	$1.7(2) \times 10^{-4}$	$1.2(1) \times 10^{-4}$	6.6×10^{-4}
IL78	28.1	65/60	$5.1(2) \times 10^{-5}$	$8.6(4) \times 10^{-5}$	7.6×10^{-4}

separately for positive and negative voltages—and the results are shown with solid lines. At negative voltages, the parabolic shape is prominent and the fit accounts for almost all data points for IL31 and IL78. For IL46 there is an evident deviation at −30 V and a contact angle saturation at about 68°. At positive voltages, all three electrowetting curves display similar behavior: initially a parabolic trend is followed, then an upward deviation occurs, and finally saturation is reached.

The symmetry between the left and right portions of the curves is very good for IL31, less perfect for IL46, and lacking in the case of IL78. In all cases the contact angle at zero external voltage, θ_0, is above the smooth parabolic curve (and has been ignored when fitting the parabolas). All results in Figure 1 have been obtained with an increment of 2 V. Electrowetting curves were also obtained with a 5 V increment and showed no significant differences in shape or absolute values. The results shown in Figure 1 are in fact the averaged result of several (2−4) separate measurements.

Discussion

The electrowetting curves obtained in this study with three different ionic liquids (Figure 1) are very similar to the electrowetting curves recorded for aqueous solutions of an indifferent electrolyte on the same smooth fluoropolymer surface.[7] The curve for IL31 is qualitatively identical to the curve for aqueous 0.1 M KCl at pH = 5.6 (Figure 5 in the above reference). This striking similarity is not unexpected. In both cases, the external voltage polarizes the insulating layer (Teflon AF1600) and its outer surface (the one in contact with the liquid) attracts oppositely charged species from the liquid. The charge density at the solid/liquid surface increases and effectively diminishes the surface free energy in accordance with Lippmann's equation.[9] Therefore the Young−Lippmann equation is expected to perform for RTILs as well as for aqueous salt solutions. However, the quantitative correspondence for ionic liquids is significantly worse than for electrolytes dissolved in water. The curvature of the parabolic fits shown in Figure 1, i.e., $C/2\gamma$, is given in Table 2. The values obtained separately from the positive and negative branch are compared with the theoretical value from eq 1.

It can be seen that despite the comparable shape and arguably a similar mechanism the electrowetting of ionic liquids is considerably less efficient than the electrowetting of aqueous salt solutions—by approximately an order of magnitude.

Another important aspect of electrowetting is saturation, i.e., reaching a limiting contact angle that would not decrease upon further increase of the applied voltage. Saturation was not achieved with negative potentials for IL31 and IL78 but was found for IL46 (Figure 1). Note that IL31 and IL78 share the same cation; the one found in IL46 is slightly different (see Table 1). It thus appears that minute structural variations in the cation structure may lead to significantly different electrowetting behavior. However, more experiments with homologous series of RTILs are needed to confirm this hypothesis. On the contrary, for positive potentials the picture is essentially the same for all three ionic liquids—the curve deviates from the parabolic behavior and saturation is achieved. It must be concluded that the nature of the anion is not of such a crucial importance with respect to electrowetting.

Table 3. Contact Angle at Saturation: Experimentally Determined and Calculated (the Surface Tension of Teflon AF1600 Is Taken as 12.5 mJ/m^2[27])

	contact angle at saturation [deg]		
RTIL	negative branch	positive branch	estimated from eq 2
IL31	64	62	63
IL46		60	67
IL78		50	64

We have recently advanced a simple model for the saturation phenomenon.[8] On the basis of thermodynamic consideration, this model predicts the lowest contact angle, at which the Young−Lippmann eq 1 still applies, as

$$\theta_{\mathrm{sat}} = \arccos \frac{\gamma_{\mathrm{S}}}{\gamma} \tag{2}$$

where γ_{S} and γ are the surface tensions of the solid and the liquid surfaces, respectively. The values calculated through eq 2 are listed in Table 3.

It can be seen that our model, eq 2, predicts the deviation point quite nicely for IL31, gives a correct order of magnitude for IL46, and yields an irrelevant value in the case of IL78. Once again it appears that simple correlations and ideas developed for electrowetting of insulated electrodes with aqueous solutions are more complicated in the instance of RT ionic liquids.

Interestingly, in the case of IL46 saturation occurs at positive as well as negative voltages but the values differ by about 10° (see Figure 1; the points of deviation rather than the saturation values are listed in Table 3). Such an asymmetry is not usually found with aqueous solutions of indifferent electrolytes and probably reflects the considerable anion−cation asymmetry of the ionic liquid.

The deviations seen on the positive side of the electrowetting curves (Figure 1) resemble the deviations observed previously with aqueous solutions and attributed to specific adsorption of anions at the hydrophobic surface.[7] Similar effects are apparent on the negative side and may reflect the specific adsorption of cations, well-known in electrical double layer studies.[15] We cannot at this stage confirm or reject this explanation for the RTILs. It should be stressed that the liquids used in this study were all of synthesis grade, i.e., neither pure nor dry, and therefore a variety of physicochemical processes may arise, e.g., adsorption, dilution, or component segregation.

The contact angle at zero external voltage does not belong to the parabolic fits (Figure 1) and has been excluded from

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consideration. Additional experimentation showed that the electrowetting curves are entirely reproducible regardless of the initial contact angle being an outlier or not. Most probably the discrepancy was due to variations in the state of the initial contact angle. Such differences are rarely observed with aqueous solutions, and we attribute this unusual behavior to the relatively high viscosity of the RTILs (see Table 1). According to the theory of contact angle hysteresis the difference between advancing and receding contact angles (without any external voltage) is fundamentally due to the restrictions for the system to jump between metastable states.[16] External vibrations may be introduced to improve the situation,[17] and it is plausible that liquid relaxation was detectably retarded under the current experimental conditions.

Finally it should be emphasized that the RTILs used in this study are commercial agents of a relatively low purity (halide content < 1000 ppm and water content < 10 000 ppm[14]) and have been used without any further purification or attempt to store them in any special way. Water and impurities have a significant impact on the properties of ionic liquids.[1,18,19] We have additionally verified that the amount of water has a relatively minor influence on the surface tension and contact angle on various substrates, but changes in time for these parameters have been documented. Nevertheless the electrowetting of ionic liquids on a smooth insulating surface has been successfully carried out. To the best of our knowledge this is the first report of this kind.

Conclusion

We have successfully demonstrated that several commercial RTILs can electrowet a smooth fluoropolymer surface. Qualitatively the process appears to be analogous to the electrowetting of aqueous electrolyte solutions, but there are several quantitative differences: (i) the efficiency is significantly lower (almost an order of magnitude); (ii) the influence of the bulky cation is larger and the importance of the smaller anion is lesser; (iii) there appears to be an asymmetry in the saturation levels for positive and negative voltages. It is plausible that water and other impurities play a role due to the low purity (synthesis grade) of the compounds used.

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