

# On the performance of thermostable electrowetting agents

Xiaodong Hu,<sup>a</sup> Shiguo Zhang,<sup>b</sup> Xiaojian Lu,<sup>a</sup> Chao Qu,<sup>a</sup> Liujin Lu,<sup>b</sup> Xiangyuan Ma,<sup>b</sup> Xiaoping Zhang<sup>a\*</sup> and Youquan Deng<sup>b</sup>

Electrowetting of ionic liquids (ILs) in different alkane ambient and at different temperatures were studied under different AC voltages. The performance of IL-based electrowetting at elevated temperatures and that at room temperature was compared. It turns out that the electrowetting of ILs at elevated temperatures resulted in faster response and lower operation voltage. Furthermore, the relationship between the structure of the ion and the contact angle change was specifically investigated and theoretically explained. Finally, the properties of IL-based electrowetting in different alkane ambient were studied. It was demonstrated that the long length of the alkyl chain guaranteed a smaller contact angle under the same applied voltage. All the experimental results showed attractive features involving wide operating temperatures and in particular high stability, fast response, and good reversibility at elevated temperatures. The performance of IL-based electrowetting could be further improved through an optimal choice of an ambient phase or a rational design and synthesis of ionic liquids. Copyright © 2011 John Wiley & Sons, Ltd.

 Supporting information may be found in the online version of this article.

**Keywords:** electrowetting; ionic liquids; temperature; alkanes ambient; AC voltage; response time

## Introduction

Electrowetting is a well-known phenomenon in which a droplet extends on a solid surface under the action of an electric field across the solid/liquid interface. It is often observed on dielectric coated surfaces. Owing to the superiority in droplet-based microfluidic devices, electrowetting on dielectric (EWOD) becomes more and more popular.<sup>[1]</sup> Drop actuation using EWOD has been used successfully in many fields as diverse as microextraction devices,<sup>[2]</sup> tunable RC filters,<sup>[3]</sup> biological sample analytical processes,<sup>[4]</sup> electrowetting displays,<sup>[5]</sup> electronic papers,<sup>[6]</sup> programmable optical filters,<sup>[7]</sup> electronic microreactors,<sup>[8]</sup> and to control fluids in multichannel structures.<sup>[9]</sup> Electrowetting is conventionally carried out with (saline) aqueous solution at room temperature. However, drawbacks such as evaporation and the absence of (saline) aqueous solution at high temperature (>80 °C) have inevitably limited its application.<sup>[10–12]</sup> Therefore, for electrowetting, development of new and robust media with low vapor pressure and good thermostability is highly desirable.

As a novel class of versatile solvents and materials possessing unique physicochemical properties, ionic liquids (ILs) have been widely studied.<sup>[13,14]</sup> There are some significant advantages of ILs compared with water and other aqueous electrolytes such as negligible vapor pressure, good thermal stability, intrinsic ionic conductivity, and acceptable electrochemistry stability. On account of these excellent physicochemical properties, ILs has recently been developed as a promising alternative medium for electrowetting by Ralston and coworkers.<sup>[15–19]</sup>

Recently, electrowetting of ILs has received increased attention. Our results and those from Nanayakkara and colleagues showed a reversible and wide contact angle modulation of ILs using oil as the ambient and under AC electric field, compared with that in air or under DC electric field.<sup>[20–22]</sup> In particular at 1 kHz

AC, stable, sensitive, reversible, and wide contact angle modulation (122–137°) was obtained.<sup>[23]</sup> In comparison with aqueous electrolytes, IL-based electrowetting systems may be run under some extreme conditions such as in vacuum, or at temperatures either above 373 K or below 273 K. Halka and Freyland reported electrowetting of few ILs at elevated temperatures under ultra high vacuum conditions.<sup>[24]</sup> In the experiments DC voltage has been employed. Here we represent an overview of the performance of ILs in electrowetting experiments under various conditions, in particular at elevated temperatures. However, all the experiments are executed under AC voltage. This manuscript is focused on the electrowetting of the several imidazolium based ILs at various temperatures (20, 60, and 100 °C) with alkane ambient under AC voltage and the effect of alkane ambient medium on the electrowetting of the ILs at elevated temperatures under AC voltage. The dependence on the alkyl chain length of imidazolium cation is also investigated.

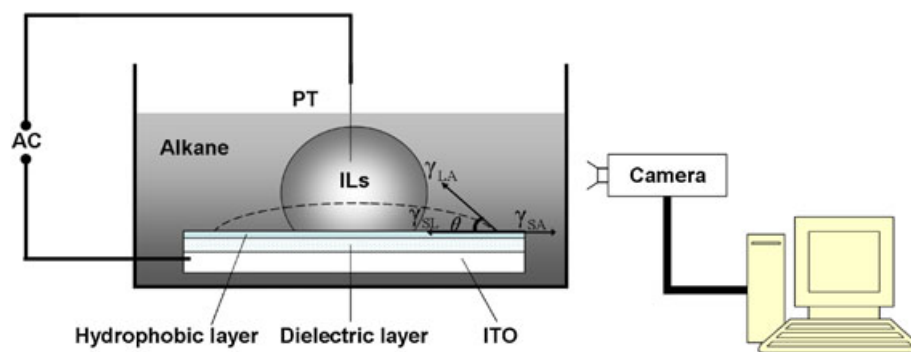
## Theory

The EWOD system is generally described by Lippmann–Young equation (Fig. 1)

\* Correspondence to: Xiaoping Zhang, School of Information Science and Engineering, Lanzhou University, Lanzhou 730000, China. E-mail: zxp@lzu.edu.cn

a School of Information Science and Engineering, Lanzhou University, Lanzhou 730000, China

b Centre for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China



**Figure 1.** Experiment setup for electrowetting measurements. Solid lines represent the drop shape at zero external voltage. Dashed lines represent the drop shape at a given external voltage. The contact angle  $\theta$  is dependent on the interfacial tensions  $\gamma_{LA}$ ,  $\gamma_{SL}$ , and  $\gamma_{SA}$  between the solid (S), liquid (L), and alkane (A) phases.

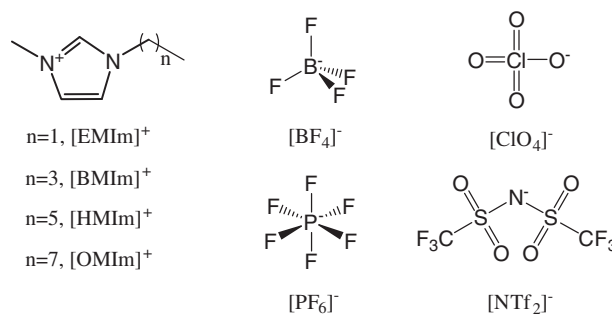
$$\cos\theta = \cos\theta_0 + \frac{1}{2\gamma_{LA}} \frac{\epsilon_0 \epsilon_r}{d} V^2 \quad (1)$$

According to Eqn (1), the contact angle  $\theta$  is a parabolic dependence of the applied voltage ( $V$ ).  $\cos\theta_0$  is cosine of the initial contact angle and equals to  $(\gamma_{SA} - \gamma_{SL})/\gamma_{LA}$ .  $\epsilon_r$  is the dielectric constant of the film and  $d$  is the thickness. In practical testing, the contact angle data are closely matched by numerical solutions of Eqn (1) at low voltage; however, above some voltage threshold, this agreement deteriorates presumably because of contact angle saturation, which the model cannot explain.<sup>[25,26]</sup> Verheijen and Prins<sup>[27]</sup> found that the insulator surfaces were charged after driving a droplet to contact angle saturation. They suggested that charge carriers were injected into the insulator layers and then partially screened the applied electric field. However, this model has not received broad acceptance because it is not clear whether this criterion is applicable for the effective solid-liquid interfacial energy in electrowetting. As a matter of fact, contact angle saturation is still not well understood. More works are required in the future.

## Experimental section

### Synthesis and characterization of ills

Seven imidazolium-based ILs with different cation and anion structures, namely, 1-ethyl-3-methylimidazolium perchlorate ([EMIm][ClO<sub>4</sub>]), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide ([BMIm][NTf<sub>2</sub>]), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm][PF<sub>6</sub>]), 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm][BF<sub>4</sub>]), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF<sub>4</sub>]), 1-hexyl-3-methylimidazolium tetrafluoroborate ([HMIm][BF<sub>4</sub>]), 1-octyl-3-methylimidazolium tetrafluoroborate ([OMIm][BF<sub>4</sub>]), were synthesized in our laboratory according to the established procedures (Fig. 2).<sup>[28–30]</sup> The physical properties of ILs in this work are shown in Table 1. The viscosity was measured on a Brookfield DV-III+ (Brookfield, Middleboro, Massachusetts, USA) viscometer. The surface tension was measured on a surface/interface analytical device (Solon Tech., Shanghai) using the Du Noüy ring method. Contact angle data was obtained by an SEO (Surface Electro Optics, Gyeonggi-do, Korea) contact angle measuring device (PHOENIX 300). The thickness of the insulating and hydrophobic layer was measured by a surface profiler (Micro-XAM, Milpitas, California USA). Chemical shifts were reported in parts per million (ppm,  $\delta$ ). The water content was determined by Karl-Fisher



**Figure 2.** Structures of ILs used.

**Table 1.** Physical properties of ILs investigated. Surface tension ( $\gamma$ ) and viscosity ( $\eta$ )

ILs	$\gamma$ [mN/m]	$\eta$ [cP]
[EMIm][ClO <sub>4</sub> ]	37	107
[BMIm][NTf <sub>2</sub> ]	37	52
[BMIm][PF <sub>6</sub> ]	38	270
[EMIm][BF <sub>4</sub> ]	49	45
[BMIm][BF <sub>4</sub> ]	40	140
[HMIm][BF <sub>4</sub> ]	36	266
[OMIm][BF <sub>4</sub> ]	31	415

analysis Metrohm KF coulometer (Metrohm, Ionenstrasse, Herisau, Switzerland). Prior to measurements all ILs were dried *in vacuo* at 80 °C for 3 h. The water content is ~520 ppm for [EMIm][ClO<sub>4</sub>], ~570 ppm for [BMIm][PF<sub>6</sub>], ~220 ppm for [BMIm][NTf<sub>2</sub>], ~860 ppm for [EMIm][BF<sub>4</sub>], ~680 ppm for [BMIm][BF<sub>4</sub>], ~260 ppm for [HMIm][BF<sub>4</sub>], ~330 ppm for [OMIm][BF<sub>4</sub>].

### Preparation and measurement

Figure 1 shows the schematic of the equipment for electrowetting of ILs measurements. Glass plates covered on one side with an indium tin oxide (ITO) are used as substrates. Parylene C (~10  $\mu$ m,  $\epsilon_r = 2.65$ ) is deposited as insulating layer by gas-phase deposition at room temperature, because of its high dielectric and conformal homogeneousness on surfaces of different shapes and compositions. A very thin Teflon AF1600 DuPont (Wilmington, Delaware, USA) coating (~1  $\mu$ m,  $\epsilon_r = 1.93$ ) is used as a top layer to obtain a hydrophobic surface with a good reversibility. This Teflon

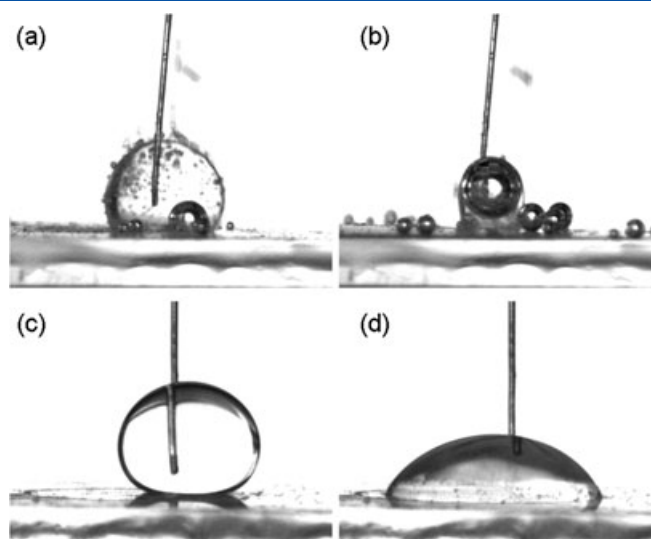
layer is deposited on the insulating coating by dipping in a 1 wt% solution of Teflon AF1600 in FC75. The substrates are withdrawn from the solution at a constant speed of 0.8 mm/s. The resulting Teflon-covered ITO glass slides were heat-treated for 6 min at 112 °C, and for 5 min at 165 °C, to remove residual solvent and improve the adhesion of the Teflon layer to the substrate. With these duplex coatings we were able to induce electrically a dramatic and reversible change in contact angle. An ILs droplet (~10 μL) was injected in the device through a 10 μL syringe. Then dodecane was transferred into the cylinder with a pipette immediately to reduce moisture. Unless otherwise specified, the alkane ambient was chosen to be dodecane, acquiescently. Our previous results showed a reversible and wide contact angle modulation of ILs under AC electric field, as compared with that under DC electric field. Thus, the AC voltage was selected in this experiment and obtained by a function generator with frequency 10, 100, and 1000 Hz, respectively, with applied voltage up to 250 V.<sup>[23]</sup> 1 kHz was selected as the major applied frequency because a 1 kHz AC electric field facilitates stable and high efficiency electrowetting of ILs.<sup>[20]</sup> All voltages in this paper are Root-Mean-Square (RMS) values. With the voltage applied to the conductive layers of the substrate plate and the platinum wire dipped into ILs, contact angle variation can be achieved. The variation is recorded using a high speed Charge Coupled Device (CCD) camera connected to a video recorder. Contact angles have been measured as a function of the potential visually from highly enlarged video pictures. Here, we define the time for the interface curve to reach its final shape after the voltage is applied as the responding time of electrowetting. The video captured by the camera could be divided into frames and the responding time was counted by cumulating slot time. Temperature was controlled by methyl silicone oil bath through a thermocouple probe connected to the digital temperature controller.

## Results and discussion

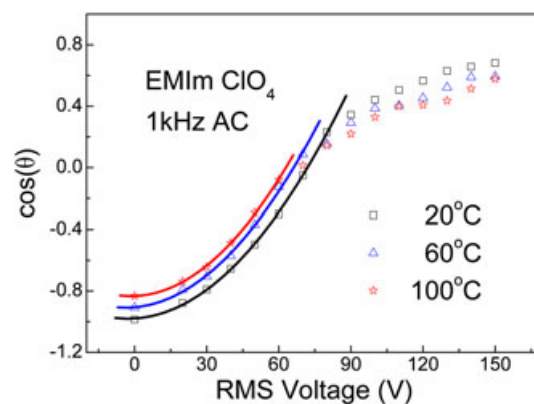
### Temperature dependence

An ILs ([EMIm][ClO<sub>4</sub>]) droplet and an aqueous electrolytes droplet were sealed in dodecane at 80 °C to compare the electrowetting performance of ILs with that of aqueous electrolytes. Aqueous electrolytes, because of high vapour pressure, completely evaporated for about just 1 min. However, the [EMIm][ClO<sub>4</sub>] droplet was unchanged after 60 min, and the contact angle remained constant for the entire experimental time at high temperature. Obviously, ILs presents a good performance of electrowetting owing to higher thermostability than aqueous electrolytes (Fig. 3). Herein, compared with water or other organic solvents, ILs has crude advantages as material in electrowetting, especially for high temperature. This clearly shows the importance of using ILs as the medium of electrowetting based devices, which could survive for long time period operations even at elevated temperatures.

Although [EMIm][ClO<sub>4</sub>] is not that thermostable compared with dicationic and tricationic ILs, in consideration of lower viscosity and higher refractive index, it was selected to investigate the impact on electrowetting of ILs caused by temperature.<sup>[31–35]</sup> The experiment setup was heated to 20, 60, and 100 °C. At each temperature, the relationship between contact angle ( $\theta$ ) and applied voltage ( $V$ ) was obtained as shown in Fig. 4. Because of the decreasing of  $\gamma_{\text{ILs}}$  (Fig. S1) and the increasing of  $\gamma_{\text{Alkane}}$  with temperature ( $T$ ) ascending,<sup>[36]</sup> the interfacial tension ( $\gamma_{\text{LA}}$ ) minishes accordingly, which yields the relationship:



**Figure 3.** Saline droplet in dodecane at 80 °C (a) and 1 min later (b). Electrowetting of [EMIm][ClO<sub>4</sub>] in dodecane under 0V (c) and 150 V (d) 1 kHz AC electric field at 100 °C.



**Figure 4.** Electrowetting curves of [EMIm][ClO<sub>4</sub>] in dodecane and under 1 kHz AC electric field at 20, 60, and 100 °C, respectively. The solid lines are fits of the Young–Lippmann equation.

$$\gamma_{\text{LA}} = \gamma_0 \left( 1 - \frac{T}{T_c} \right) \quad (2)$$

$\gamma_0$  equals the interface tension at  $T = 0$  K and  $T_c$  represents critical temperature. Both of them are constants. Thus, the initial contact angle ( $\theta_0$ ) decreased. The temperature dependence could be obtained by combining Eqns (1) and (2)

$$\cos \theta = \cos \theta_0 + \frac{T_c}{2\gamma_0(T_c - T)} \frac{\epsilon_0 \epsilon_r}{d} V^2 \quad (3)$$

Consequently, it could be concluded that high temperature ( $T$ ) guarantees a smaller contact angle ( $\theta$ ) under the same applied voltage ( $V$ ).

The line in Fig. 4 represents the theoretical value based on the coating properties. The experimental contact angle data are closely matched by numerical solutions of Lippmann–Young equation; however, above some voltage threshold, this agreement deteriorates. This behavior at higher voltages is presumably because of contact angle saturation phenomenon observed in

electrowetting experiments. If the voltage is decreased, the liquid drops back to the initial shape with minimal hysteresis (i.e., the variation of contact angle behind the changing electric field). Even after several cycles, hysteretic effects are not particularly significant as long as the hydrophobic film is applied to the electrodes.

As shown in Fig. 5, the relationship between viscosity of ILs and temperature follows the negative exponential attenuation. Also, low viscosity guarantees short response time. Thus, the response time of electrowetting of ILs decreased as temperature increased.

Although the contact angle variation range declined slightly, both the dramatically shortened response time and better reversibility guarantee that electrowetting of ILs at high temperature is superior to that at room temperature.

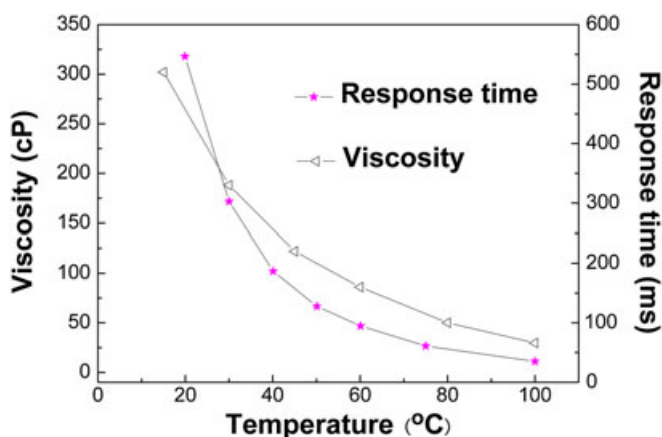
### Structure dependence at high temperature

To investigate electrowetting of ILs with different cation or anion at high temperature, three [BMIm]<sup>+</sup>-based ILs with different anions ([BMIm][PF<sub>6</sub>], [BMIm][NTf<sub>2</sub>], and [BMIm][BF<sub>4</sub>]) and four [BF<sub>4</sub>]<sup>-</sup>-based ILs with different cations ([EMIm][BF<sub>4</sub>], [BMIm][BF<sub>4</sub>], [HMIm][BF<sub>4</sub>], and [OMIm][BF<sub>4</sub>]) were selected. All tests were executed at 100 °C.

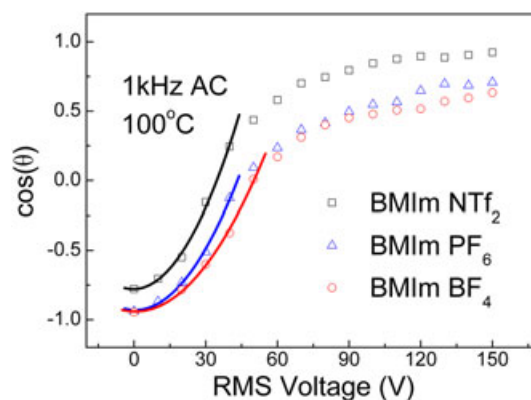
As for [BMIm]<sup>+</sup>-based ILs (Fig. 6), although no significant difference in electrowetting behavior occur upon changing the anions, [BMIm][NTf<sub>2</sub>], owing to the lower surface tension, had lower initial contact angle ( $\theta_0$ ) and outstandingly ultimate wettability.

While for the [BF<sub>4</sub>]<sup>-</sup>-based imidazolium ILs, the applied voltage (V) to obtain the same  $\theta$  (90°) (horizontal dashed line in Fig. 7) presents  $V_{[OMIm][BF_4]} (30\text{ V}) < V_{[HMIm][BF_4]} (41\text{ V}) < V_{[BMIm][BF_4]} (49\text{ V}) < V_{[EMIm][BF_4]} (58\text{ V})$  and  $\cos\theta_{[OMIm][BF_4]} (-0.06) > \cos\theta_{[HMIm][BF_4]} (-0.42) > \cos\theta_{[BMIm][BF_4]} (-0.61) > \cos\theta_{[EMIm][BF_4]} (-0.72)$  when applied voltage (V) was set a certain value of 30 V (vertical dash line in Fig. 7).

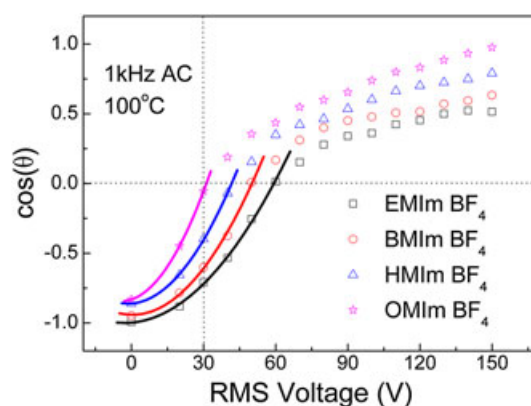
This phenomenon could be explained by the Young–Lippmann equation. Equation (1) shows that the applied voltage (V) is in proportion to the interfacial tensions ( $\gamma_{LA}$ ) (thus the surface tension of ILs  $\gamma_{ILs}$ ). Considering that the longer length of alkyl chain guarantees lower surface tension (Fig. S2), it could be easily obtained that the longer the length of alkyl chain, the lower the applied voltage (V) needed to obtain identical contact angle ( $\theta$ ). Consequently, [OMIm][BF<sub>4</sub>] required a lower voltage to spread over the hydrophobic surface than the other three [BMIm]<sup>+</sup>-based



**Figure 5.** Change of viscosity and response time of electrowetting of [EMIm][ClO<sub>4</sub>] at variable temperature.



**Figure 6.** Electrowetting curves of three [BMIm]<sup>+</sup>-based ILs in dodecane and under 1 kHz AC electric field at 100 °C. The solid lines are fits of the Young–Lippmann equation.



**Figure 7.** Electrowetting curves of four [BF<sub>4</sub>]<sup>-</sup>-based ILs in dodecane and under 1 kHz AC electric field at 100 °C. The solid lines are fits of the Young–Lippmann equation.

**Table 2.** Fitted values of  $\cos\theta_0$  and  $\epsilon_0\epsilon_r/2\gamma_{LA}d$  for the four [BF<sub>4</sub>]<sup>-</sup>-based ILs investigated

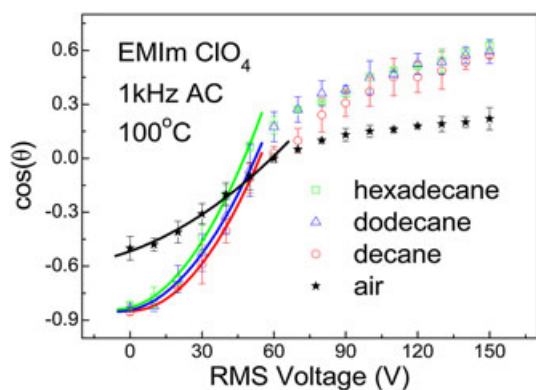
ILs	Length of alkyl chain	Surface tension at 100 °C (mN/m)	$\cos\theta_0$	$\frac{\epsilon_0\epsilon_r}{2\gamma_{LA}d}$
[EMIm][BF <sub>4</sub> ]	2	43	-0.99762	0.00026
[BMIm][BF <sub>4</sub> ]	4	35	-0.94164	0.00038
[HMIm][BF <sub>4</sub> ]	6	31	-0.86038	0.00046
[OMIm][BF <sub>4</sub> ]	8	26	-0.83167	0.00067

imidazolium ILs. The fitted values of  $\cos\theta_0$  and  $\epsilon_0\epsilon_r/2\gamma_{LA}d$  almost changed with the order of their surface tensions (Table 2). That is in good conformity with the experimental results in Fig. 7. Hence, our electrowetting results demonstrate that ILs with long alkyl chain could be a better choice to enhance the surface hydrophilicity at high temperature.

### Ambient dependence at high temperature

Previous studies have shown that electrowetting of ILs using alkane as the ambient exhibits greatly enhanced, sensitive, and reversible contact angle modulation in comparison to that in air.<sup>[20,23]</sup> Also, our experiment results confirmed this again at elevated temperatures. It could be obtained from Fig. 11 that the usage of alkane ambient not only enlarged the contact angle





**Figure 8.** Electrowetting curves of [EMIm][ClO<sub>4</sub>] under 1 kHz AC electric field at 100 °C and in decane, dodecane, and hexadecane, respectively. The solid lines are fits of the Young-Lippmann equation.

**Table 3.** Surface tension and fitted value for three alkanes investigated

Alkanes ambient	Length of alkyl chain	<i>a</i>	<i>b</i>	Surface tension at 100 °C (mN/m)
Decane	10	25.670	0.0920	16.47
Dodecane	12	27.120	0.0884	18.28
Hexadecane	16	29.180	0.0854	20.64

modulation but also enhanced the reversibility. However, the ambient impact on electrowetting behaviors of ILs under AC voltage conditions has not yet been studied to our knowledge. Herein, we presented three alkanes with different lengths of alkyl chain (decane, dodecane, hexadecane) to investigate electrowetting of ILs with different alkane ambient (Fig. 8). All tests were executed at 100 °C.

Some effort has been devoted to the dependence of the surface tension on the temperature for the large majority of compounds, including alkanes, by Jasper.<sup>[36]</sup> It can be given as

$$\gamma = a - bt \quad (9)$$

where *a* and *b* are constants and *t* is the temperature in °C. The values of *a* and *b* given in Table 3 can be used to calculate the values of surface tension for the alkanes within its liquid range. From Table 3, it can be easily obtained that  $\gamma_{\text{decane}} < \gamma_{\text{dodecane}} < \gamma_{\text{hexadecane}}$ . Considering surface tension of [EMIm][ClO<sub>4</sub>] (25.9 mN/m), the interface tension  $\gamma_{\text{ILs-decane}}$ ,  $\gamma_{\text{ILs-dodecane}}$ , and  $\gamma_{\text{ILs-hexadecane}}$  between ILs-decane, ILs-dodecane, and ILs-hexadecane interfaces present  $\gamma_{\text{ILs-decane}} > \gamma_{\text{ILs-dodecane}} > \gamma_{\text{ILs-hexadecane}}$ . Consequently, the long length of alkyl chain leads to lower interfacial tension ( $\gamma_{\text{LA}}$ ). Additionally, low interfacial tension ( $\gamma_{\text{LA}}$ ) guarantees smaller contact angle ( $\theta$ ) under the same applied voltage (*V*) and lowers applied voltage (*V*) to reach the same contact angle ( $\theta$ ), according to Eqns (1) and (6). Thus, it could be concluded that the long length of alkyl chain guarantees smaller contact angle ( $\theta$ ) under the same applied voltage (*V*) and lowers applied voltage (*V*) to reach the same contact angle ( $\theta$ ).

## Conclusion

In this work, the electrowetting behavior of several imidazolium-based ILs on dielectric substrate, using alkane as the ambient and under AC electric field at high temperature (up to 100 °C), has

been investigated. In conclusion, ILs because of their excellent properties, are superior to aqueous electrolytes or other organic solvents as the media in electrowetting. The results showed attractive features involving wide operating temperatures and in particular high stability, fast response, and good reversibility at high temperatures. Besides, the structure of cation and anion was found to be directly related to the contact angle change of the ILs. The longer the length of alkyl chain of the cation, the higher the applied voltage was needed to obtain identical contact angle. Moreover, long length of alkyl chain of alkanes guarantee smaller contact angle under the same applied voltage and lower applied voltage to reach the same contact angle. The performance of IL-based electrowetting affected by the structure and physicochemical properties of ILs such as surface tension, alkyl carbon chain length of cation, type of the anion, etc., and the efficiency could be further improved through optimal choice of ambient phase or rational design and synthesis of ILs.

## SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

## Acknowledgements

We are grateful to the National Natural Science Foundation of China (No.20533080) and the science and technology support program of Gansu Province (No. 1011GKCA018).

## References

- [1] M. G. Pollack, R. B. Fair, A. D. Shenderov, *Appl. Phys. Lett.* **2000**, *77*, 1725.
- [2] H. Moon, P. A. L. Wijethunga, Y. S. Nanayakkara, P. Kunchala, D. W. Armstrong, *Anal. Chem.* **2011**, *83*, 1658.
- [3] Y. S. Nanayakkara, H. Moon, D. W. Armstrong, *ACS Appl. Mater. Interfaces* **2010**, *2*, 1785.
- [4] V. Srinivasan, V. K. Pamula, R. B. Fair, *Lab on a Chip* **2004**, *4*, 310.
- [5] R. A. Hayes, B. J. Feenstra, *Nature* **2003**, *425*, 383.
- [6] H. You, A. J. Steckl, *Appl. Phys. Lett.* **2010**, *97*.
- [7] W. J. J. Welters, L. G. J. Fokkink, *Langmuir* **1998**, *14*, 1535.
- [8] P. Dubois, G. Marchand, Y. Fouillet, J. Berthier, T. Douki, F. Hassine, S. Gmouh, M. Vaultier, *Anal. Chem.* **2006**, *78*, 4909.
- [9] D. Huh, A. H. Tkaczyk, J. H. Bahng, Y. Chang, H. H. Wei, J. B. Grotberg, C. J. Kim, K. Kurabayashi, S. Takayama, *J. Am. Chem. Soc.* **2003**, *125*, 14678.
- [10] M. S. Dhindsa, N. R. Smith, J. Heikenfeld, P. D. Rack, J. D. Fowlkes, M. J. Doktycz, A. V. Melechko, M. L. Simpson, *Langmuir* **2006**, *22*, 9030.
- [11] F. Mugele, J. C. Baret, *J. Phys. Condens. Matter* **2005**, *17*, R705.
- [12] N. Verplanck, E. Galopin, J. C. Camart, V. Thomy, Y. Coffinier, R. Boukhroub, *Nano Lett.* **2007**, *7*, 813.
- [13] R. D. Rogers, K. R. Seddon, *Science* **2003**, *302*, 792.
- [14] J. H. Davis, P. A. Fox, *Chemical Communications* **2003**, 1209.
- [15] D. Chatterjee, B. Hetayothin, A. R. Wheeler, D. J. King, R. L. Garrell, *Lab Chip* **2006**, *6*, 199.
- [16] S. Millefiorini, A. H. Tkaczyk, R. Sedev, J. Efthimiadis, J. Ralston, *J. Am. Chem. Soc.* **2006**, *128*, 3098.
- [17] H. L. Ricks-Laskoski, A. W. Snow, *J. Am. Chem. Soc.* **2006**, *128*, 12402.
- [18] M. Paneru, C. Priest, R. Sedev, J. Ralston, *J. Phys. Chem. C* **2010**, *114*, 8383.
- [19] M. Paneru, C. Priest, R. Sedev, J. Ralston, *J. Am. Chem. Soc.* **2010**, *132*, 8301.
- [20] Y. S. Nanayakkara, S. Perera, S. Bindiganavale, E. Wanigasekara, H. Moon, D. W. Armstrong, *Anal. Chem.* **2010**, *82*, 3146.
- [21] E. Wanigasekara, X. T. Zhang, Y. Nanayakkara, T. Payagala, H. Moon, D. W. Armstrong, *ACS Appl. Mater. Interfaces* **2009**, *1*, 2126.
- [22] Y. S. Nanayakkara, H. Moon, T. Payagala, A. B. Wijeratne, J. A. Crank, P. S. Sharma, D. W. Armstrong, *Anal. Chem.* **2008**, *80*, 7690.

- [23] S. G. Zhang, X. D. Hu, C. Qu, Q. H. Zhang, X. Y. Ma, L. J. Lu, X. L. Li, X. P. Zhang, Y. Q. Deng, *Chemphyschem* **2010**, *11*, 2327.
- [24] V. Halka, W. Freyland, *Zeitschrift Fur Physikalische Chemie-International Journal of Research in Physical Chemistry & Chemical Physics* **2008**, *222*, 117.
- [25] A. G. Papatasiou, A. G. Boudouvis, *Appl. Phys. Lett.* **2005**, *86*.
- [26] J. Buehrle, S. Herminghaus, F. Mugele, *Phys. Rev. Lett.* **2003**, *91*.
- [27] H. J. J. Verheijen, M. W. J. Prins, *Langmuir* **1999**, *15*, 6616.
- [28] P. Bonhote, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Gratzel, *Inorg. Chem.* **1996**, *35*, 1168.
- [29] J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker, R. D. Rogers, *Green Chem.* **2001**, *3*, 156.
- [30] D. R. MacFarlane, S. A. Forsyth, J. Golding, G. B. Deacon, *Green Chem.* **2002**, *4*, 444.
- [31] T. Payagala, Y. Zhang, E. Wanigasekara, K. Huang, Z. S. Breitbach, P. S. Sharma, L. M. Sidisky, D. W. Armstrong, *Anal. Chem.* **2009**, *81*, 160.
- [32] T. Krizek, Z. S. Breitbach, D. W. Armstrong, E. Tesarova, P. Coufal, *Electrophoresis* **2009**, *30*, 3955.
- [33] Z. S. Breitbach, D. W. Armstrong, *Anal. Bioanal. Chem.* **2008**, *390*, 1605.
- [34] M. L. Qi, D. W. Armstrong, *Anal. Bioanal. Chem.* **2007**, *388*, 889.
- [35] J. L. Anderson, R. F. Ding, A. Ellern, D. W. Armstrong, *J. Am. Chem. Soc.* **2005**, *127*, 593.
- [36] J. J. Jasper, *J. Phys. Chem. Ref. Data* **1972**, *1*, 841.