

Electrically Switchable Capillarity of Ionic Liquids

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Abstract

Electrocapillarity is the basis of modern electrowetting. And room temperature ionic liquids, an increasingly important set of electrolytes and organic salts that are liquid at room temperature, are considered a novel class of electrowetting agents, because of non-significant vapor pressure, nonflammability, good thermal stability, and a wide useable temperature range. In this paper, a simple device has been fabricated to investigate the electrocapillarity of ionic liquids. It shows attractive features involving wide operating temperature and in particular high stability, fast response and good reversibility at high temperatures. Besides, electrocapillarity of ionic liquids is strongly dependent on power supply frequency. In particular, high frequency, stable, reversible and wide height of rise modulations were obtained. The phenomenon of ionic liquids-based electrocapillarity was found to be affected by the structure and physicochemical properties of ionic liquids such as density, 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 ionic liquids.

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Keywords

Electrocapillarity, ionic liquids, height of rise, response time, high temperature, AC electric fields

1. Introduction

Electrowetting (EW) is the decrease in contact angle achieved by applying an external voltage across the solid/liquid interface. It has been studied by researchers from various fields, such as applied physics, physical chemistry, electrochemistry and electrical engineering, but has recently attracted considerable interest in relation to directed and switchable fluid movement [1-4]. As the basis of modern electrowetting, electrocapillarity (EC) was first described in detail in 1875 by Lippmann [5]. Since then, capillary rise as a result of a potential-induced change in the contact angle has been demonstrated. Welters and Fokkink [6] showed that

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electrowetting could be used to control capillary rise in a polymer coated capillary. A fast and reversible rise can be achieved by switching the potential. Consequently, a simple theory based on a circuit model and the Maxwell stress tensor has been used to determine the height of rise of a conducting liquid between parallel coated electrodes by Jones *et al.* [7], and also the frequency-dependent relationship has been clarified. Pellat observed that at least in a terrestrial gravitational field, rapid Joule heating sets in at field strength well below the value required to achieve a significant liquid elevation [8]. Even distilled or deionized water is easy to boil before a 1 cm height of rise can be achieved. However, the heating problem is ameliorated to a tolerable extent, it should be further improved. Besides, the most frequently used conductive liquid in EC is limited to saline, which may suffer from problems such as evaporation or freezing at relatively higher/lower temperatures. Therefore, development of new and robust media for electrocapillarity with higher thermostability and low vapor pressure is highly desirable.

Room temperature ionic liquids (RTILs or ILs), an increasingly important set of electrolytes and organic salts that are liquid at room temperature, are considered as a novel class of electrowetting agents [9, 10]. These liquids have unique physicochemical characteristics: non-significant vapor pressure, nonflammability, good thermal stability and a wide useable temperature range. They are nonvolatile with high ionic conductivity and, therefore, are very promising in various electrochemical and industrial applications [11–13].

As ionic liquids gain industrial significance, the manipulation of these fluids becomes increasingly important. ILs have emerged and employed as promising alternative EW media because of their unique physicochemical properties [14–17]. As with EW, EC is also a prime candidate for the actuation of these fluids since it is reversible, has no moving parts, and is conducive to computerized triggering. Successful electrocapillarity-based manipulation of ILs for reaction control would enhance their role as more environmentally sustainable industrial solvents.

2. Theory

Years ago, Jones *et al.* used an apparatus similar to that depicted in Fig. 1 to demonstrate that a conductive liquid rises upward between vertically oriented, parallel electrodes against gravity when a voltage is applied [18]. Here we define t as the thickness of the dielectric layer, d as the gap width of the two dielectric layers. Let the conductive liquid have mass density ρ_{IL} , electrical conductivity σ_{IL} and dielectric constant ϵ_{IL} . If voltage V is applied between the electrodes at spacing d , the liquid responds by rising to height h above its equilibrium level, refer to Fig. 1. The capacitance c and conductance g , for convenience expressed per unit area, are $c_d = \epsilon_d/d$, $c_{air} = \epsilon_0/d$, $c_{IL} = \epsilon_{IL}/d$ and $g_{IL} = \sigma_{IL}/d$. Using the circuit model, the

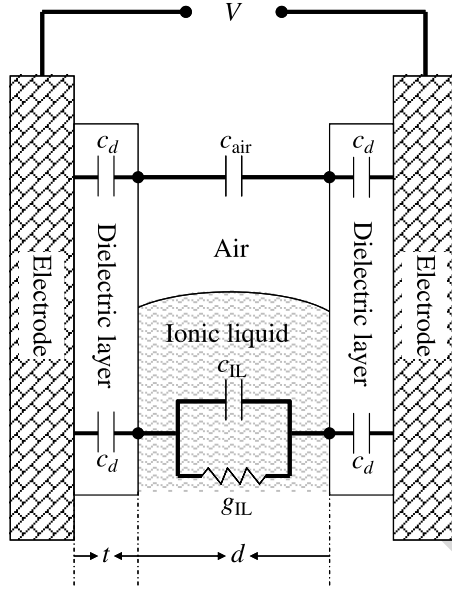


Figure 1. RC circuit model used.

root-mean-square (RMS) electric field quantities are

$$E_d = \frac{c_{air}}{2c_{air} + c_d} V/t, \quad (1a)$$

$$E_{air} = \frac{c_d}{2c_{air} + c_d} V/d, \quad (1b)$$

$$E'_d = \text{Re} \left[\frac{j\omega c_{IL} + g_{IL}}{j\omega(2c_{IL} + c_d) + 2g_{IL}} V/t \right], \quad (1c)$$

$$E_{IL} = \text{Re} \left[\frac{j\omega c_d}{j\omega(2c_{IL} + c_d) + 2g_{IL}} V/d \right]. \quad (1d)$$

Examination of equations (1c) and (1d) reveals a critical frequency as:

$$f_c = \frac{g_{IL}}{p(2c_{IL} + c_d)}. \quad (2)$$

For $f \ll f_c$, $E_{IL} \approx 0$, which means that the liquid acts like a perfect conductor so that the entire voltage drop occurs in the dielectric layers. On the other hand, for $f \gg f_c$, the electric field below the liquid surface is nonzero and is related by the electric flux continuity condition to the field in the dielectric layer: $\varepsilon_{IL} E_{IL} = \varepsilon_d E'_d$. If we let the ionic liquid have mass density ρ_{IL} , based on the critical frequency, f_c , low- and high-frequency limits for the height of rise can be identified as:

$$h = \begin{cases} \frac{\varepsilon_d}{4\rho_{IL}gt} V^2, & f \ll f_c, \\ \frac{\varepsilon_{IL} - \varepsilon_0}{2\rho_{IL}td^2} V^2, & f \gg f_c. \end{cases} \quad (3a)$$

$$(3b)$$

The low-frequency limit is identical to the result obtained using the contact angle model [6], while the high-frequency expression agrees with equation (1) as long as $t \ll d$ [19].

Equations (1)–(3) combine to give a parabolic relationship between height of rise h and voltage V :

$$h = H(f)V^2, \quad (4)$$

where

$$H(f) = \frac{\varepsilon_d^2 [4\pi^2 f^2 (\varepsilon_{IL} - \varepsilon_0) (\varepsilon_{IL} t - \varepsilon_0 d/2) + \sigma_{IL}^2 t]}{4\rho_{IL} g (2t\varepsilon_0 + \varepsilon_0 d) [\omega^2 (\varepsilon_{IL} t + \varepsilon_d d/2)^2 + \sigma_{IL}^2 t^2]}.$$

This expression is convenient when comparing the predictions of the model to the experiments. From this relationship it follows that the absolute height of rise h is proportional to the square of the applied potential and is not dependent on the surface tension of the liquid. The surface tension of the liquid will only determine the initial liquid level, not the extent of the electrically induced height of rise.

3. Experimental Section

3.1. Synthesis and Characterization of ILs

Six kinds of imidazolium ILs with three different anions, namely, 1-ethyl-3-methylimidazolium perchlorate ([EMIm][ClO₄]), 1-ethyl-3-methylimidazolium dicyanamide ([EMIm][N(CN)₂]), 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm][BF₄]), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF₄]), 1-hexyl-3-methylimidazolium tetrafluoroborate ([HMIm][BF₄]) and 1-octyl-3-methylimidazolium tetrafluoroborate ([OMIm][BF₄]), were synthesized in our laboratory according to established procedures. The ion conductivity was measured using a Mettler-Toledo Seven Multimeter. The viscosity was measured on a Brookfield DV-III+ viscometer. The surface tension was measured on a Surface Tension Analyzer (Solon Tech. Shanghai) using the Du Noüy ring method. The thickness of the insulating and hydrophobic layers was measured by a surface profiler (Micro-XAM, USA). The water content was determined by Karl–Fisher analysis (Metrohm, Switzerland). Prior to measurements all ILs were dried in vacuo at 80°C for 3 h, except [EMIm][N(CN)₂], which was dried in vacuo at 60°C for 3 h. The water content was ≈160 ppm for [EMIm][ClO₄], ≈190 ppm for [EMIm][N(CN)₂], ≈287 ppm for [EMIm][BF₄], ≈289 ppm for [BMIm][BF₄], ≈268 ppm for [HMIm][BF₄] and ≈363 ppm for [OMIm][BF₄].

3.2. Sample Preparation and Measurements

Figure 2 shows the schematic of equipment for investigating EC of ILs. Glass plates covered on one side with an indium tin oxide (ITO) were used as substrates. Parylene C (≈10 μm, ε_r = 2.65), because of its high dielectric constant and conformal

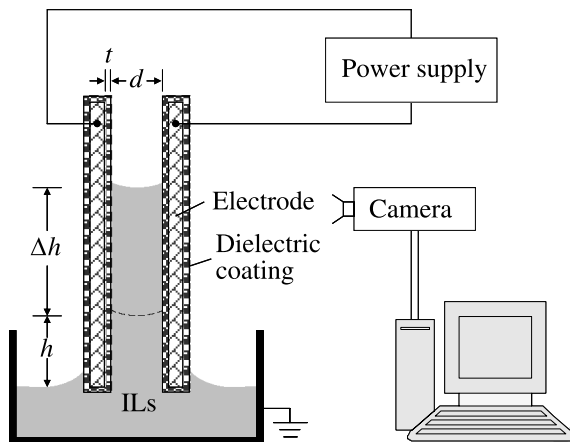


Figure 2. Schematic of equipment for investigating EC of ILs.

coating of surfaces of different shapes and compositions, was deposited as the insulating layer by gas-phase deposition at room temperature. A very thin ($\approx 1 \mu\text{m}$, $\epsilon_r = 1.93$) Teflon coating was used as the top layer to obtain a hydrophobic surface with a low contact angle hysteresis. With these duplex coatings we were able to induce electrically a dramatic and reversible change in contact angle as well as a fast and substantial rise and depression in capillary slits. This Teflon AF1600 (DuPont, USA) layer was deposited on the insulating coating by dipping in 1 wt% solution of Teflon AF1600 in FC75 (GORUBER, USA). The substrates were 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 , in order to remove residual solvent and improve the adhesion of the Teflon layer to the substrate. The AF1600 layer does not have sufficient insulating properties to be used without the Parylene C coating. An AC voltage was applied on the two electrodes by a function generator with frequency varying from 10 Hz to 1 kHz and applied voltage up to 250 V. All voltages in this paper are root-mean-square (rms) values. Switchable capillary rise was measured between two coated glass plates. A transparent layer of ITO was used as the conductive coating. After the deposition of the coatings, the glass plates were clamped together with a 0.35-mm spacer in between. With this setup a transparent capillary slit was obtained. With the same voltage applied to the conductive layers of both plates, a capillary rise can be achieved. The height of the liquid between the plates was recorded using a camera connected to a video recorder and measured as a function of the potential. For speed measurements a video setup was used.

4. Results and Discussion

All height of rise data were obtained at a spacing of $d = 0.7 \pm 0.05 \text{ mm}$, where curvature-related error is negligible, overshoot is not observed, and no liquid os-

cillation is evident. For convenience in observation, the height, h , was measured from the liquid level outside the electrodes to the lowest point of the meniscus. This choice, while arbitrary, introduces minimal error because, except right after the voltage is turned on, the height of rise is large compared to the observed radius of curvature [20]. For applied voltages below the saturation limit, the height of rise data agree remarkably well with the electromechanical model. This good agreement extends from 10 Hz to 1 kHz and covers all ILs mentioned.

4.1. Ion Type Dependence

Switchable capillary rise was measured between two glass plates coated with the same duplex coating. At any fixed frequency, the column rises within 4 s, approaching a steady value identical to the static height measured by slowly increasing the voltage and the meniscus rose in proportion to the square of the potential, as can be seen in Fig. 3. It could be concluded that EMIm BF₄, EMIm ClO₄ and EMIm N(CN)₂ behave similarly, because they have similar density. On the other hand, for different cations, the length of carbon chain determines height of rise ($h_{\text{OMIm BF}_4} > h_{\text{HMIm BF}_4} > h_{\text{BMIm BF}_4} > h_{\text{EMIm BF}_4}$). Because, of conductivity being more than 100 times higher than that of DI water, the critical frequency, which for DI water is 5.2 kHz, is of the order of 480 kHz, and according to equation (3), low density ($\rho_{\text{OMIm BF}_4} < \rho_{\text{HMIm BF}_4} < \rho_{\text{BMIm BF}_4} < \rho_{\text{EMIm BF}_4}$) guarantees high h , when $f \ll f_c$. The line in Fig. 3 represents the theoretical meniscus height based on the coating properties and the measured plate distance. The height of rise data are closely matched by numerical solutions of equation (4); however, above some voltage threshold, this agreement deteriorates. This behavior at higher voltages, presumably due to contact angle saturation, is strongly correlated to the saturation phenomenon observed in EW experiments and will be considered further. If the voltage is decreased, the liquid drops back to the reference level with minimal hysteresis. Even after several rise–fall cycles, hysteretic effects are not particularly

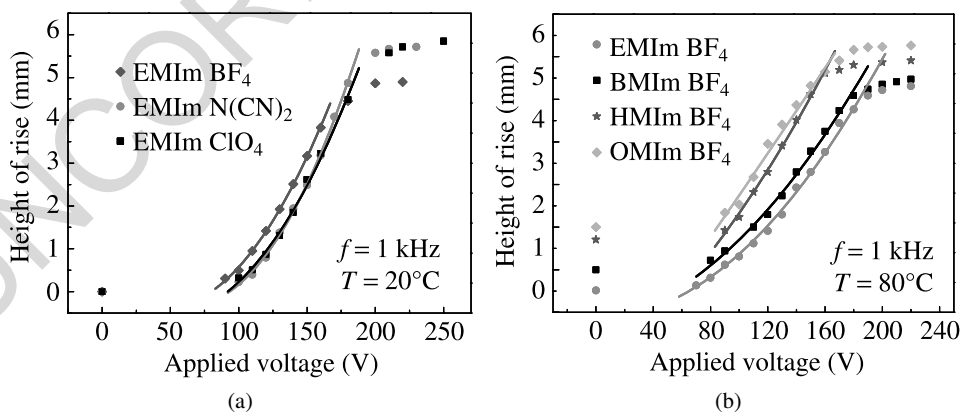


Figure 3. Height of rise versus applied voltage for (a) three ILs with different cations and (b) four ILs with different anions at a spacing of $d = 0.35 \pm 0.05$ mm and 1 kHz voltage from 0 to 250 V-rms.

significant as long as the hydrophobic film is applied to the electrodes. Sometimes at higher voltages, the IL surface drops abruptly, possibly due to breakdown through pinholes in the insulating layers.

4.2. Frequency Dependence

The frequency dependence of height of rise was examined under AC voltage from 10 Hz up to 1 kHz. As shown in Fig. 4(right), the height of rise (h) has a linear relationship with the square of applied voltage (V) in the beginning. Then, starting around some voltage threshold, the height of rise data start to deviate markedly from the parabolic dependence predicted by the model, i.e., $h \propto V^2$. Welters and Fokkink reported a similar deviation from square-law behavior [6]. They correlated the voltage at which the deviation occurred to independent measurements of the voltage at which contact angle saturation manifested itself. It seems justified to make the hypothesis that the observed deviation from V^2 is likewise related to contact angle saturation; however, using AC voltage provides an opportunity to exploit frequency as a tool to study the nature of contact angle saturation and its influence on the electromechanical force. Using AC instead of DC electric field leads to a wider modulation, because AC electric field could prevent the adsorption of ions from ILs onto the substrate surface. In the AC experiments, measurements were made both starting at low frequency and moving to higher values and from high frequency to low, the latter to minimize possible accumulation of trapped electric charge on the parylene films. We have found that the voltage at which the deviation from square-law behavior occurs is strongly dependent on frequency (Fig. 4). In our work, the strong dependence of h on frequency is registered in the range from 10 Hz up to 1 kHz. Increasing the frequency from 10 Hz to 1 kHz further resulted in wider modulation of height of rise, and the largest height of rise values are observed for the highest frequency, which is similar to the result obtained by Jones *et al.* [18], in which the height of rise of DI water was frequency dependent and increased from 10 Hz to 1 kHz. This is as expected because the smaller height of rise modulation in low frequency case can be correlated to contact angle saturation because of charge-induced ion adsorption on the substrate, while in the high frequency case it is reduced by the fast change of the electric field polarity.

4.3. Temperature Dependence

Traditional water/organic solvent EC setup was able to operate within narrow temperature range (-20 to $+60^\circ\text{C}$). In addition, microdroplets inevitably generated by temperature gradient on the inner surfaces of the two electrodes affected the EC effect in a serious way. However, IL-based EC exhibits a better performance at high temperature than at room temperature. For instance, EMIm BF₄-based EC at high temperature shows not only a large range of height of rise (Fig. 5) but also fast response (Fig. 6) and good reversibility. As shown in Fig. 5, although the initial height at zero voltage is barely increased with increasing temperature, the driving voltage to obtain identical height of rise is obviously decreased. The different driving volt-

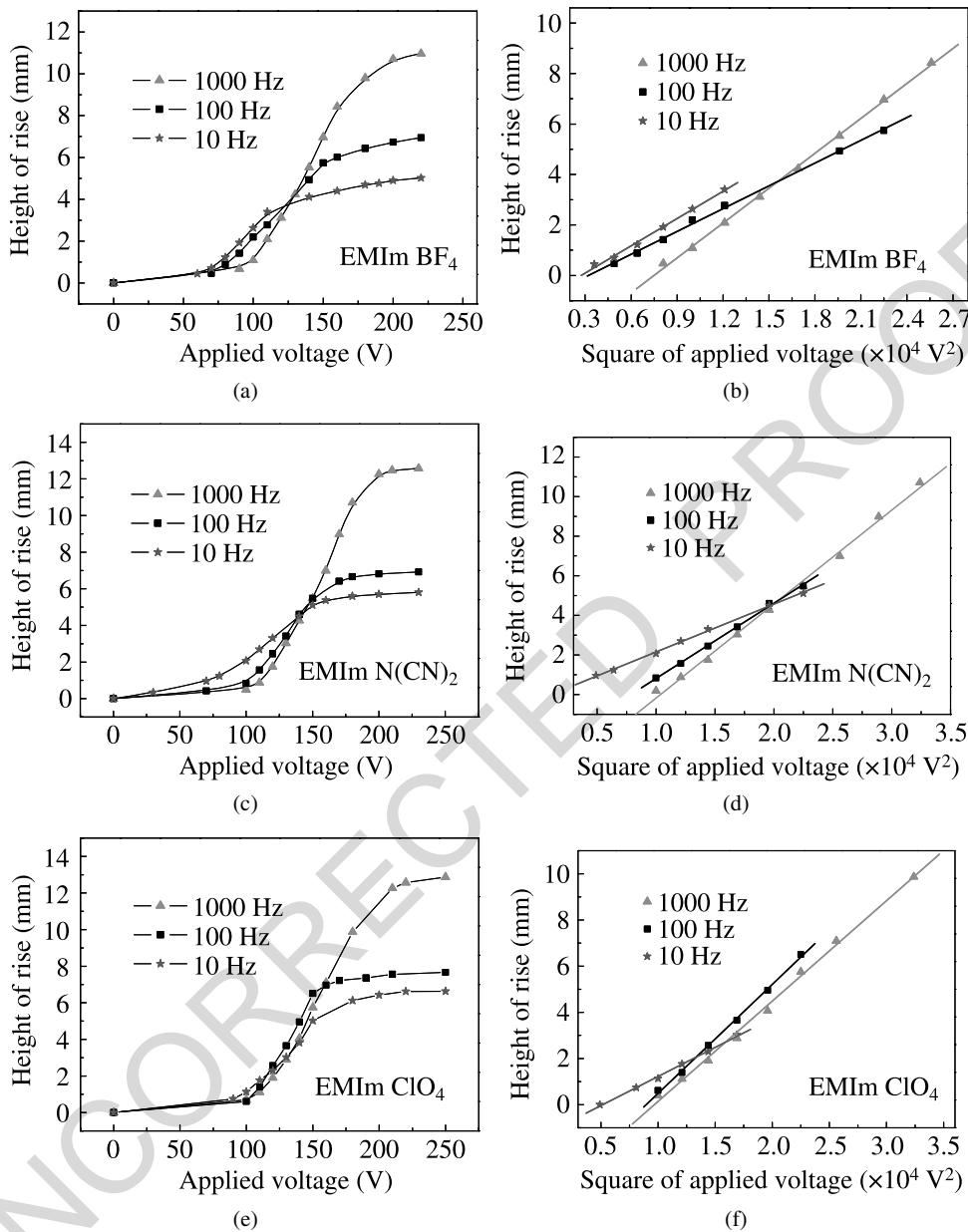


Figure 4. Height of rise versus applied voltage for three ILs with different anions at a spacing of $d = 0.35 \pm 0.05$ mm under 10, 100 Hz and 1 kHz AC electric field.

ages could be due to the high temperature-induced decrease of density according to equation (3a).

Note that IL-based EC at high temperature can work well with not only high efficiency but also with fast response. This speed is mainly dependent on the viscosity

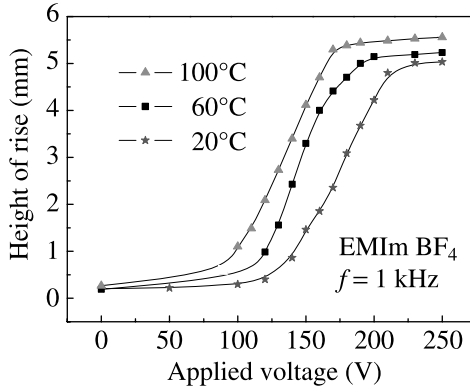


Figure 5. Height of rise *versus* applied voltage for EMIIm BF₄ at a spacing of $d = 0.35 \pm 0.05$ mm under 1 kHz AC electric field at temperatures of 20, 60 and 100°C.

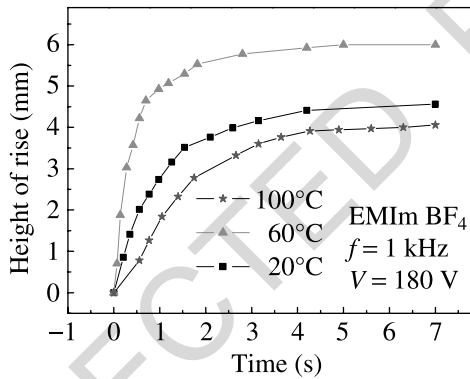


Figure 6. Height of rise *versus* response time for EMIIm BF₄ at a spacing of $d = 0.35 \pm 0.05$ mm under 1 kHz AC electric field at temperatures of 20, 60 and 100°C.

of the liquid and the dynamic contact angle during the rise of IL. Low viscosity guarantees fast speed leading to shorter response time [21]. Thus, the response time obviously decreased from ≈ 4 s at 20°C to ≈ 2 s at 100°C due to the significant decrease of viscosity. In sum, an IL with low viscosity and low density is likely to give fast response and wide height of rise range in EC.

5. Conclusions

A simple IL-based EC device, according to the theory based on the circuit model, has been established to investigate the height of rise of ILs between parallel, coated electrodes. As compared to conventional EC, EC of ILs under AC electric field shows attractive features involving wide operating temperature and, in particular, high stability, fast response and good reversibility at high temperature. Besides, EC of ILs is strongly dependent on power supply frequency. In particular at the high fre-

quency of 1 kHz, stable, reversible and wide height of rise modulation was obtained. The phenomenon of IL-based EC is influenced by the structure and physicochemical properties of IL such as density, 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.

Acknowledgements

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