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Preparation and Analysis of 1-Chloronaphthalene for Highly Refractive Electrowetting Optics

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High-index oils are critical to the performance of optical electrowetting devices, such as lenses, prisms, and retroreflectors. Herein, the preparation and electrowetting analysis of 1-chloronaphthalene are reported. When 1-chloronaphthalene is mixed with small amounts of an alkane, the following properties can be achieved: refractive index > 1.60, viscosity < 5 cP for rapid switching, operation at < 10 V, and ±45° of electrowetting modulation around the condition for a flat meniscus (90°).

Optical electrowetting[1] devices[2−9] are fully self-contained and, therefore, are distinct from general optofluidic devices,[10,11] which often require bulky peripheral equipment, such as syringe pumps. However, optofluidic devices do possess an advantage in that they impose no electrical requirements on the liquids and, therefore, can utilize a wider range of liquid options. Optical electrowetting devices must utilize a polar fluid, which is preferably water and a nonpolar oil fluid. In nearly all practical embodiments, the oil is implemented as the higher-index liquid because the water has a low refractive index of 1.33. The oil is further useful, as it reduces contact angle hysteresis,[12] greatly retards the evaporation of the water, and eliminates the effects of gravity or vibration. According to basic electrowetting theory, the water is treated as a perfect conductor and the oil as a perfect electrical insulator. As shown in Figure 1, for electrowetting optical devices, such lenses,[3,4,8] microprisms,[5] and retroreflectors,[9] a voltage is applied between a capacitor comprising water, a hydrophobic dielectric, and an electrode. At equilibrium, the three phases (water/oil/dielectric) rest at Young's contact angle for the water (θ_Y). As voltage is applied, an electromechanical force[13] reduces the water contact angle (θ_V) according to the electrowetting equation:

$$\cos\theta_V = \cos\theta_Y + CV^2/2\gamma_{AO} \qquad (1)$$

where C is capacitance per unit area of the hydrophobic dielectric and γ_{AO} is the interfacial surface tension between the aqueous and oil phases. As plotted in Figure 2, optical electrowetting devices that rely on refraction benefit from higher refractive index oil by having a smaller minimum focal length, larger beam deflection, or greater scattering (respectively, lenses, prisms, retroreflectors). However, selection of high-index oils is generally challenging because the oil must also be: (1) electrically insulating, > 100 of kV/cm, and very "dry" like a transformer oil; (2) low viscosity as to not compromise switching speed; (3) compatible with surface-active content in the water for lower interfacial tension (γ_{AO}) and, therefore, a reduced voltage (V); (4) weakly polarizable such that electrowetting relaxation does not occur during low-frequency ac bias; and (5) as high as possible in Abbe number[14] if used in polychromatic applications. Reported herein are the preparation and analysis of chloronaphthalene (CN), a high-index (n = 1.632) and low-viscosity (4.13 cP at 20 °C) oil that might be an excellent "building block" to achieve many or all of the above criteria for electrowetting optics. According to the Refutas equation,[15,16] when oils are mixed, the lowest-viscosity oil dominates the viscosity of the final mixture. Therefore, it is plausible that CN might be useful when solvated with other high-index and high Abbe number liquids or solids.

To begin experimentation, CN (> 85%, Sigma-Aldrich Company) was purified to reduce dichloronaphthalene (di-CN) and other contaminants from the commercial source. The boiling point of di-CN is higher (bp = 286 °C) than that of CN (bp = 259 °C). Therefore, steam distillation of the crude material was performed, followed by liquid−liquid extraction of the distillate using hexane (14.8 g of CN to 10.1 g by hexane). Hexane was then evaporated under vacuum until a change in weight was no longer observed. The steam distillation purification setup is systematically diagramed in Figure 3. After this distillation process was repeated twice, a material balance of over 70% remained. Figure 4a shows the gas chromatographic analysis, using flame ionization detection (GC−FID) before and after purification. GC analysis confirms 99.7% purity for 1-CN and 2-CN, with the remainder being 0.3% of di-CN (on the basis of peak areas).

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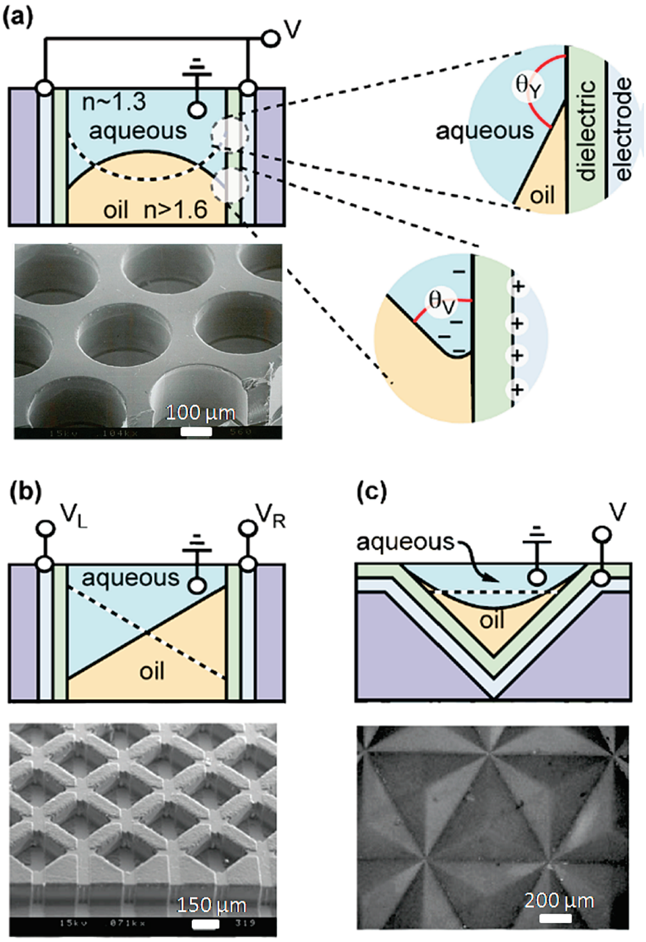

Figure 1. Examples of arrayed electrowetting optical devices, (a) lens, (b) prism, and (c) retroreflector, wherein high refractive index oils improve performance. The dotted line in each diagram represents an electrowetting-altered optical response for each device.

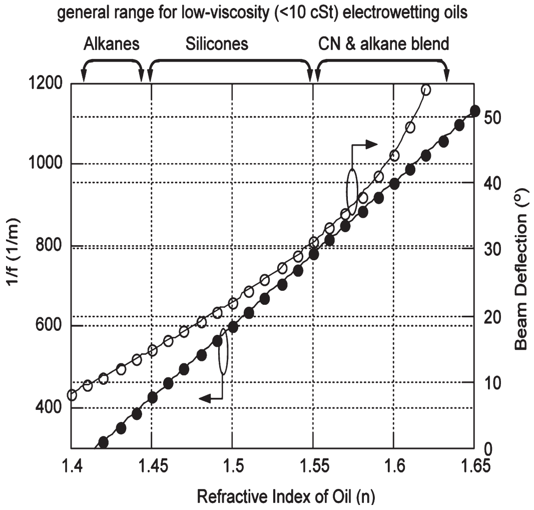

Figure 2. Theoretical properties of ~0.3 mm electrowetting devices with water ($n_w = 1.33$) and $\theta_V = 45°$ vs oil refractive index: 1/f for an electrowetting lens and deflection angle for an electrowetting double-prism. The general range for refractive index of other electrowetting oils with low viscosity (< 10 cSt) is provided at the top of the figure. Although several higher-index ($n > 1.55$) siloxane and phenylated oils exist, generally, their viscosity is very high or their electrowetting response poor.

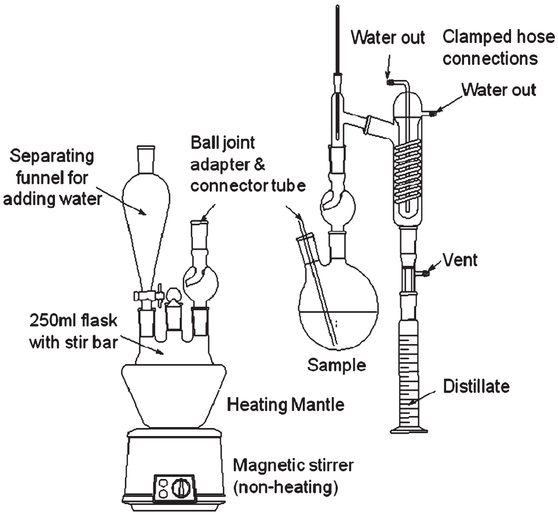

Figure 3. Diagram of steam-distilling setup for purification of CN.

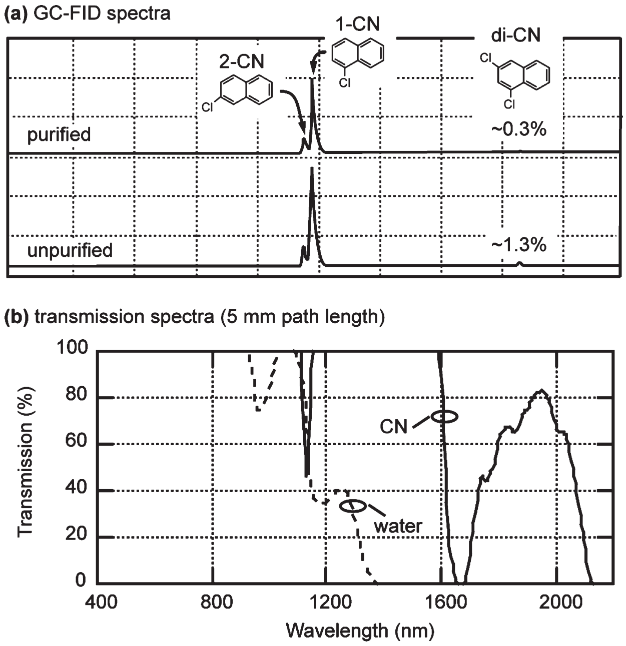

Figure 4. (a) GC−FID chromatogram of the purified and unpurified CN. (b) Transmission spectrum of CN and water from 400 to 2200 nm.

As shown in Figure 4b, CN is a colorless material, and it has infrared transmission superior to that of water. Other properties of CN include: 4.13 cP, 1.19 g/mL, mp = −20 °C, an interfacial surface tension with DI water of $\gamma_{AO} = 40$ mN/m, and a highly unpleasant smell. Toxicity should also be discussed because electrowetting is also of interest for medical applications, such as optical catheters. Cornish et al.[17] showed that 1 g of 1-CN can be metabolized in rabbits within 4 days. According to material safety data sheets, LD_{50} for 1-CN is 1540 mg/kg for ORL-RAT. Therefore, at this time, it is postulated that CN can be appropriately purified and might be safe for many applications, especially because only several milligrams of CN are needed for a 2 mm lens.

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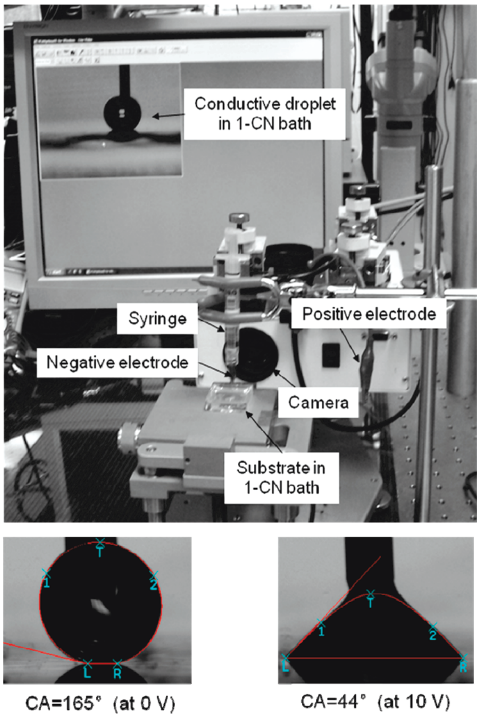
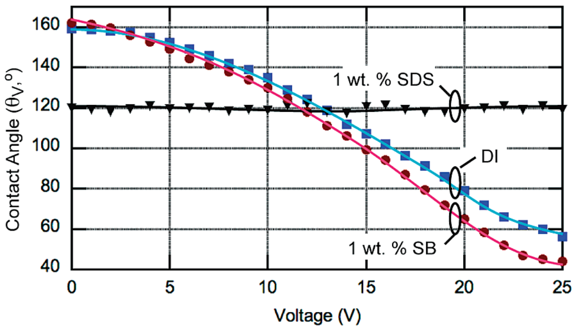


Figure 5. Picture and labeling of the experimental setup for pendant drop and electrowetting drop experimentation.

To test electrowetting properties, hydrophobic capacitors were formed on glass substrates. First, a 100 nm film of In_2O_3/SnO_2 was deposited on glass substrates. This thin-film electrode was then coated by atomic layer deposition with 100 nm of Al_2O_3 for use as an electrically insulating dielectric ($\varepsilon = 8.0$). Subsequently, 50 nm of Cytop fluoropolymer was then applied to create a hydrophobic dielectric surface. The Cytop CTL-809 M (Asahi) was spin-coated at 1% in CT-solv-180 (Asahi) and thermally cured at 180 °C to form a solid hydrophobic film with a surface energy of 19 mN/m. One corner of the substrate was scratched with a diamond scribe, then a tungsten wire was connected to the In_2O_3/SnO_2 film with Pelco colloidal silver paste, followed by application of a hermetic epoxy overcoat. All electrical tests were performed by connecting the electrowetting plate to ground, placing the electrowetting plate in a bath of CN, injecting a <1 mm diameter water droplet via a metal microsyringe, and applying a 1 kHz ac square wave to the droplet through the metal syringe. Figure 5 provides a photograph and labeling of the setup used for pendant droplet and electrowetting contact angle testing. Because 1-CN oil ($\rho = 1.19$ g/cm^3) is denser than the aqueous solutions ($\rho \sim 1$ g/cm^3) used in the experiments, the syringe used to insert the aqueous droplet was also used to hold down the droplet inside the oil. Contact angles were measured using an AST VCA-Optima system. The VCA-Optima system was integrated with a custom LabVIEW program, which automatically stepped the voltage and captured a photograph every 1 s. The contact angles were calculated in the VCA-Optima software via fitting to the meniscus near the contact line. Contact angle data were plotted from the average of three curves. Because of the use of an oil ambient, the effects of contact angle hysteresis were reduced to $<2°$ and the remaining measurement deviation was generally $<5°$ due to the combined effects of the impaling syringe and inhomogeneous dielectric quality (charge injection). Several aqueous solutions were tested, including DI water and water with 1 wt % sodium dodecyl sulfate (SDS), sodium benzoate (SB), or nonionic Triton X-100. Dodecane oil was used as an experimental control because it is highly electrically insulating and has a weak electrical polarization. The dodecane control would confirm that any degradation in the electrowetting response is due to the use of CN and not other materials.

(a) pure CN and various aqueous solutions



(b) CN blended with various wt. % of dodecane, 1 wt. % SDS in the aqueous solution

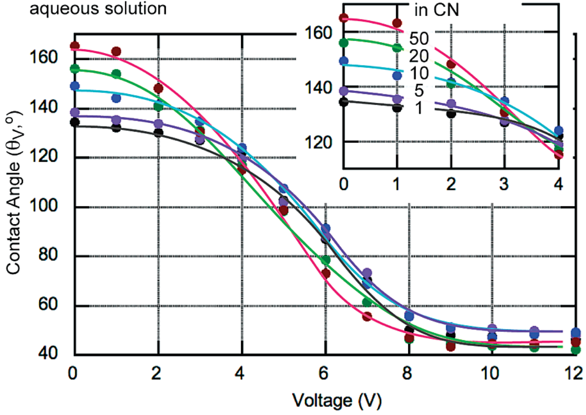


Figure 6. Contact angle vs 1 kHz square wave voltage of DI water droplets, 1 wt % SB solution, and 1 wt % SDS solution in baths of CN and CN-dodecane solution.

The following experimental results were achieved. Without voltage, the Young's angle of DI water in a CN ambient was observed to be 160°, which is similar to the value expected for dodecane. Therefore, CN does not behave like silicone oils, which often exhibit a Young's angle of 180° (oil film between the aqueous droplet and the fluoropolymer). This is generally expected because the surface tension of the CN and that of the fluoropolymer are not closely matched. The interfacial surface tension γ_{AO} was independently measured for CN and water and found to be 40 mN/m, which is less than the 50 mN/m for an alkane/water system. The electrowetting response for DI water and CN is shown in Figure 6a. The water could be reversibly electrowetted down to $\theta_V = 60°$, but this required 25 V and is beyond the onset of electrowetting saturation at 20 V. To reach a smaller contact angle and lower operating voltage, aqueous surfactants were next explored to reduce γ_{AO}. SDS works very well for water/dodecane[18] ($\gamma_{AO} = 5$ mN/m), but its inclusion with CN resulted in an unusually small Young's angle and no electrowetting response (Figure 6a). Similarly, poor results were seen for the surfactant blend Triton-X-15. Next, 1 wt % SB in water was utilized to assess the potential of a phenylated nonpolar group for lowering tension between water and CN. As shown in Figure 6a, slightly lower voltage is required for electrowetting, suggesting a lower value for γ_{AO} (eq 1). Several other surfactant and hydrotropic additives were explored and exhibited difficulties similar to

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Table 1. Interfacial Tension between Different Conductive Liquids and Oils Tested by the Pendant Drop Method[a]

aqueous phase	DI water	1 wt % SB	1 wt % SDS	1 wt % SDS	1 wt % SDS	1 wt % SDS	1 wt % SDS	1 wt % SDS	1 wt % SDS
oil phase	1-CN	1-CN	1-CN	C_{12}	1 wt % C_{12}/ 1-CN	5 wt % C_{12}/ 1-CN	10 wt % C_{12}/ 1-CN	20 wt % C_{12}/ 1-CN	50 wt % C_{12}/ 1-CN
interfacial tension (mN/m)	40.3	32.6	N/A	5.8	9.8	7.5	7.4	7.7	6.9

[a] Abbreviations: 1-CN, 1-chloronaphthalene; SB, sodium benzoate; SDS, sodium dodecyl sulphate; C_{12}, n-dodecane.

Table 2. Refractive Index of 1-CN Mixed with Different Ratios of Dodecane (at 25°C)

oils	1-CN	1 wt % C_{12}/1-CN	5 wt % C_{12}/1-CN	10 wt % C_{12}/1-CN	20 wt % C_{12}/1-CN	50 wt % C_{12}/1-CN
refractive index	1.632	1.628	1.617	1.603	1.575	1.539

those observed for the SDS and SB. To investigate further, γ_{AO} was measured via the pendant drop method for the above-described aqueous/oil combinations (Table 1). Adding 1 wt % SB was measured to reduce γ_{AO} from 40 to 33 mN/m, in agreement with the reduced voltage requirement observed in Figure 6a. Adding 1 wt % SDS resulted in what visually appeared to be a $>10\times$ increase in interfacial surface tension (the denser CN pendant drop sagged less). Such an increase is not physically possible; thus, the density of the oil pendant drop must have been reduced via water uptake and/or the formation of a distinctly new phase. SDS has a very high HLB number of ~40, which makes a water-in-oil emulsion unlikely. At this time, we speculate that the CN uptakes some percentage of water/SDS. This would explain the lack of an electrowetting response for the SDS solution in Figure 6a because water/SDS in the CN phase would give rise to electrical conductivity and neutralize the electrowetting force in the aqueous phase.

Next, alkane oil blending was explored and yielded greatly different experimental results. 1-CN was blended with a small percent of dodecane by using a magnet stirring bar for > 1 h and a 1 wt % SDS aqueous solution retested. The electrowetting results, presented in Figure 6b, show that γ_{AO} was reduced to < 10 mN/m and that $\theta_V = 45°$ can be achieved at < 10 V. This result is not entirely surprising because of the excellent nonpolar match for the dodecyl chains now present in both the water and the oil phases. The exact nature of the interaction is under further investigation; however, the results are repeatable and striking in comparison to previous attempts. Shown in the inset for Figure 6b, Young's angle also varies substantially with dodecane content. It should be noted that, because dodecane is less dense than CN, the measured increase in Young's angle with increasing dodecane content is not an "apparent" change due to change in oil density. Also, as shown in Table 1, γ_{AO} barely changes with > 5 wt % dodecane content. Therefore, the increase in contact angle is clearly due to an oil/fluoropolymer interfacial tension that decreases as dodecane content is increased. Similar electrowetting results were also achieved with tetradecane in place of the dodecane. Furthermore, in place of SDS, 1 wt % of the nonionic surfactant Triton X-100 was tested and exhibited a change in θ_V from 160° to 60° for 10 wt % dodecane in the CN. The frequency dependency of the electrowetting response was also measured. The above-described electrowetting results were relatively unchanged from 50 to 1 kHz but degraded for an ac frequency of < 50 Hz. It is, therefore, likely that the dipole of the CN molecule causes relaxation of the electrowetting response over a time period of approximately tens of milliseconds. Electrical breakdown of CN was removed from consideration from this frequency dependence because dc electrowetting of CN with no surfactants could sustain $\theta_V < 90°$ at 25 V. This further confirms that there is no content in the purified CN that is electrically conductive or that carries a net charge. Lastly, we note that adding alkane content to the CN does reduce refractive index, but only slightly at usable mixtures. As shown in Table 2, pure dodecane is a low-index oil (~1.418 at 25 °C). When CN is mixed with 1, 5, 10, 20, and 50 wt % dodecane, the index of the oil blend decreases gradually from 1.632 to 1.628, 1.617, 1.603, 1.575, and 1.539. However, the 5 and 10 wt % dodecane blends showed robust electrowetting and still have a refractive index greater than 1.6.

In summary, it has been shown herein that electrowetting in a CN/alkane ambient can be performed at low voltage (< 10 V) and with > 100° of contact angle modulation. The reduced values for γ_{AO} reported herein are highly compatible with the arrayed electrowetting optics formats shown in Figure 1, where the small size of individual electrowetting elements offsets some of the undesired effects of reduced γ_{AO} (meniscus sagging, slower switching speed).[12] Further studies, such as temperature dependence and long-term aging, are certainly of interest. However, CN can now be considered as a candidate for some applications requiring highly refractive electrowetting optics.

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