Abstract—Water remains the most extensively studied electrowetting fluid, but few reports exist on nonaqueous conducting solvents. Reported herein is a complete analysis of alternate fluids for electrowetting devices and displays. Emphasis is provided on real-world testing parameters, including contact angle response and immiscibility with oil, environmental range, interfacial tension, ionic content and influence on dielectric reliability, compatibility with additives such as soluble dyes or particle dispersions, and cross-diffusion of fluids or solutes. Out of 16 presellected fluids, six exhibited electrowetting performance comparable to the best aqueous:surfactant solutions. Use of the nonaqueous fluids in advanced display devices is also demonstrated.

Index Terms—Electrowetting, fluid, reflective displays.

I. INTRODUCTION

Electrowetting research in new physical understanding and devices [1] has substantially outpaced work in developing practical and reliable electrowetting materials. There are several advanced commercialization efforts in labs-on-chip [2]–[4], lenses [5], and displays [6]–[8], but, not surprisingly, these groups do not disclose their state-of-the-art materials results. Only lately has our group begun publishing on materials for robust electrowetting. For example, we reported a strong correlation between ion size in solution and dielectric failure [9]. More recently, we have published work on thin-film fluorinated Parylene as a low-voltage and reliable substitute for thicker film chlorinated Parylene [10]. Continued materials work is needed such that new electrowetting exploration can be performed, but using the most practical materials for real applications. Such applied work typically only increases the scientific breadth of the field when further commercialization is enabled (e.g., consider the expanse in basic liquid crystal research).

Consistent with this pursuit of more practical electrowetting materials, in this study, we report a complete analysis of alternate conductive fluids for electrowetting devices and displays. Water has very high surface tension, easily accepts ionic content, and, for other obvious reasons, has been the most extensively studied and commonly used electrowetting fluid. However, water poses several challenges, including corrosion of electrodes, lack of robust environmental range, a tendency to permeate through or swell numerous polymers, and a greater ability to degrade some materials. Our report is not the first demonstration of nonaqueous electrowetting fluids. For example, there have been numerous electrowetting studies on ionic liquids [11]–[14], which show contact angle modulation greater than 100° at 250 V [14]. Chatterjee et al. [15] were the first to report electrowetting for a wide range of organic fluids. These prior reports provide the initial scientific investigation of nonaqueous fluids for electrowetting, however, further analysis is still needed, especially when considering use in displays. As one example, the Chatterjee study [15] was carried out in air (not in oil), which may be acceptable for lab-on-chip, but which is impractical for electrowetting [6] and electrofluidic [7] displays. Compatibility with oil eliminates many of the candidate fluids reported by Chatterjee et al. [15].

In this report, we continue exploration of nonaqueous fluids and optimal ionic content for robust electrowetting control. Systematically, we have analyzed and reduced the fluids to six that meet our key set of parameters, including contact angle response and immiscibility with oil, environmental range, interfacial tension, ionic content and influence on dielectric reliability, compatibility with additives such as soluble dyes or particle dispersions, and cross diffusion of fluids or solutes. These parameters are chosen mainly based on requirements for electrowetting [6] and electrofluidic [7] displays, but may extend to other applications in optics and labs-on-chip. We complete our study by demonstrating use of the nonaqueous fluids in electrowetting display devices. This work provides the first thorough analysis of nonaqueous fluids for electrowetting and the first design of experiments for screening such fluids.

II. EXPERIMENTAL

A. Materials and Experimental Setup for Electrowetting

Electrowetting testing was performed using the conventional setup shown in Fig. 1(a). Test substrates consisted of commercial Corning aluminosilicate glass coated with a transparent film of electrically conducting indium tin oxide (SnO$_2$ : In$_2$O$_3$, 100 Ω/sq, ~50-nm thickness). This transparent electrode was then coated with ~1 μm Parylene C using a Specialty Coating Systems 2010 lab coater. A Cytonix Fluoropel 1601 V solution was subsequently spin-coated onto the Parylene C, annealed at 120 °C for 30 min, yielding a hydrophobic fluoropolymer layer of ~50 nm thickness. Electrowetting tests
[Fig. 1(a)] were performed in a mixture of electrically insulating silicone oils (80 wt% Dow Corning OS-20–16.5 mN/m, 10 wt% OS-10–15.2 mN/m, 10 wt% OS-30–17.3 mN/m). A clear acrylic box was used to contain the immersed substrate and fluids. A $\sim 1-\mu$L conducting fluid droplet was placed on the substrate and viewed through the transparent acrylic sidewalls. To provide electrical bias to the polar fluid solution, a probe wire was inserted into the polar droplet. The other end of this probe was connected to the voltage supply. A VCA Optima contact angle measurement system was used to record the contact angle data. A LabVIEW program was written to allow a repeatable 1 V/s step of voltage and synchronized video capture of the droplet profile. DC and ac (1 kHz, square wave) voltages up to 30 V were applied. The SnO$_2$ : In$_2$O$_3$ was held at electrical ground in all experiments. The experiments were repeated at least three times at fresh sample locations for each of the solutions studied.

AC voltage usually leads to the best electrowetting response, partly since charging of the dielectric and/or the oil is less likely to occur in comparison to dc voltage. However, dc voltages were still tested to determine if charging was a major issue for any of the tested fluids. To ensure the AC electrowetting response was not limited by an $RC$ time constant, the conductivity of the fluids was measured with an OAKTON CON6/TDS6 conductivity meter (in $\mu$S/cm, $\pm0.5\%$).

B. Materials and Experimental Setup for Dielectric Failure

The dielectric failure testing setup is shown in Fig. 1(b). The test substrates were the same as the electrowetting tests except for two changes. First, the Parylene C thickness was reduced to $\sim400$ nm, in order to more aggressively investigate dielectric failure. Secondly, dielectric failure tests were performed in air to prevent the droplet from spontaneously ejecting away from the probe tip. For each failure test, the voltage was swept from 0 to $\pm98$ V dc at 1 V/s. The positive and negative polarity voltage sweeps were independently measured at fresh sample locations. A platinum probe was used to ensure that the results would not be affected by any contamination from the wire material. The diameter of the contacting droplet was $\sim2$ mm for each experiment. Three current–voltage plots were taken for each solution tested, and the averaged results are reported.

C. Initial Fluids Property Requirements and Selection

The initial selection criteria included at least the possibility of satisfying contact angle response in oil and immiscibility with oil, proper environmental range, interfacial tension, accepting of ionic content and possible influence of ionic content on dielectric reliability, compatibility with additives such as soluble dyes or particle dispersions, and cross diffusion of fluids or solutes. Initially, 16 nonaqueous fluids were selected: acetonitrile, acetonitrile-nitromethane, diacetone alcohol, diethyl carbonate, dimethyl malonate, dimethyl sulfoxide, ethylene glycol, ethyl acetoacetate, ethyl-L-lactate, formamide, $\gamma$-butyrolactone, N,N-dimethylacetamide, N-methylformamide, propylene carbonate, propylene glycol, and 2-pyrrolidinone. All fluids were reagent grade or better and were purchased from Fisher Scientific. Some of the fluids chosen had an unacceptably high freezing point. These high-freezing-point fluids were still tested because blending of fluids is a simple means for extending the melting/boiling range.

The full list of candidate fluids was then initially screened in terms of miscibility with the OS oils blend. Dimethyl malonate, ethyl acetoacetate, and ethyl-L-lactate were found to be miscible with the OS oils mixture and were removed from the list of fluids to be tested. The OS fluid is already an oil that is more hydrophobic than alkane and other oils, therefore simply changing the oil is not likely a feasible solution.

D. Fluid Interfacial Tension Requirement

The electrowetting effect can be described in terms of the conductive fluid contact angle ($\theta_V$) as

$$\cos \theta_V = \frac{\gamma_{id}}{\gamma_{ci}} + \frac{C \cdot V^2}{2 \gamma_{ci}}$$

where $C$ is the capacitance per unit area of the hydrophobic dielectric, $V$ is the applied dc voltage or ac rms voltage, and $\gamma$ is the interfacial tension between the insulating fluid or oil ($i$), the electrically conductive fluid ($c$), and the dielectric surface ($d$). Typically, contact angle modulation of conducting aqueous fluids in insulating oil ranges from 180° to $\sim45-60°$, beyond which the contact angle modulation ceases due to contact angle saturation [16]. The interfacial tension between the conducting fluid and the insulating oil ($\gamma_{ic}$) is a critical factor in the voltage response in (1) and was therefore measured for each fluid by the pendant drop method with an IT Concept Tracker instrument (results are shown in Table I). Acetonyl acetone, diacetone alcohol, and N,N-dimethyl acetamide presented too low of an interfacial tension with the surrounding oil medium, visually forming a “jelly bean” shape, as shown in Fig. 2. The OS silicone oils are already very hydrophobic (low surface tension), and therefore alternate oils were not explored to increase the interfacial tension.

E. Ionic Content and Fluid Conductivity Requirements

Ionic content typically must be added to provide sufficient charge carriers to drive the electromechanical electrowetting effect [17]. For some pure fluids, such as propylene carbonate, no significant electrowetting response can be achieved with 1-kHz ac voltage. By adding a salt (such as, tetrabutylammonium acetate), the conductivity of the solution can be increased to 20 $\mu$S/cm, and the $RC$ time constant decreased, resulting
TABLE I
PROPERTIES OF THE VARIOUS FLUIDS TESTED

<table>
<thead>
<tr>
<th>Fluid</th>
<th>m.p. (°C)</th>
<th>b.p. (°C)</th>
<th>μ (cP) at 25°C</th>
<th>σ (µS/cm)¹</th>
<th>TBAB conc. (wt%)²</th>
<th>γ₀ (mN/m)¹</th>
<th>SDS conc. (wt%)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>18.5</td>
<td>189</td>
<td>1.99</td>
<td>0.62</td>
<td>0.018</td>
<td>8.5</td>
<td>0.026</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>-13</td>
<td>197.3</td>
<td>16.1</td>
<td>0.03</td>
<td>0.072</td>
<td>15.6</td>
<td>Not studied</td>
</tr>
<tr>
<td>Formamide</td>
<td>2.6</td>
<td>220</td>
<td>3.34</td>
<td>1.500</td>
<td>Not needed</td>
<td>23.8</td>
<td>Not studied</td>
</tr>
<tr>
<td>γ-butyrolactone</td>
<td>-43.3</td>
<td>204</td>
<td>1.7</td>
<td>0.84</td>
<td>0.016</td>
<td>7.0</td>
<td>0.033</td>
</tr>
<tr>
<td>N-methyl formamide</td>
<td>-3.8</td>
<td>199.5</td>
<td>1.68</td>
<td>160</td>
<td>Not needed</td>
<td>6.8</td>
<td>Not needed</td>
</tr>
<tr>
<td>Propylene carbonate</td>
<td>-48.8</td>
<td>242</td>
<td>2.53</td>
<td>5.3</td>
<td>0.027</td>
<td>8.6</td>
<td>0.039</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>-60</td>
<td>187.6</td>
<td>40.4</td>
<td>~0</td>
<td>0.305</td>
<td>8.5</td>
<td>0.372</td>
</tr>
<tr>
<td>2-pyrolidone</td>
<td>25</td>
<td>251</td>
<td>13.3</td>
<td>4.6</td>
<td>0.086</td>
<td>7.8</td>
<td>0.135</td>
</tr>
</tbody>
</table>

¹Data were measured as described in the experimental section; unmarked data are from [18]. ²Tetrabutylammonium bromide and sodium dodecyl sulfate were added to reach a conductivity of 20 µS/cm.

Fig. 2. Drop formed by: (a) N,N-dimethylacetamide and (b) propylene glycol in the oil ambient.

in expected electrowetting behavior. Through optimization, ~ 20 µS/cm was chosen as the threshold conductivity needed for all fluids, beyond which additional conductivity (ionic content) had little effect on electrowetting response. All fluids tested herein were therefore provided with ionic content ([Cl]Br, see Table I) to achieve conductivity > 20 µS/cm for the electrowetting experiments, except formamide and N-methyl formamide, which present an inherently high conductivity.

Ions were chosen with a small size to determine if the choice of fluid (and size of fluid molecule) would influence dielectric failure. This approach assumes that, if a small ion is used, it easily moves with fluid through the dielectric, and therefore this would determine if large fluid molecules penetrate the dielectric [9]. Tetraethylammonium bromide (TEAB) and sodium dodecyl sulphate (SDS) were dissolved in the fluids to achieve a conductivity of 20 µS/cm, as summarized in Table I. These salts were chosen for their small ions (Na⁺, Br⁻) and large organic counterions which allow high solubility in the fluids tested. Continuing the initial fluid screening, acetonophene and diethyl carbonate were eliminated from the tested fluid list because they could not dissolve TEAB. N-methyl formamide has an inherently high conductivity, and therefore no additional ionic content was required.

Ions were also selected with varied size. This would determine if large ions would lead to less dielectric failure with selected fluids and, therefore, be consistent with our previous work showing ionic size dependence of dielectric failure with aqueous solutions [9]. The ions studied and the solutions formed are summarized in Table II.

III. RESULTS AND DISCUSSION

A. Electrowetting Results

DC electrowetting tests are plotted in Fig. 3. For comparison purposes, the electrowetting behavior of a 1 wt% SDS in deionized (DI) water solution is also displayed on the plots. Formamide and ethylene glycol have the least contact angle change with voltage, which is fully expected considering that they have higher interfacial tension with the oil (γ₀, Table I). These fluids therefore eliminated from the analysis, but it should be noted that surfactants could likely be added to reduce γ₀. The other fluids provided an electrowetting behavior comparable to that of water:SDS. Contact angle saturation is noticed for γ-butyrolactone and 2-pyrrolidone at ~28 V. Strong asymmetry of the curves can be observed for most of the fluids. A difference as high as 20° between +30 and −30 V is sometimes obtained, as shown in Table III. This might be partially attributed to the presence of bromide ions. Halides have been reported to adsorb on the surface of fluoropolymers [19]. However, such a large asymmetry in the electrowetting curves likely requires additional factors, which are beyond the scope of this study.

The results under 1-kHz ac voltages are presented in Fig. 4. The total change in contact angle with N-methyl formamide (~80°), γ-butyrolactone (~70°), 2-pyrrolidone (~70°), and propylene glycol (~70°) are satisfactory but not as high as that for 1 wt% SDS in water solution (around 90° total). DMSO and propylene carbonate exhibited the least contact angle change (around 60°), which is consistent with the dc results.

The dc and ac results conclusively show that, with the correct ionic content, a strong electrowetting response can be achieved
Dielectric failure in an electrowetting system can occur through one of several mechanisms [9], the most challenging of which is due to current flow through the dielectric. We had previously observed for Al₂O₃ dielectrics that liquid molecule size might play a significant role in preventing dielectric failure [9]. Any such dependence is likely highly dependent on fluid absorption in the dielectric. In this work, 400 nm of Parylene C was investigated, since it is a very commonly utilized dielectric in electrowetting and an often used hermetic seal in electronics. This Parylene C thickness is consistent with approximately 15–20 V operation (which allows thin-film transistor compatibility).

Fig. 5 shows the results of the dielectric failure tests performed on the various fluids using small inorganic ions (Br⁻ under negative voltages and Na⁺ for positive voltage). The theoretical breakdown field strength of Parylene C is around 260 V/µm, which is beyond the test voltages employed herein for 0.4-µm-thick films [20]. For fluid testing, dielectric failure was determined to be when the current reaches $10^{-6}$ µA for the droplet diameter of 2 mm, as denoted by the dashed lines on the plots. For negative voltage, in comparison with water:SDS, less dielectric failure was observed for some but not all nonaqueous fluids. The case of reduced dielectric failure with...
nonaqueous fluids is especially prominent for positive voltage. This would support our previous arguments for use of fluids with larger molecules [9]. However, the voltages for dielectric failure are too low in positive voltage for most of the nonaqueous fluids.

It was clear that, with a thin Parylene C dielectric, liquid molecule size alone will not sufficiently prevent dielectric failure. Therefore, like our previous study [9], we turned to larger ion size to improve dielectric reliability. The effect of ion size on dielectric failure with propylene glycol is provided in Fig. 6. Propylene glycol displayed poor dielectric reliability in positive voltage with small ions [Na⁺, Figs. 5(e) and 6(a)]. A significant improvement in dielectric reliability is seen when using large ions. Ammonium [NH₄⁺, Fig. 6(b)] and tetrabutyl ammonium [TBA⁺, Fig. 6(c)] exhibited no dielectric failure.

Larger size ions also revealed significant improvement in dielectric reliability for negative voltage. With negative voltage, propylene carbonate was specifically explored. As shown in Fig. 7, increasing the anion size only slightly increases the voltage at which the dielectric failure occurs: from below -75 V for Cl⁻ to > -75 V for Br⁻ and not measured (higher than -98 V) for CH₃COO⁻. Larger ions are less likely to penetrate the pores and defects of the dielectric materials because of size exclusion.

To summarize, the benefit of improved dielectric reliability with larger ion in aqueous fluid [9] clearly extends to the nonaqueous fluids reported herein.

C. Factors Related to Fluid Colorants

Although the fluid results for this paper are of value to general electrowetting applications, the main applied focus of this work was motivated by displays. There are two types of displays that may benefit from the used of nonaqueous electrowetting
fluids. First, there are conventional electrowetting displays [6],

where the electrowetting fluid is clear and the pixel switches the
coverage area of a dye-colored oil film. Second, there are elec-
tronfluidic displays [7] where the oil is clear and the electrowet-
ting fluid, which contains a pigment, is electrowetted into and
out of thin microfluidic channel. There are also droplet-driven
displays [8] which can use colored oil or colored electrowetting
fluids. However, each display platform poses unique challenges
relating to adding colorants, and those challenges were investi-
gated as follows.

1) Cross Diffusion of Dyes: Generally, electrowetting dis-
plays require a dye percent of >10 wt%, which is achieved by
using dyes that are oil soluble but somewhat polar in nature [21].
These dyes might diffuse out of the oil and into the electrowet-
ting fluid, especially those nonaqueous fluids with lower surface
tensions. Using a more polar electrowetting fluid such as propy-
lene glycol was therefore investigated in an electrowetting dis-
pay. Arrays of electrowetting display pixels of 300 × 900 μm
were created using fabrication techniques reported elsewhere
[21]. The pixels contained a black dye mix in tetradecane oil. In
the off state, the black oil occupied the entire area of the pixels,
as can be seen in Fig. 8(a). When a voltage was applied, the
electrowetting fluid displaced the black oil (into the corners),
resulting in clear pixels [Fig. 8(b)]. The pixels operated as ex-
pected, even with substituting propylene glycol for water, and
without diffusion of the dye from the oil into the electrowet-
ting fluid (propylene glycol). It is also interesting to note that
propylene glycol allowed self-assembled oil dosing, as previ-
ously demonstrated for aqueous electrowetting fluids [22].

2) Dispersed Pigments in Nonaqueous Electrowetting
Fluids: Electrofluidic pixels were also tested using device
structures and fabrication techniques reported elsewhere [7].
It was found that some nonaqueous fluids can incorporate as
much as 15 wt% pigment (color, white, and black, similar to
those used for ink jet fluids), possibly more, with no variation
in the electrowetting response from those described for Figs. 3
and 4. Moreover, they displayed a wide environmental range,
(operating from −30 °C to +70 °C). The fluid details are not
shown herein as they are proprietary to Sun Chemical and
Gamma Dynamics. The detailed results can be found elsewhere
[23]. Nonaqueous fluids are therefore fully adaptable for use in
electrofluidic displays.

IV. CONCLUSION

This study demonstrated that polar nonaqueous solvents can
be used to replace water for electrowetting-based applications.
It was shown that, with a careful selection of ionic content and a good solvent/oil match (high interfacial tension), electrowetting behaviors comparable to those of aqueous solutions can be achieved, while limiting or even eliminating the risk of dielectric failure. Furthermore, nonaqueous fluids were demonstrated as fully effective in electrowetting and electrofluidic display pixels. These findings advance environmental robustness and reliability issues for the commercialization of electrowetting/electrofluidic displays, and more broadly other electrowetting devices and applications such as lenses and labs-on-chip.

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REFERENCES


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