



Published in final edited form as:

*Langmuir*. 2012 January 10; 28(1): 31–36. doi:10.1021/la203729t.

## Influence of Simple Electrolytes on the Orientational Ordering of Thermotropic Liquid Crystals at Aqueous Interfaces

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### Abstract

We report orientational anchoring transitions at aqueous interfaces of a water-immiscible, thermotropic liquid crystal (LC; nematic phase of 4'-pentyl-4-cyanobiphenyl) that are induced by changes in pH of the aqueous solution and the addition of simple electrolytes (NaCl) to the aqueous phase. Whereas measurements of the zeta potential on the aqueous side of the interface of LC-in-water emulsions prepared with 5CB confirm pH-dependent formation of an electrical double layer extending into the aqueous phase, quantification of the orientational ordering of the LC leads to the proposition that an electrical double layer is also formed *on the LC-side of the interface* with an internal electric field that drives the LC anchoring transition. Further support for this conclusion is obtained from measurements of the dependence of LC ordering on pH and ionic strength, as well as a simple model based on the Poisson-Boltzmann equation from which we calculate the contribution of an electrical double layer to the orientational anchoring energy of the LC. Overall, the results presented herein provide new fundamental insights into ionic phenomena at LC-aqueous interfaces, and expand the range of solutes known to cause orientational anchoring transitions at LC-aqueous interfaces beyond previously examined amphiphilic adsorbates.

### Keywords

electrical double layers; oil-water interfaces; liquid crystals; anchoring transitions; emulsions; electrolytes

### Introduction

Ions play a central role in a wide range of interfacial phenomena, including the stability of colloids, formation of emulsions, events involving the fusion of biological membranes, and the charging of electrochemical interfaces.<sup>1</sup> At relatively low concentrations, the qualitative effects of ions often reflect the presence of electrical double layers.<sup>1–4</sup> In contrast, at high concentrations of ions, the effects of short-range ion-hydration interactions are typically dominant and pronounced specific ion phenomena are observed.<sup>4–7</sup> Whereas past studies have reported extensively on ionic phenomena at oil-water interfaces<sup>3, 8–15</sup> and oil-solid interfaces,<sup>3, 16–19</sup> in this paper, we report initial observations of the effects of simple electrolytes on interfaces formed between a thermotropic liquid crystal (LC) and aqueous phases. Because the orientational ordering of the molecules in the LC phase is long-ranged,

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Supporting Information Available. Experimental procedures. Calculation of tilt angles of LCs from measurements of optical retardance. Calculation of the chemical potentials of the ionic species, and details of a model for calculating the contribution of an electrical double layer to the LC anchoring energy. Figures S1, S2, and S3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

the ionic phenomena at the LC-aqueous interface are amplified into bulk ordering transitions within the LC phase that are readily imaged by using polarized light microscopy. The results reported in this paper are significant in that they offer new fundamental insights into the balance of intermolecular forces that determine the ordering of thermotropic LCs at aqueous interfaces, and they provide new guidance to the design of dynamic and responsive LC interfaces such as those that enable reporting of chemical and biological interactions.<sup>20–38</sup> In particular, whereas past studies of LC-aqueous interfaces have reported that a wide range of *amphiphilic* molecules can adsorb at LC-aqueous interfaces to induce anchoring transitions mediated by interactions involving the tails of the amphiphiles,<sup>25–27, 39–42</sup> anchoring transitions in LCs induced by simple electrolytes at aqueous interfaces have not been previously reported.

## Experimental Section

In a typical experiment, a thin film of nematic LC (5CB, Scheme 1) with an approximately flat interface was prepared by hosting the LC in the pores ( $283\mu\text{m} \times 283\mu\text{m}$ ) of a  $20\mu\text{m}$ -thick gold-coated specimen grid (Figure 1a), as detailed elsewhere.<sup>20, 39</sup> Briefly, glass microscope slides were cleaned according to published procedures<sup>39</sup> and coated with octadecyltrichlorosilane (OTS) to anchor the LC in an orientation that was perpendicular (homeotropic) to the LC-glass interface (Figure 1b).<sup>27</sup> Immersion of the supported LC-filled grid under an aqueous phase led to the formation of a stable interface between the aqueous phase and LC. In the experiments reported below, LC interfaces thus obtained were equilibrated against aqueous solutions of sodium chloride (at the indicated concentrations). To quantify the time-dependent orientation of the LC at the aqueous interface, the optical retardance of each LC film was measured using a Berek U-CTB compensator as a function of time. The orientation of the LC at the aqueous interface was calculated from the measured retardance using methods described in Supporting Information. In some of the experiments described below, the LC-fill specimen grid was supported on a gold-coated glass microscope slide on which a monolayer was formed from hexadecanethiol (C16). The gold film was formed by physical vapor deposition at an oblique angle of incidence ( $64^\circ$  measured from normal), which leads to a uniform azimuthal orientation of the LC. As reported previously, the C16 monolayer causes nematic 5CB to assume an orientation that is parallel to the surface.<sup>43</sup> Additional experimental details are presented in Supporting Information (SI).

## Results and Discussion

In our first experiments, we contacted nematic phases of the nitrile-containing mesogen 5CB with aqueous solutions containing 1 M NaCl ( $T=25^\circ\text{C}$ ) at either pH 6 or pH 12.8. Under illumination with white light (and crossed polars), the 5CB in contact with the aqueous solution exhibited bright interference colors (Figure 1a) consistent with a LC film that was anchored parallel to the aqueous interface (so-called planar anchoring), and splayed and bent in the bulk of the LC film to accommodate the hybrid boundary conditions (Figure 1b).<sup>27</sup> Upon replacing the water with 1 M NaCl at pH 12.8, we observed the 5CB to undergo a time-dependent transition in optical appearance to a dark state (Figure 1c), corresponding to homeotropic ordering of the LC at the aqueous interface (Figure 1d). The anchoring transition was reversible, with the LC film adopting a planar alignment when the pH was lowered by the addition of HCl. Measurements of the optical retardance of the LC film were used to calculate the angle of tilt of the director of the LC at the aqueous interface, revealing a continuous anchoring transition (Figure 1e, see SI for additional details). The dynamics of the anchoring transition were observed to vary from sample-to-sample (see below for comments regarding this observation), but all samples ultimately transitioned at pH 12.8 to the homeotropic orientation at the aqueous interface.

The orientation of the LC that was observed after 1 hr at pH 12.8 was found to depend on the concentration of electrolyte added to the aqueous phase (Figure 2). At the lowest ionic strength investigated (the addition of NaOH to achieve the pH of 12.8 generated an ionic strength of 0.06 M), we measured the tilt angle (measured from the surface normal) of the 5CB to be  $56^{\circ} \pm 13^{\circ}$ . An increase in ionic strength from 0.06 M to 0.7 M, achieved by the addition of NaCl, caused a continuous decrease in the tilt angle of the LC to  $0^{\circ}$  (i.e., homeotropic ordering at the aqueous interface). This result indicates that the orientational ordering of the LC at the aqueous interface is strongly influenced by the concentration of salt added to the aqueous phase.

The dependence of the orientational ordering of the LC on ionic strength, as shown in Figure 2, led us to hypothesize that the anchoring transition was due to formation of an electrical double layer on the LC side of the aqueous interface. Nematic 5CB has anisotropic dielectric properties, with a static dielectric constant ( $\epsilon$ ) that is greatest in the direction parallel to the optical axis ( $\epsilon_{\text{para}} = 19.7$  and  $\epsilon_{\text{perp}} = 6.7$ ; see Figure 3a).<sup>44</sup> According to our hypothesis, the formation of an electrical double layer on the LC side of the interface would lead to an electric field in the diffuse part of the double layer that is perpendicular to the interface. Such an electric field would exert a torque to align the LC with its largest dielectric constant parallel to the electric field, thus promoting the homeotropic ordering of the LC (see later discussion of model calculations). To find additional support for this hypothesis, we measured both the zeta potential of LC-in-water emulsions and the tilt angle of films of nematic 5CB, both as a function of pH (Figure 3b and c).

To measure the zeta potential on the aqueous side of the interface, LC-in-water emulsions (prepared by sonication) were added to aqueous solutions of either 100 mM or 1 M NaCl at various values of pH. Zeta potentials of LC droplets measured in solutions of 100 mM NaCl (squares in Figure 3b) confirmed that the interface of the LC acquired an increasingly negative potential at the aqueous shear-plane as a function of increasing pH. This result is consistent with past studies of the zeta potential of the aqueous side of various oil-in-water emulsions.<sup>11-14</sup> Although a complete understanding of the surface charging process remains to be fully established, several past studies suggest that hydroxide ions adsorb to oil-water interfaces with increasing pH<sup>10-12, 14</sup> while others propose an alternative charge transfer mechanism involving hydrogen bonding.<sup>45</sup> At high concentrations of NaCl (diamonds in Figure 3b correspond to 1 M NaCl), we measured the zeta potential to be close to zero, a result we attributed to screening of the charge of the interface within the hydrodynamic shear plane.<sup>12, 14, 46-48</sup> In light of the result obtained at high ionic strength, we interpret the plateau in the zeta potential measured in solutions containing 0.1 M NaCl at pH values between 10 and 12 to result from the increase in ionic strength caused by the addition of the base (NaOH) to achieve the desired pH. We emphasize this point because we do not interpret the zeta potential measurements at high ionic strength to indicate the absence of charging of the interface (a conclusion that is supported by our observations reported below of the orientational ordering of the LC).

Figure 3c shows the tilt angle of nematic 5CB at the aqueous interface, plotted as a function of pH in 1 M NaCl (variation in ionic strength is small: 1–1.06 M). Below pH 9, the LC exhibits near-planar anchoring. Above pH 9, however, the tilt angle decreases *continuously* with increasing pH to a value of  $0^{\circ}$  (i.e., a homeotropic orientation) at pH~12.8. This observation supports our proposition that the charging of the LC-aqueous interface not only creates an electrical double layer on the aqueous side of the oil-water interface (as evidenced by the zeta potential measurements at low ionic strength), but that it also generates a double layer on the LC-side of the interface that is capable of exerting sufficient torque on the interfacial region of the LC film to induce an ordering transition that propagates far from the interface via the long range ordering of the LC. The result also reinforces our conclusion

that the absence of a measurable zeta potential in 1 M NaCl does not indicate the absence of charging of the interface. The consequences of the charging of the interface are evidenced by the LC anchoring transition.

The simplest description of the equilibrium orientation of a confined LC considers elastic contributions to the free energy of the bulk of the LC (due to bend, splay or twist of the LC) as well as an orientation-dependent free energy of the interface of the LC ( $\gamma_{\text{aniso}}$ ).<sup>49, 50</sup> The latter contribution is typically defined in terms of the anchoring energy of the interface ( $W$ ) as well as the deviation of the orientation of the director ( $\theta$ ) from the so-called easy axis (the orientation corresponding to the lowest interfacial free energy, characterized here by the angle  $\varphi_e$ ) of the LC:

$$\gamma_{\text{aniso}} = \frac{1}{2} W \sin^2(\theta - \varphi_e) \quad (1)$$

To obtain further insight into the origins of the anchoring transitions described above, we performed experiments to determine if they were the result of a change in the easy axis of the LC ( $\varphi_e$ ) or the magnitude of the anchoring energy at the LC-aqueous interface ( $W$ ). Here we note that prior to the salt/pH-induced anchoring transition in the LC, in the experiments described above (see Figure 1b), the LC was strained by the initial hybrid boundary conditions. For this situation, a decrease in the anchoring strength  $W$  at the aqueous-LC interface is sufficient to permit the transition seen in Figure 1 (the orientation of the easy axis does not need to change). Such an anchoring transition is driven by the OTS-treated surface via the elasticity of the LC. To determine the origin of the anchoring transition observed in our experiments, we quantified the orientation of the LC as a function of pH, when the LC film was supported on a gold film treated with hexadecanethiol (C16) (Figure 4a-d). In this situation, the C16 monolayer specifies a preferred azimuthal direction (i.e. parallel to the direction of gold deposition<sup>51</sup>), and the LC at the aqueous interface assumes the same orientation. Since the initial state of the LC is not strained, an anchoring transition to the homeotropic orientation at the aqueous interface would necessarily induce strain in the LC (and cannot, therefore, be driven by a decrease in  $W$ ). Inspection of Figure 4c and 4d reveals that the LC film, when supported on the C16 surface, does indeed undergo an anchoring transition when the pH of the aqueous solution was increased to a pH of 12.8 in the presence of 1 M NaCl. Quantification of the optical retardance of the LC film and calculation of the tilt of the LC at the aqueous interface (Figure 4e) revealed that the anchoring transition was continuous, ending with the homeotropic orientation at the LC-aqueous interface. This result indicates that the anchoring transition induced by the change of pH must be caused by a change in the easy axis of the LC (not a decrease in  $W$ ). Specifically, we conclude that the easy axis of the LC at the LC-aqueous interface rotates to become perpendicular to the interface (tilt angle of  $0^\circ$ ) at high pH, consistent, as shown below, with the calculated effects of an electrical double layer formed on the LC side of the interface.

We calculated the order of magnitude of the contribution of an electrical double layer formed on the LC side of the LC-aqueous interface to the anchoring energy of the LC by solving the linearized Poisson-Boltzmann (PB) equation (we considered the effects of small potentials since linearization requires is the potential to be  $< 25.4$  mV).<sup>1</sup> The description we adopt builds, in part, from prior studies of electrical double layers at LC-solid interfaces.<sup>52-55</sup> The equilibrium partitioning of the electrolyte from the aqueous phase into the LC phase was determined by equating the chemical potentials of the ionic species in the aqueous and LC phases (see SI for additional details), where the chemical potential was evaluated as

$$\mu_{\pm}^i = k_B T \ln(c_{salt}^i) + \frac{e^2}{2\epsilon^i a_{\pm}} \pm e\psi^i \quad (2)$$

where  $a_{\pm}$  is the radius of the cation and anion, respectively. The second term in Eq (2) describes the Born (self) energy of the ions in each phase, and the third term accounts for the electrical potential of the bulk phase. In our evaluation of Eq (2), we approximated the LC as an isotropic solvent with an effective dielectric constant of  $\epsilon_{eff} = (2 \cdot \epsilon_{perp} + \epsilon_{para})/3$ .<sup>56</sup> For a bulk aqueous phase containing 1 M NaCl, we calculated the concentration of  $\text{Na}^+$  and  $\text{Cl}^-$  ions within the LC to be 3.5  $\mu\text{M}$ . Next we solved the linearized PB equation (see SI) to calculate the contribution of the internal electric field of the double layer to the anchoring energy as:

$$W = \pi \epsilon_0 \psi_0^2 (\epsilon_{para} \kappa_{para} - \epsilon_{perp} \kappa_{perp}) \quad (3)$$

where  $\epsilon_0$  is the permittivity of free space,  $\psi_0$  is the electrical potential at the aqueous-LC interface, and  $\kappa_{para}$  and  $\kappa_{perp}$  are the Debye lengths calculated using  $\epsilon_{para}$  and  $\epsilon_{perp}$ , respectively. For an assumed value of  $\psi_0$  of  $-20$  mV, we calculated the contribution of the internal electric field of the double layer to the anchoring energy of the LC to be 1.1  $\mu\text{J}/\text{m}^2$ . This value is comparable to the lower end of past estimates of anchoring energies of LCs at the LC-aqueous interfaces ( $1-10 \mu\text{J}/\text{m}^2$ ),<sup>38</sup> and thus is consistent with our observation that the effects of the electrical double layer are dominant at high pH (where the interfacial potential is large compared to 20mV) but not at low pH (where the interfacial potential is small compared to 20mV) (Figure 3b). We note that we also measured the NaCl concentration in the LC by using inductively coupled plasma emission spectroscopy (ICP-ES, experimental details in SI) to be 409  $\mu\text{M}$ . The fraction of this salt that dissociates into ions in the LC was estimated from measurements of ionic conductivity reported by Shah et al.<sup>55</sup> Those measurements lead to an estimated dissociation constant of  $K \approx 3.4 \cdot 10^{-9}$  M, and thus concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$  in the LC in our experiments of  $1.2 \pm 0.2 \mu\text{M}$ . These values are in good agreement with the ion concentrations calculated above (3.5  $\mu\text{M}$ ) based on the Born energies of the ions. Our simple calculation thus provides support for our hypothesis that an electrical double layer in the LC phase causes the orientation of the easy axis of the LC to rotate to the interface normal. We also note that Eq. (3) predicts that the effects of the double layer will be pronounced at high ionic strength ( $\kappa \sim \sqrt{c_{io}}$ , where  $c_{io}$  is the concentration of the ionic species  $i$  in the bulk), a prediction that is also consistent with experimental observations (Figure 2). In future studies, we will refine the above-described model to incorporate the anisotropic dielectric properties of the LC in the evaluation of the chemical potential of the ions in the LC as well as utilize the non-linearized form of the PB equation.

## Conclusions

In summary, the results reported in this Letter provide support for the hypothesis that an electrical double layer is formed on the LC side of an LC-aqueous interface via the partitioning of ions from the aqueous phase into the LC (a polar oil). We infer the existence of the double layer on the LC-side of the interface via the orientational ordering of the LC. The pH-dependence of the ordering suggests that the origins of the double layer in the LC are similar to those which control the zeta-potential measured on the aqueous side of the interface (e.g., adsorption of  $\text{OH}^-$  ions).<sup>10-12, 14</sup> Our conclusions are also supported by order-of-magnitude estimates of the electric field strength in the vicinity of the interface, and

the influence of that field on the orientation of the easy axis of the LC at the aqueous interface. Although the diffusion of simple ions across a 20  $\mu\text{m}$ -thick film of LC occurs on time-scales of seconds, we observe the LC anchoring transitions triggered by a change of pH/salt concentration to occur over minutes to hours. This result suggests that substantial barriers may exist to the transfer of ions from the aqueous phase into the LC, and that the dynamics of the anchoring transitions may be influenced by energetic barriers, interfacial viscosity, interfacial backflows, and variations in impurity ion and water concentrations in the LC.<sup>55</sup> Additional studies will be performed to investigate these dynamics, including the effects of specific ion types.

The observation that simple electrolytes can trigger anchoring transitions at aqueous-LC interfaces is significant in light of previous reports which have examined the ordering of LCs at interfaces decorated with proteins, ionic surfactants, polyelectrolytes and DNA at aqueous-LC interfaces.<sup>25–27, 39–42</sup> The results in this paper suggest that modulation of the charge of the LC interfaces caused by the presence of these species, and the accompanying changes in electrical double layers formed at these interfaces, are likely an important part of the overall balance of intermolecular interactions governing the ordering of LC at these interfaces (in addition to the widely recognized role of the interactions of the aliphatic tails of amphiphiles with LCs).<sup>27</sup> We also comment that understanding ionic phenomena in non-aqueous phases is relevant in a number of other contexts including recent studies of polyelectrolyte multilayers<sup>35–37</sup> and the electrophoresis of particles in oils.<sup>16, 57, 58</sup>

Many past studies have reported measurements of zeta potentials of oil-in-water emulsions as a means to characterize interfacial charge.<sup>10–14, 46</sup> Those measurements, however, only probe the aqueous side of the oil-water interfaces. The ordering of the LC provides information regarding the presence of internal electric fields on the “oil”-side of the interface. In addition, we note that the use of zeta potential to infer the charged state of an interface at high ionic strength can also be misleading (as evidenced in Figure 3b for the data at 1 M NaCl), whereas we conclude that the orientational ordering of the LC indicates the charging of the interface at high ionic strengths. We also note that identification of the role of the electrical double layer in ordering LCs at aqueous interfaces, as reported herein, provides new guidance to the design of interfaces than can report chemical and biological interactions.<sup>20–38</sup>

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

## Acknowledgments

This work was supported by the NSF (DMR-0520527, DMR-0602570, CBET 075921), the ARO (W911NF-10-1-0181) and NIH (CA108467 and CA105730, and AI092004).

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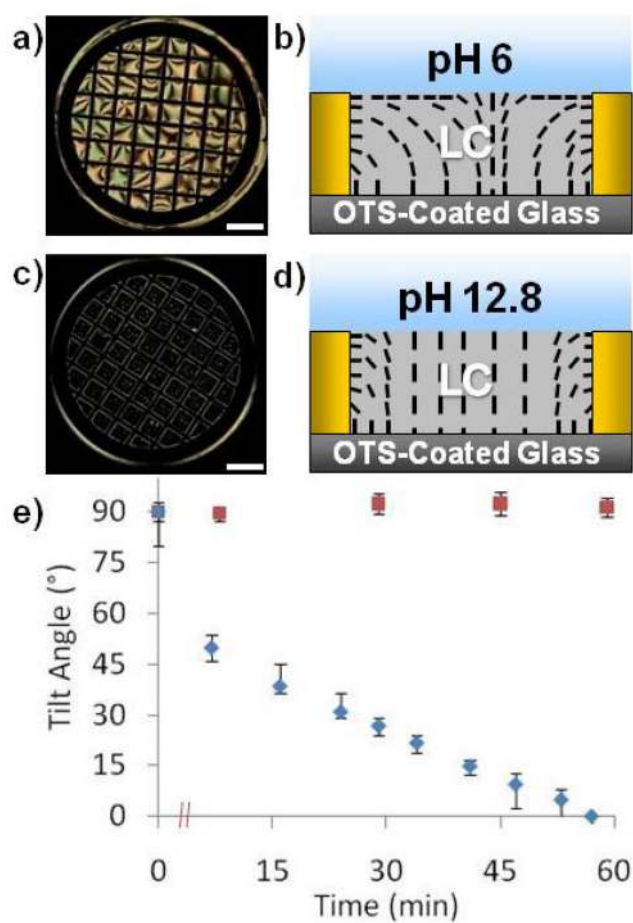
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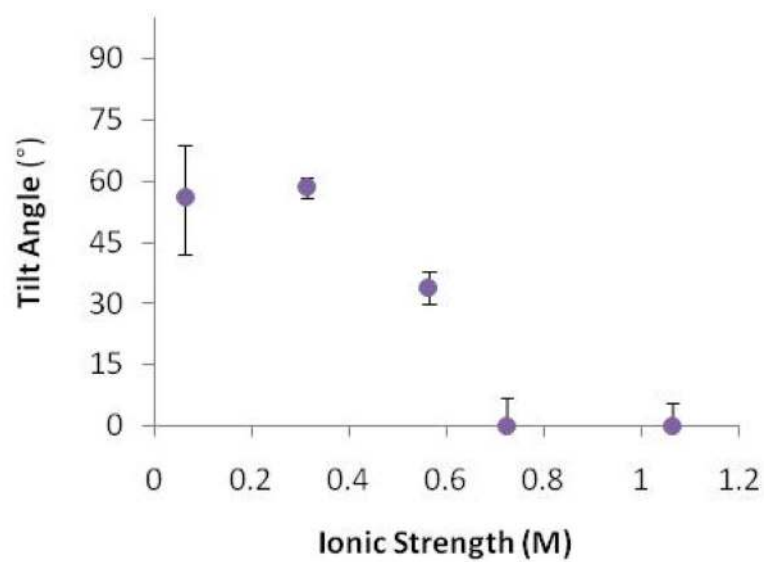
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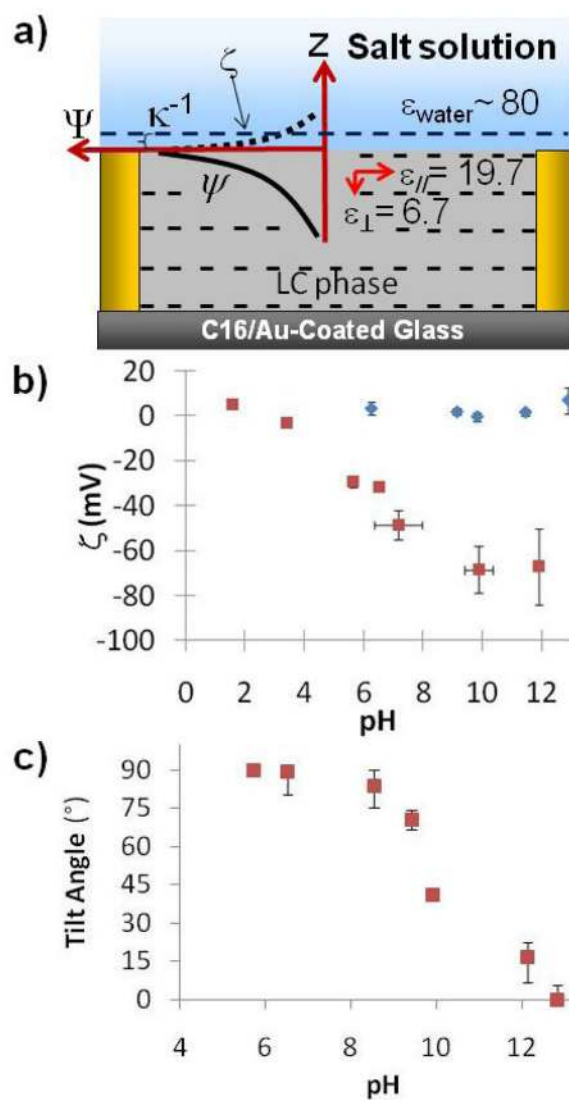


**Figure 1.**

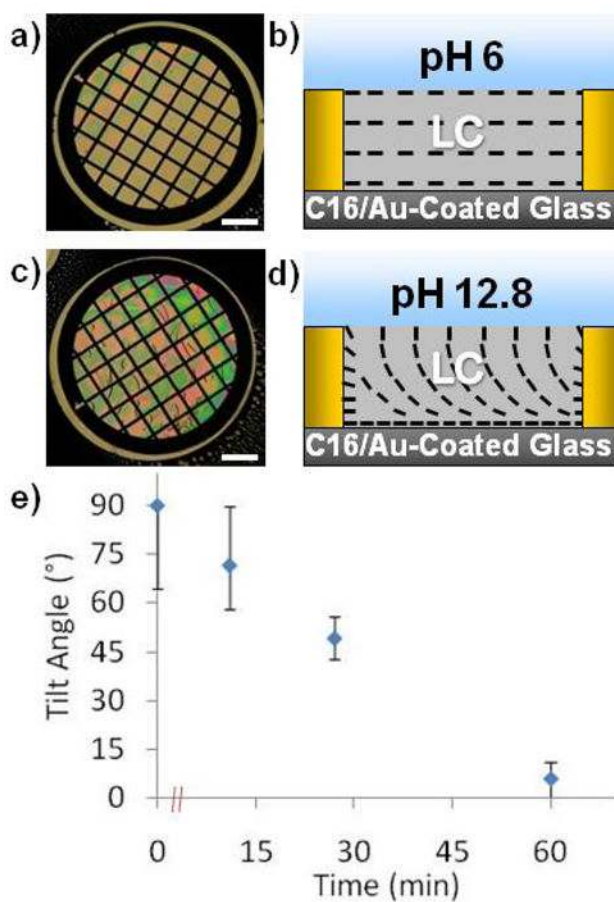
(a–d) Polarized micrographs (PMs, crossed polars) and schematic illustrations of nematic films of 5CB in contact with aqueous 1 M NaCl at (a, b) pH 6 or (c, d) pH 12.8 for one hour. In a–d, the 5CB is supported on an OTS-treated glass surface. Scale bars ~ 500  $\mu\text{m}$ . (e) The tilt angle of the director of the LC at the LC-aqueous interface (measured from the surface normal) plotted against the time of contact of the LC film with the aqueous solution of 1 M NaCl at either pH 6 (squares) or pH 12.8 (diamonds).



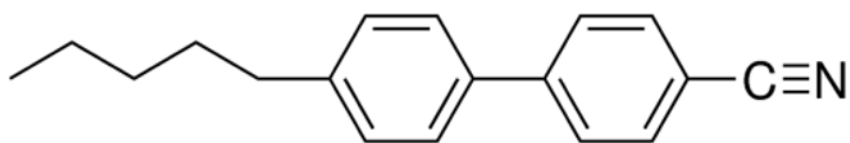
**Figure 2.** The tilt angle of nematic 5CB (angle from surface normal) after one hour of contact with an aqueous solution of NaCl (at pH 12.8), plotted as a function of the ionic strength of the aqueous solution.



**Figure 3.** (a) Schematic illustration of electrical double layers formed on both sides of an LC-aqueous interface. (b) Zeta potential ( $\zeta$ ) of 5CB-in-water emulsions, plotted as a function of pH in either 100 mM NaCl (squares) or 1 M NaCl (diamonds). (c) Tilt angle (angle from surface normal) of nematic 5CB following contact with aqueous 1 M NaCl, plotted as a function of pH.



**Figure 4.** (a–d) Optical micrographs (crossed polars) and schematic illustrations of the orientations of nematic 5CB (determined from the PMs) in contact with aqueous 1 M NaCl at either (a, b) pH 6 or (c, d) pH 12.8. In a–d, the 5CB is supported on a monolayer of hexadecanethiol formed on an obliquely deposited gold film. Scale bars  $\sim 500 \mu\text{m}$ . (e) The tilt angle of the director at the LC-aqueous interface plotted as a function of the time of immersion in aqueous 1 M NaCl at pH 12.8.



**Scheme 1.**  
Molecular structure of 5CB.