

A Tunable Ionic Liquid Based RC Filter Using Electrowetting: A New Concept

Yasith S. Nanayakkara,[†] Hyejin Moon,[‡] and Daniel W. Armstrong^{*·†}

Department of Chemistry and Biochemistry and Department of Mechanical and Aerospace Engineering, The University of Texas at Arlington, Arlington, Texas 76019, The University of Texas at Arlington, Arlington, Texas 76019

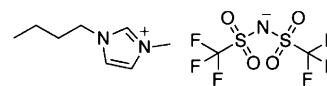
ABSTRACT RC filters are used to discriminate unwanted frequency elements of a specific signal. Here we report a new concept for a tunable RC filter. The concept was demonstrated by developing a tunable RC filter “consisting of an ionic liquid drop placed on a dielectric layer.” Cut-off frequency of the filter can be altered and controlled by changing the drop shape via electrowetting. The dielectric layer and the solid–liquid interface behave as serially connected capacitors, where the total capacitance is a function of drop shape (or contact angle). The drop shape and hence the total capacitance can be instantly controlled by electrowetting. The change in the capacitance will change the cutoff frequency of the filter. For a 5 μL ionic liquid drop, the achieved “tunability range” was 4.5–9.8 kHz. This demonstrates that the new concept is attainable. This RC filter system could potentially be used as a detecting technique.

KEYWORDS: RC filter • electrowetting • ionic liquids • cutoff frequency, • critical frequency • [bmim][NTf₂]

INTRODUCTION

A resistor-capacitor (RC) filter is an electronic circuit, which is used to discriminate unwanted frequency elements of a specific signal. The cutoff frequency (f_c) value of a filter typically is a function of R (resistor) and C (capacitor) values. Therefore, changing either the R value, the C value, or both can alter the f_c value. Hence almost all tunable RC filters have been using the same principle of tuning resistor value or capacitor value to tune f_c value (1).

It is well-known that a solid–liquid interface can act as a capacitor in the presence of an external electric field. If a liquid drop is placed on a dielectric surface such as Teflon, then that system can be modeled as a series of capacitors (2). Thus the total value of the capacitance is a combination of solid–liquid interface capacitance and dielectric layer capacitance (2). The total capacitance is a function of the area between drop and the dielectric layer (3, 4), and this area is dependent on the shape of the drop or the contact angle (4, 5). The shape (or the contact angle) of the drop can be controlled by electrowetting (2); therefore the total capacitance can be easily tuned by electrowetting. If this system is serially connected to a traditional resistor then one can produce a simple RC filter with tunable f_c values. We used the system explained above to demonstrate the concept of a new type of tunable RC filter. The RC filter effect has been observed for both sessile drops and parallel plate type in previous electrowetting/dielectrophoretic experiments (3, 4, 6–9). However, those studies had no intention



[bmim][NTf₂]

FIGURE 1. Structure and the acronym of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid.

of developing a workable RC filter, rather they explained their experimental observations using the RC filter effect. Here, we report a novel liquid drop based tunable RC filter. This kind of liquid RC filter system can easily be combined with most microfluidic devices to analyze data online and has several applications, such as: (i) to determine approximate water and other impurity contents of different ionic liquids, (ii) to detect ionic liquids synthesized on microfluidic chips (10a), (iii) as a detector in microfluidic liquid–liquid extraction chips (10b).

EXPERIMENTAL SECTION

The ionic liquid (IL), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, is commonly abbreviated [bmim][NTf₂] (Figure 1) was synthesized in our laboratory as reported previously (11). Before use, the IL was kept in a vacuum oven for 18 h with phosphorus pentoxide (P₂O₅) at room temperature to minimize the water content. The final water content of the IL measured by Karl Fischer titration was 470 ppm.

The experimental setup for the RC filter is shown in Figure 2. Unpolished float glass slides coated with 30 nm indium tin oxide were purchased from Delta Technologies Ltd., (Stillwater, MN). Then they were dip-coated with Teflon solution prepared by dissolving 4% (w/v) Teflon AF1600 (www.dupont.com) in Fluoroinert FC75 solvent (www.fishersci.com). The approximate dipping speed of the custom-made dipcoater was set to 0.78 ± 0.03 mm/s. Once 75% of the slide was dipped in the solution, dipping was stopped

* Corresponding author. Phone: (817) 272-0632. Fax: (817) 272-0619. E-mail: sec4dwa@uta.edu.

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[†] Department of Chemistry and Biochemistry, The University of Texas at Arlington.

[‡] Department of Mechanical and Aerospace Engineering, The University of Texas at Arlington.

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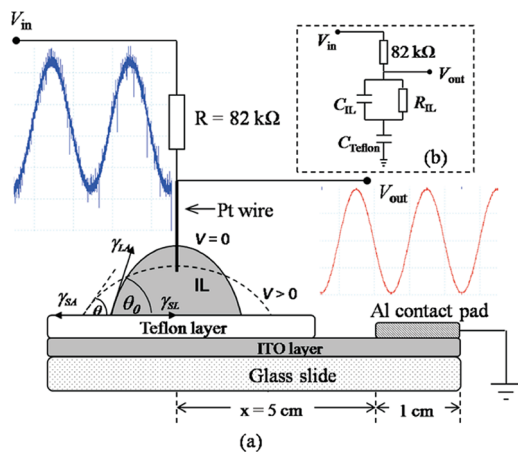


FIGURE 2. (a) Ionic-liquid-based RC filter experiment setup. θ_0 is the contact angle at zero external voltage, θ is the contact angle at any given voltage and frequency. For ionic liquid [bmim][NTf₂], $\theta_0 \approx 75^\circ$, $\theta_{(1 \text{ kHz}, 30 \text{ V})} \approx 58^\circ$, $\theta_{(1 \text{ kHz}, 50 \text{ V})} \approx 43^\circ$, $\theta_{(1 \text{ kHz}, 70 \text{ V})} \approx 35^\circ$. γ_{SA} , γ_{LA} , and γ_{SL} are solid–air, liquid–air, and solid–air interfacial tensions, respectively. The sinusoidal signal in left (blue) is an unfiltered signal with noise. The filtered signal is shown on the right (red). (b) Equivalent circuit model for the ionic-liquid-based RC filter.

for 5 s, and the slide was then raised at the same speed. The coated slides were kept in an oven for 6 min at 112 °C, 5 min at 165 °C, and 15 min at 328 °C. Finally, Teflon-coated glass slides were allowed to reach room temperature, washed thoroughly with acetone and deionized water, and then air-dried. The resulted Teflon coating thickness was 260 ± 10 nm, as measured by a Tencor Alphastep 200 Profilometer.

A drop of ionic liquid ($5.0 \pm 0.5 \mu\text{L}$) was placed on top of the Teflon layer using a capillary tip. The volume and the contact angle of the drop were calculated using CAM 200 software (www.ksvlt.com). A waveform generator (Agilent model 33220A) connected to a voltage amplifier (Trek model PZD 350) was used as the signal source for the experiments. The ground electrode was connected to the ITO layer using an Al contact pad, the IL drop was always placed 5 cm apart from this Al contact pad. The other electrode was connected to a 82 kΩ resistor. The resistor was serially connected to one end of a Pt wire (32 gauge) and the other end of the wire was dipped in the IL drop. In this way, the wired system is an analogue to a low-pass type RC filter (Figure 2b). The distance between Pt tip and Teflon surface was set to 0.8 mm. First, 10 V_{rms} sinusoidal signal was supplied to the system, increasing the frequency from 20 Hz to 18.5 kHz logarithmically with a 140 s sweep time. Output signal data was collected using a PC based oscilloscope (www.picotech.com). This procedure was repeated for 30 V_{rms}, 50 V_{rms}, and 70 V_{rms} sinusoidal signals.

RESULTS AND DISCUSSION

To make practical, tunable, liquid RC filter an ionic liquid, [bmim][NTf₂] was used. Use of [bmim][NTf₂] has several practical advantages: (i) having negligible or no vapor pressure so that evaporation is not a concern and no special sealing or packaging is needed for the filter (11), (ii) resistance to vibrations and satellite drop formation, particularly compared to water or aqueous electrolytes (3), (iii) a lower

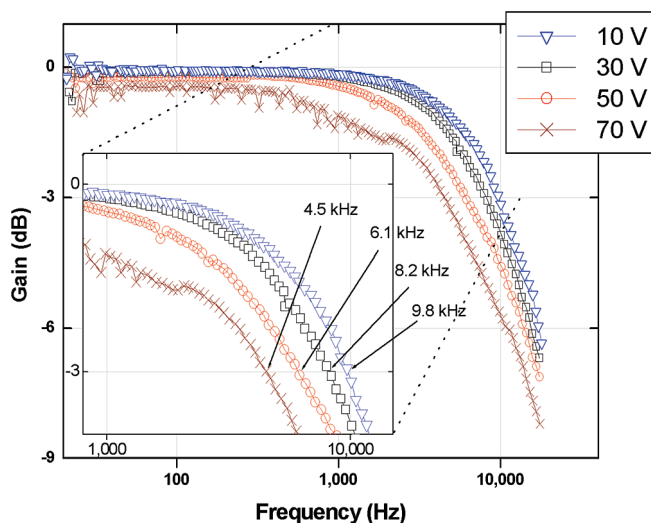


FIGURE 3. Frequency vs gain plot for the ionic-liquid-based RC filter.

viscosity than most ILs so that response times are faster than other ILs (11), (iv) the apparent contact angle change ($\Delta\theta$) of [bmim][NTf₂] due to frequency (not voltage) is lower than that of other ILs (3), (v) ion adsorption to the Teflon surface is minimal for [bmim][NTf₂], since it contains a bulky NTf₂⁻ anion (3, 11), and (vi) negligible effect of water when compare to other ionic liquids (3, 11).

Typically, frequency versus gain plots are used to characterize RC filters, in which the intersection point of the curve and the -3 dB line represents the f_c of the filter. Figure 3 shows frequency versus gain plot of the IL-based low-pass RC filter. It can be observed from the plot that at 10 V_{rms} the obtained f_c is 9.8 kHz, whereas at 30 V, 50 and 70 V the obtained f_c values are 8.2, 6.1, and 4.5 kHz, respectively. At higher voltages, lower f_c is obtained. Cutoff frequency (f_c) dependence on electrowetting voltage (V_{in}) can be explained by formulating a relationship between V_{in} and f_c (see the Supporting Information for the step by step derivation). The final derived relationship states that for a given IL

$$f_c = f(V_{in}) \quad (1)$$

When the applied voltage (V_{in}) increases, θ will decrease as described by the Young–Lippmann equation (2). As a consequence, the contact area of the drop on the Teflon surface (A) will increase (3, 4), thus increasing the total capacitance of the system. Finally, an increase in capacitance will result in a decrease in the f_c value.

The performance and the range f_c of the RC filter can be optimized by altering or controlling any of the following factors: (i) The value of the resistor (R) can be changed. (ii) The total capacitance of the filter can be easily changed by changing the drop size (here we used a $5 \mu\text{L}$ drop). Note that there are reported examples of drops as large as $25\text{--}50 \mu\text{L}$ and as small as few tens of picoliters used to demonstrate electrowetting (2, 12). (iii) Since different ILs have different capacitance due to their structure and the nature of their functional groups, the IL itself can be changed depending

on the required capacitance value (13). Also, the $\Delta\theta$ is different for different ILs, i.e., some ILs exhibit higher $\Delta\theta$ at a given voltage, whereas other ILs show lower $\Delta\theta$ at the same voltage (3, 11, 12). Therefore, if one needs a wide tunability range of f_c , it is desirable to use the first type of ILs, and for fine-tunability the latter types of ILs are desirable. (iv) The C_{total} value also can be controlled by changing the dielectric layer material. Here, we used Teflon as our dielectric layer, since it shows good reversibility and ease of use. However, Teflon layers usually have small pin holes in them, and electrons can penetrate through these holes creating a leakage current, this can reduce the performance of the filter. Coating another dense dielectric material like SiO_2 beneath the Teflon layer can minimize the leakage current (14). (v) The voltage, which requires achieving a certain $\Delta\theta$, can be reduced by reducing the thickness of the dielectric layer. In our work, we used a 260 nm dielectric layer. Previous studies have shown the use of thinner dielectric layers than 260 nm (14). However, most thin dielectrics exhibit numerous failure modes (15). Hence one should decrease the dielectric thickness with analysis of reliability for better operation. If the reliable thinner dielectric is achievable, then that may allow the use of even lower voltage to tune the f_c values. (vi) The resistivity of the ITO coating in this study was higher than that of the connecting wires ($\sim 100 \Omega/\text{cm}$). Thus it behaves more like an extra resistor in the system, and the resistance value depends on the position of the IL drop, which affects the f_c value. Therefore, distance from the Al contact pad to the drop position (i.e., x in Figure 2a) was kept constant (5 cm) for every experiment. Using gold- or silver-coated glass slides, this effect can be minimized. (vii) The amount of connecting wires used should be minimized, since at higher frequencies the impedance coming from these wires can affect the system. (viii) This filter can be assembled in oil instead of air, which would provide more contact angle change giving a larger cutoff frequency range.

This liquid drop RC filter system has low tunability range compared to traditional solid state electronic RC filter systems (16). However, liquid drop RC filter systems have many potential applications where traditional solid-state electronic RC filters cannot be used. One potential application would be determination of water content in water-miscible ionic liquids. Previous studies show water has a significant role in water-miscible ionic liquids, where contact angles vary with the amount of absorbed water. Since different contact angles provide different f_c values, this RC filter system can easily be used to determine the water content of water-miscible ionic liquids. In addition, this RC filter system can be easily integrated with microfluidics chips and can be used as a detector when synthesizing ionic liquids on chip and in microfluidic liquid–liquid extractions. Finally, one another advantage of this RC filter is its ability of continuous tunability. Most tunable RC filters have multiple discrete switches

to achieve different capacitances (17, 18), and hence their corresponding f_c values are discrete, whereas in our RC filter, the f_c values are continuous due to its continuous change of capacitance.

CONCLUSION

We have demonstrated the new concept by developing a novel low-pass RC filter using an ionic liquid droplet. The cutoff frequency of the filter can be tuned by electrowetting. The cutoff frequency range can be further optimized and varied by changing the factors outlined above.

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Supporting Information Available: Step-by-step derivation of eq 1 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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