

Nematic Liquid Crystal Reorientation at Aqueous-LC Interface for Monitoring Biochemical Interactions by Specific Ions Effects

FengJie He¹, HuiLong Liu¹, XingLiang Xiong¹ and Shengjie Zhai^{2,*}

Abstract: In this paper, we attempt to show that contacting aqueous solution made of either kosmotropic or chaotropic ions within a certain concentration range can trigger concentration-dependent transitions of the nematic liquid crystal (LC) at the aqueous-LC interface, going from planar to homeotropic. The effects of different ions (both anions and cations) with different concentrations on the LC orientation have thus been investigated. Nearly every ion, irrespective of being chaotrope or kosmotrope, is found to have its critical concentration, and upon reaching this concentration, homeotropic alignment in LC can be induced. Most chaotropic ions, however, induce homeotropic alignment in LC with a much lower critical concentration than their kosmotropic counterparts. Furthermore, the LC ordering transitions are related to the ion types, concentrations, and pH values, as revealed by the polarized light micrographs of LC thin films in contact with various ionic solutions. The homeotropic ordering of LC at the aqueous-LC interfaces upon the addition of kosmotropic ions is attributed to an internal electric field that results from the concentration difference between the interface and the bulk solutions. As a sharp contrast, this internal electric field, together with the ion-induced dipole interaction between the nitrile group of 4-cyano-4'-pentylbiphenyl (5CB) and the chaotropic ions, determines the orientations of LC upon the addition of chaotropic ions. Understanding the underlying mechanism of the ionic phenomena at aqueous-LC interface is of great importance for the design of aqueous-LC interface for detecting interactions involving ions, as the case in biosensing and many important applications.

Keywords: Ion Effect, Liquid Crystal, Reorientation, Electric Double Layer, Aqueous Interface.

1. Introduction

The orientation behavior of nematic liquid crystals (LCs) molecules is extremely sensitive to physical or chemical properties of a bounding interface. The changes in structure and constitutions of the interfaces caused by molecular binding events can trigger orientational ordering transitions in LCs, which can be rapidly propagated as far as 100 μm into bulk LCs. Such transitions result in visible optical signal transduction, as observed by polarized microscopy (A dark image indicates homeotropic alignment in LCs). With the inherent optical anisotropy of LC molecules and the abovementioned properties, the LC material can be an ideal stimuli-responsive element in biosensing applications^[1-3]. Therefore, controlling the orientation behavior of LCs at interfaces in the presence or absence of molecular binding events and understanding their underlying molecular-levels mechanisms are crucial issues in LC-based biosensors. Abbott and other groups have explored a series of chemically functionalized surfaces to induce the homeotropic orientation in LCs supported on these surfaces through interactions between LCs molecules and the chemical functional groups coated on the interfaces. These interactions include hydrogen binding, electrical double layer, and metal ion-ligand coordination^[1,4-9]. Furthermore, interactions between analytes

¹Laboratory of Bioengineering, Chongqing Medical University, China

²Mechanical Engineering Department, University of Nevada, Las Vegas, USA

*Corresponding Author: Shengjie Zhai. Email: Shengjie.Zhai@unlv.edu.

and the chemical functional groups at the interfaces could trigger the orientation transition of LC film from homeotropic to planar. Based on these strategies, a variety of label-free LC-based biosensors have been applied in the detection of proteins, viruses, toxic agents, and metal ions^[7–13].

The abovementioned orientation transitions of LCs are predominantly based on the solid-LC interface. However, the particular interest in interface has recently shifted to the aqueous-LC interface as it has several unique characteristics that are absent in solid-LC interface. First, the aqueous-LC interface is deformable and soft. Second, the mobility of molecules at the aqueous-LC interface is substantially greater than that at the solid-LC interface, thereby allowing rapid and large-scale lateral molecules rearrangement. Third, the LC-aqueous interface permits investigations of the dynamics of molecular lateral organization, and amphiphile desorption and adsorption^[14]. The lipid-laden aqueous-LC interface analogous to cell membrane facilitates imaging and mimics the molecular reorganization and biochemical reactions occurring on the cell membrane. In the past decades, several strategies based on the LC reorientation at the aqueous-LC interfaces have succeeded in the detection and analysis of specific protein binding events, enzyme-catalyzed reaction and DNA hybridization^[15–21].

The biosensing systems based on aqueous-LC interface generally consist of the aqueous phase, aqueous-LC interface and the thin film of bulk LCs ($\sim 20 \mu\text{m}$).³ The aqueous phase provides a biochemical reaction environment, and the aqueous-LC interface laden with surfactant or phospholipid serves as alignment agent to induce homeotropic orientations in LCs. Subsequently, the coverage or structure of surfactant at the aqueous-LC interface can be modified upon target binding and diffusion from aqueous phase onto the aqueous-LC interface. Then the orientation transition of bulk LC film is triggered. In most cases, various electrolytes are added into the aqueous phase to promote the biochemical reactions, such as DNA hybridization and enzyme-catalyzed reaction^[16,17]. The ions, particularly the anions, can significantly affect the properties of the aqueous interface. According to specific ion effects (also called Hofmeister effects), the ions are classified as kosmotrope and chaotrope. Kosmotropic ions are generally sulfate, chloride and acetate. These are strongly hydrated and could be repelled from the aqueous interface. Chaotropic ions are specifically thiocyanate, perchlorate and potassium. These are weakly hydrated and could accumulate at the aqueous interface^[22–26]. Consequently, it is necessary to ascertain the effect of ions on the aqueous-LC interface for the extreme response of LCs to the changes of the interfacial properties.

Although previous studies have extensively explored the specific ion effects on air-water interface, oil-water interface and oil-solid interface^[27–32], few experiments or theories showed the influence of the ionic phenomena on the orientation of LCs at the aqueous-LC interface. Abbott and coworkers have found that changes in pH and the addition of simple electrolytes (1 M NaCl) to the aqueous-LC interface caused the orientational ordering transitions in LC films. Also, they concluded that a homeotropic electric double layer forming on the LC-side of the interface triggered the 5CB orientation transition^[33]. They further investigated the influence of specific anions on the orientational ordering of LCs at aqueous interfaces. They reported that the addition of chaotropic anions to aqueous-LC interfaces triggered 5CB ordering transitions from planar to homeotropic because of the anion-specific interactions with the nitrile group of 5CB and the change in the easy axis of the 5CB.³⁷ Although the abovementioned studies investigated the effects of changes in pH and anions at high concentrations on the ordering transition of 5CB, respectively, several aspects of specific ions effects require further exploration, as follows: (i) the effects of several factors (i.e., the ion types, the ion concentration, the equilibrium time) on LCs reorientation at the aqueous-LC

interface; and (ii) the underlying molecular mechanisms of the specific effects of ions and pH on the LCs ordering transition. We emphasize that understanding the ionic phenomena occurring at aqueous-LC interfaces are essential for guiding the detection of chemical and biological molecules binding events.

MATERIALS AND METHODS

Materials

n, n-Dimethyl-n-octadecyl-3-amino-propyltrimethoxysilyl chloride (DMOAP) was purchased from Sigma Aldrich (St. Louis, USA). The thermotropic LC, 4-cyano-4'-pentylbiphenyl (5CB) was provided by Huajing Scientific and Technological Development Co., Ltd. (Hebei, China). Copper grids (100-mesh, 20 μm thickness) were obtained from Zhongjingkeyi Technology Co., Ltd (Beijing, China). Microscope glass slides were purchased from Xinhua Laboratory Glassware Company (Haimen, China). All reagents used in this study were analytical grade and all aqueous solutions were prepared with ultrapure water.

Treatment of Glass slides with DMOAP

First, the glass slides were cut into square measuring 2 cm \times 2 cm and immersed in freshly prepared piranha solution (98% H_2SO_4 and 30% aqueous H_2O_2 3:1 v/v) at approximately 80 $^\circ\text{C}$ for 1 h. Warning: piranha reacts strongly with organic compounds and should be handled with extreme caution; do not store in a closed container. Then, the slides were rinsed with deionized water (18.2M Ω) and ethanol and dried under a stream of ultrapure nitrogen (N_2) followed by heating to 110 $^\circ\text{C}$ for about 3 h prior to DMOAP deposition. Subsequently, the clean glass slides were immersed into an aqueous solution containing 0.1% (v/v) of DMOAP for 5 min. Then, the DMOAP-coated slides were rinsed with copious amounts of ultrapure water and dried under a stream of N_2 . Finally, these slides were heated at 110 $^\circ\text{C}$ for 1 h. The water contact angle of the DMOAP-treated surface measured by a contact angle goniometer was greater than 95 $^\circ$, which was sufficient to trigger strong homeotropic anchoring.

Preparation of LC Cells

The clean copper grid was placed onto the surface of DMOAP-deposited glass. Then, the pores of the grid were filled with 5CB by pipetting $\sim 0.3 \mu\text{l}$ into the grid. The 5CB in the grid was heated into its isotropic transition temperature and cooled to room temperature. This led to the formation of an approximately 20 μm -thick LC layer of. Subsequently, 30 μl aqueous salt solution was added on top of the 5CB-filled grid to contain the LC layer, thereby forming a stable interface between the aqueous phase and 5CB. The aqueous salt solutions used in the experiments were described in the Supporting Information(SI) (see Table S1). Meanwhile, each ion solution was diluted into a series of gradient concentrations.

Polarized light microscope measurements of LC anchoring

The optical appearance of 5CB within each copper grid was determined by using plane-polarized light in transmission mode on a XP-201POL polarized light microscope (Shanghai Changfang Optical instrument Co., Ltd.). All images were captured by a Power Shot A640 Canon digital camera mounted on the microscope. The effective average birefringence in the LC films of thickness 20 μm was determined by comparing the colors of the images with those on a Michel-Levy chart (see Figure S1). Based on the obtained birefringence, we were able to calculate the tilt angle of the LC films at the aqueous-LC interface from the following equation:

$$\Delta n_e \approx \frac{1}{d} \int_0^d \left(\frac{n_0 n_e}{\sqrt{n_0^2 \sin^2 \left(\frac{z}{d} (\theta - \theta_s) + \theta_s \right) + n_e^2 \cos^2 \left(\frac{z}{d} (\theta - \theta_s) + \theta_s \right)}} - n_0 \right) dz$$

where Δn_e is the effective average birefringence, n_e is the extraordinary index of refraction for 5CB parallel to the director, n_0 is the ordinary index of refraction for 5CB perpendicular to the director, and d is the thickness of the 5CB films. θ_s is the tilt angle of the LC director at the DMOAP-coated solid interface and is assumed to always be equal to 0° (homeotropic orientation).

RESULTS AND DISCUSSION

Abbott’s previous studies have indicated that contacting the 5CB with aqueous solutions of

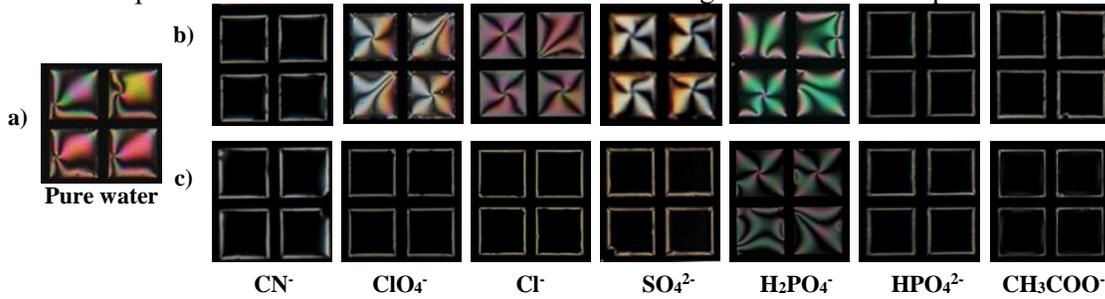


Figure 1. Polarized light microscopy images of 5CB after contacting with pure water (a), 25 mM (b), or 0.5 M (c) aqueous solutions of different ions for 5 min.

chaotropic ions at high concentrations (~2–8 M) induced homeotropic orientations of 5CB at aqueous-LC interface, whereas contacting with aqueous solutions of kosmotropic ions could not change the 5CB orientation from that observed with deionized water.³⁷ Therefore, we first explored the influence of the ion types on the ordering of the 5CB by contacting aqueous solutions of different anions (the cation is sodium ion), which involved both chaotropic and kosmotropic anions. All the anions added into the aqueous phase were chosen from the Hofmeister series (Table S1). The ion types affected the orientation of the nematic 5CB, in agreement with Abbott’s studies (Figure 1b). Some kosmotropic anions with relatively high concentrations (~0.5 M) can also cause homeotropic ordering in 5CB at the aqueous-LC interface (Figure 1c), which is not consistent with results of previous studies. Thus, we hypothesize that other factors, including the concentration of the ion solutions, the pH value, and the equilibrium time upon addition of ion solutions, may also contribute to the reorientation of the LC films.

To investigate the influence of the concentration of ionic aqueous solutions on the LC alignment, the 5CB films were placed in contact with each salt aqueous solution with a series of concentrations, separately. Sodium thiocyanate (NaSCN) and sodium thiocyanate (Na₂SO₄) were chosen from opposite ends of the anion Hofmeister series as representative examples for chaotropic and kosmotropic anions, respectively. The occurrence of planar-homeotropic orientation transitions of 5CB films increased with increasing concentration of aqueous solutions of both NaSCN and Na₂SO₄ (Figure 2). However, several differences between SCN⁻ (chaotropic ion) and SO₄²⁻ (kosmotropic ion) regarding the detail influence of ions on the orientation transitions of 5CB films are observed. First, the minimum concentration of SCN⁻ (25 mM), which caused a planar-homeotropic orientation transition of 5CB, is much lower than that of SO₄²⁻ (0.1 M). Second, at the same concentration of ions (beyond the minimum concentration), the time to reorient to a homeotropic alignment is less than 40 s for SCN⁻, whereas this is about several minutes for SO₄²⁻.

Moreover, when the concentrations of the ion solution are lower than its minimum concentration, the 5CB films still remain planar orientations similar to the result of pure water. Thus, we defined the minimum concentration that can initially induce a planar-homeotropic orientation transition of LCs as critical concentration. Coupled with the results of other anions solution with pH values between 6 and 7.5 (avoiding the influence of pH) studied in this work, we conclude that chaotropic anions do induce 5CB homeotropic orientations. This finding is consistent with those of previous studies. Kosmotropic anions also caused homeotropic orientations in 5CB. Both orientation transitions were concentration-dependent. In addition, the results of cations (anion is chloride ion) were similar to those of anions, but cations have less effect on the LC orientation compared with anions (see Figure S2).

In particular, previous studies have demonstrated that ions were also classified as kosmotropes and chaotropes based on the values of their Jones-Dole viscosity B coefficients (Table S1). Ions with negative B coefficients are chaotropes, which have generally large monovalent ions of low charge

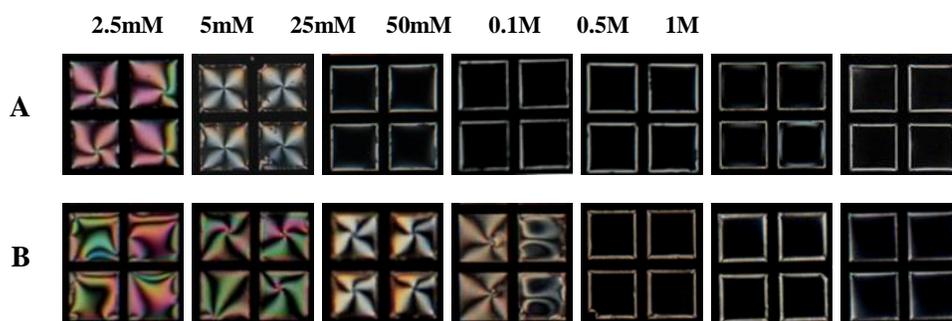


Figure 2. LC response at varying ionic concentrations: Polarized light microscopy images of 5CB films in contact with aqueous solutions of NaSCN(A), or Na₂SO₄ (B) for ~5min.

density. They are weakly hydrated because chaotropic ion-water interactions are weaker than water-water interactions in solution. Ions with positive B coefficients are kosmotropes, usually small ions with high charge density, they are strongly hydrated because kosmotropic ion-water interactions are stronger than water-water interactions in solution^[26]. Chaotropic ions could be adsorbed into the water-oil interface, whereas kosmotropic anions were repelled from the interface^[33]. Our results on the influence of ions on the orientation transition in the 5CB films correlate directly with these specific properties and phenomena. Therefore, this close correlation with ionic properties and past theories led to the following hypothesis: the LC reorientation reported in this work is mainly triggered by an internal electric field formed by molecular interactions at the aqueous-LC interface.

Chaotropic ions mostly accumulate at the aqueous-LC interface to decrease the interfacial tension upon weak hydration and in the presence of dispersion force caused by a ion-induced dipole interaction between chaotropes and the nitrile group of 5CB. From surface energy viewpoint, the concentration of chaotropic ions at the interface is higher than in the bulk solution, thereby decreasing the surface energy, in terms of the accumulation of chaotropic ions at the LC-aqueous interface. Subsequently, the positive excess concentrations of chaotropes at the interface bring about charge transfer. Later, an electrical double layer perpendicular to the interface is formed as a result of the charge balance of solution. Ultimately, the electric field of the electrical double layer will trigger the ordering transitions of the 5CB molecules ($\epsilon_{\parallel}=19.7$, $\epsilon_{\perp}=6.4$) at the aqueous interfaces (see schematic in Figure 3a). Additionally, the LC orientation transitions depend on the concentrations of chaotropic ions at the aqueous phase. We interpreted that the intensity of internal

electric field and dispersion forces increased as the accumulation of ions at the interface increased with the concentration of ions. Eventually, increasing electric field intensity and dispersion forces exert a torque to induce the homeotropic orientation of the 5CB with its largest dielectric constant parallel to the electric field. Specifically, the concentration of ions sufficient for the LC homeotropic ordering is the *critical concentration*.

In contrast, kosmotropic ions are generally small ions with strong hydration and high charge density. Thus, the concentration of kosmotropic ions in bulk solution is higher than that at the aqueous-LC interface due to interactions between kosmotropic ions and water molecules in solution. The positive excess concentration of ions in bulk solution also results in a perpendicular electrical double layer, which ultimately triggers the orientational anchoring transitions of 5CB at aqueous interface. Similar to the behavior of chaotropic ions, the electric field intensity also depends on the concentration of kosmotropic ions; the difference is in the formation mechanism of the electrical double layer (see schematic in Figure 3b). Furthermore, the results described above reveal that the ion solutions (either chaotropes or kosmotropes) with relatively low concentrations (i.e., lower than its *critical concentration*), analogous to the behavior of pure water, failed to induce homeotropic ordering of 5CB at the aqueous-LC interface because of too-weak electrical field intensity (see schematic in Figure S4). The concentration of kosmotropic ions in the interface-LC is expected to be so low that the dipole interaction between kosmotropic ions and the nitrile group of 5CB does not occur. Hence, the critical concentration of kosmotropic ions is universally higher than that of the chaotropic ions, i.e., the chaotropic ions induce the homeotropic orientation of 5CB better than kosmotropic ions. Nevertheless, every chaotropic and kosmotropic ion has distinct ion size, charge, ionic polarizability, as well as ionic hydration. Under the same conditions, different chaotropic or kosmotropic ion solutions can generate different electric field strengths and dispersion forces so that the *critical concentration* varies in association with the rank of the Hofmeister series.

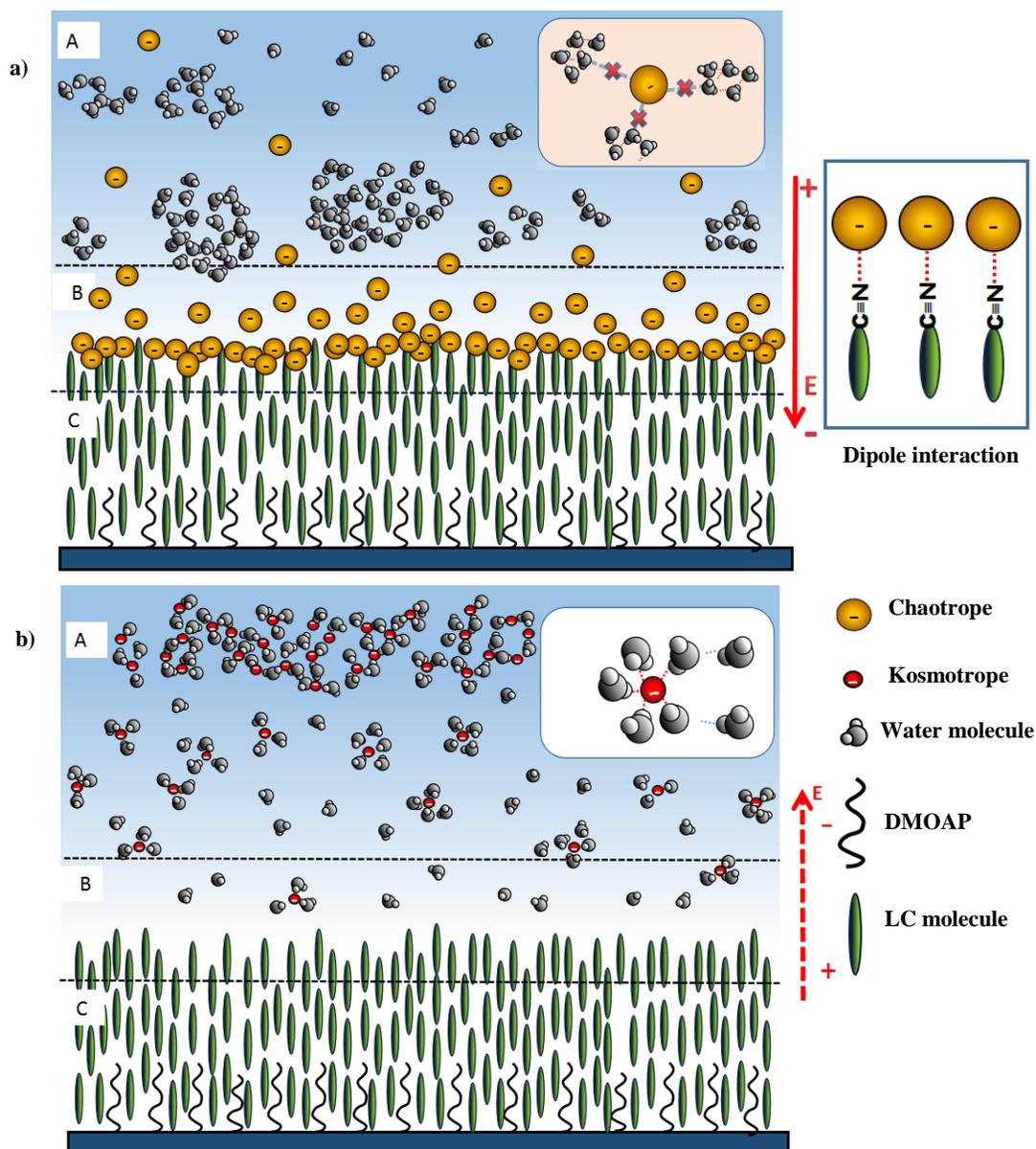


Figure 3. Schematic illustration of the mechanism for a LC reorientation in contact with a) high concentration of aqueous chaotropic ions, b) high concentration of aqueous kosmotropic ions. The system is divided into three layers: the bulk solution phase (A), the aqueous-LC interface (B), the bulk LC phase (C).

To obtain further insight into the mechanism of the LC ordering transitions in contact with ion solutions, we investigated the dynamics of the ordering transitions of 5CB films. Figure 4 illustrated a series of time-dependence images that showed the dynamics of the LC alignment after contacting with 2 M NaClO₄, 25 mM NaClO₄, 2 M NaCl, and 0.1 M NaCl, respectively. Inspection of these images reveals that the 5CB films undergo a rapid orientation transition to a homeotropic ordering within less than 40 s upon addition of a much higher concentration (~2 M) of salt solutions, whereas they undergo a relatively slow ordering transition to a homeotropic orientation upon contact with low concentration (near its *critical concentration*) of salt solutions (generally over 5 min). We also calculated the tilt angles of the LC films at the aqueous-LC interface (Figure 4B). All observations are in perfect agreement with our proposed mechanism that high concentrations of ions in solution

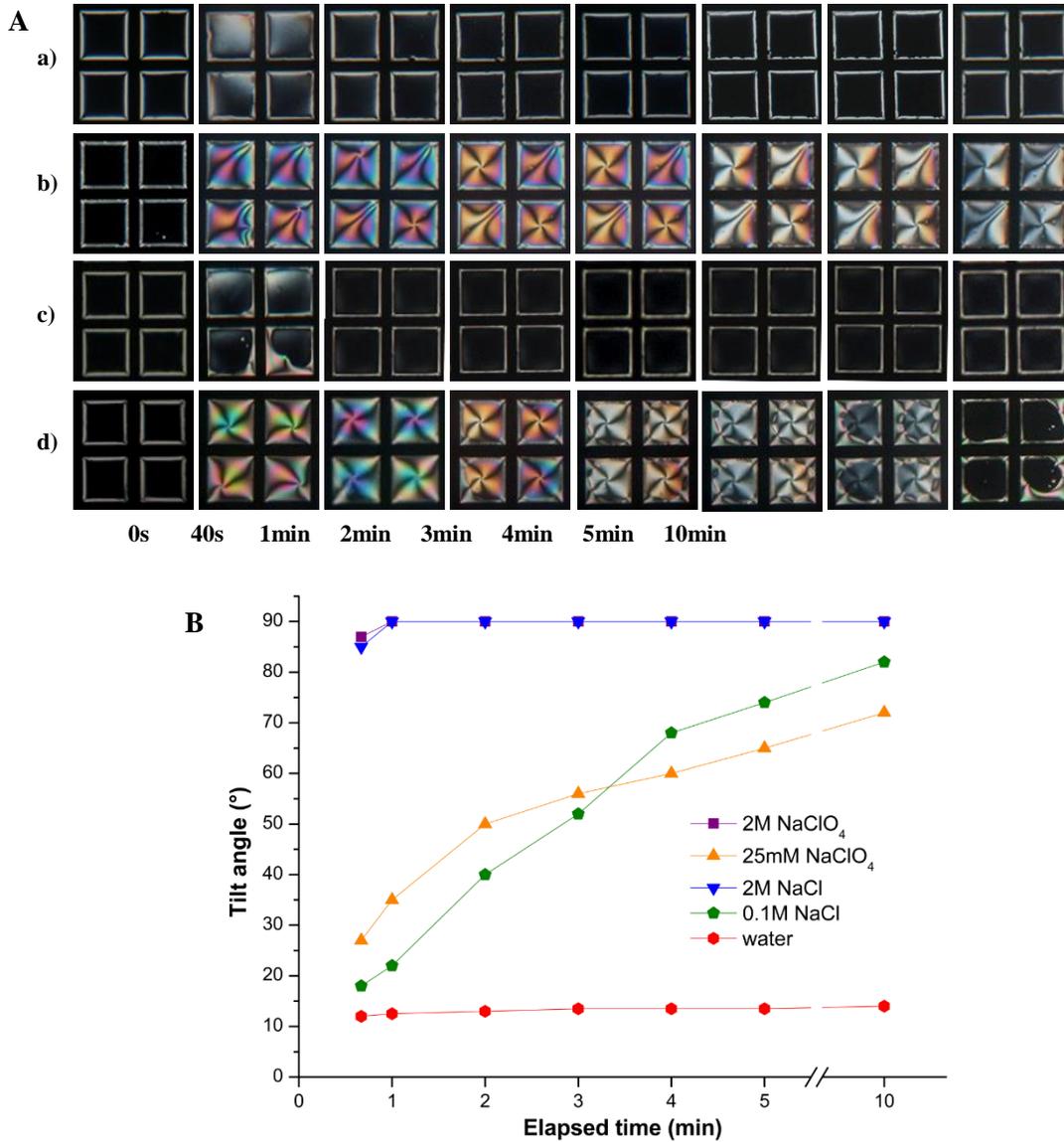


Figure 4. The dynamics of changes in orientation of the 5CB films: (A) Time-lapse polarized light microscopy images of the LC films in contact with (a) 2 M NaClO₄, (b) 25 mM NaClO₄, (c) 2 M NaCl, (d) 0.1 M NaCl, respectively. (B) Tilt angles of 5CB films in contact with the above four kind of salt solutions.

shorten the formation process of the internal electric field at the aqueous-LC interface, as characterized by a rapid ordering transition from planar to homeotropic in LCs, whereas relatively low concentration of ions (near its critical concentration) need longer time to form such electric field for inducing homeotropic orientation in LC films.

The mechanism described above does not consider the influence of pH. The pH values of some kosmotropes or chaotropes solutions are beyond the range of 6–7.5 due to hydrolysis equilibrium. Therefore, the pH shall be considered when investigating the effect of these ions on the LC orientation at the aqueous phase. For example, acetate solutions (anion is chloride ion, pH>7.5) are kosmotropic ion solutions, in which the concentration of hydroxide ions (OH⁻) is higher than that of hydrogen ions (H⁺). We observed that it induces LC homeotropic orientation with a relatively low *critical concentration* (~25 mM, see in Figure 5). We propose that contacting 5CB with acetate

solutions, an additional homeotropic electric double layer is formed because the behavior of OH^- in solution was analogous to kosmotropic salts. Together with the initial homeotropic electric field formed by acetate, the critical concentration of acetate solutions decreases. In contrast, aluminum ion solutions (anion is chloride ion, $\text{pH} < 6$) are as kosmotropic ion solutions, in which the concentration of H^+ is higher than that of OH^- . The aluminum ion solutions do not trigger homeotropic LC orientations even at 2 M (Figure 5). The positive excess concentration of hydrogen ions in aluminum ion solutions largely inhibits the hydrogen bonding between water molecules and weakens the hydration between ions and water. All these result in a great decrease in the homeotropic electric field intensity formed at the aqueous-LC interface, and such a decrease leads to the substantial increase in the critical concentration of aluminum ion solutions.

As a further confirmation of our hypothesis of the specific ions effects on the LC orientation, we performed several additional experiments to present the role of ions in the orientation of LC films

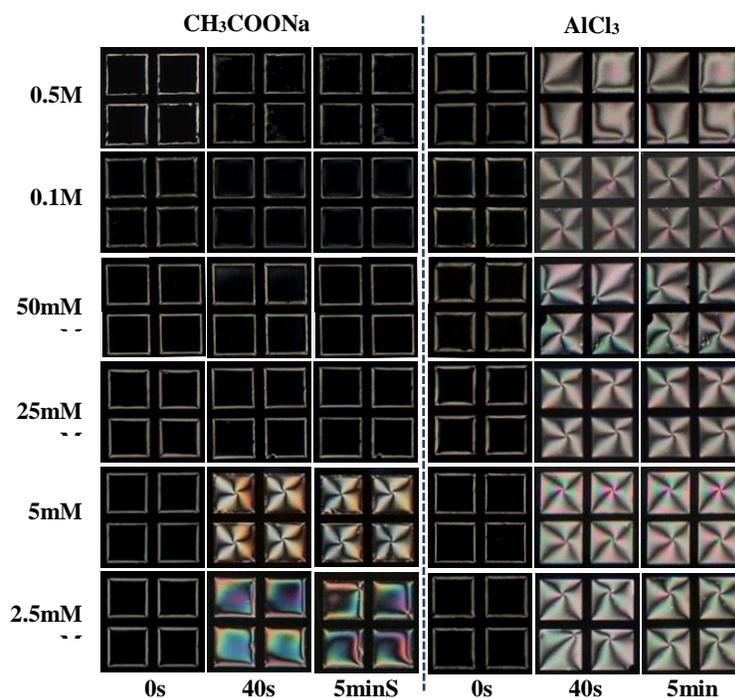


Figure 5. The effect of pH on LC orientation: Polarized light microscopy images of an aqueous-LC interface in contact with CH_3COONa ($\text{pH} > 7.5$, left) and AlCl_3 ($\text{pH} < 6$, right) at seven various concentrations, respectively.

at the surfactant-laden aqueous-LC interface (Figure 6). Octadecyltrimethylammonium bromide (OTAB) is a cationic surfactant and is known to induce LC homeotropic orientation when its concentration exceeds $80 \mu\text{M}$. OTAB at $10 \mu\text{M}$ is insufficient to induce LCs homeotropic orientation. The addition of either 0.5 M or 0.1 M into the $10 \mu\text{M}$ OTAB-laden aqueous-LC interface causes homeotropic orientations in 5CB films, which is in good agreement with our hypothesis on the specific ion effect on LC reorientation. Ions addition into the aqueous phase could greatly decrease the critical concentration of surfactant for the orientation transitions from planar to homeotropic of LCs. These phenomena could be due to the fact that the addition of salts into aqueous phase screens the electrostatic repulsion between the ionic head groups of surfactants at the interface, and thereby increasing surface coverage density of cationic surfactant. Moreover, the salts itself can decrease the solubility of surfactant in aqueous phase and repel the surfactant molecules to the interface. The concentration of salt solution must be controlled down to its distinct

critical concentration in the fabrication of biosensor based on the surfactant-laden aqueous-LC interface.

Finally, our interpretation on the experimental results is generally consistent with previous experiments and theories, as well as the Hofmeister series. Although some researchers argued that not all ions of the Hofmeister series interacted with water under the same principle, electrostatic effects (ion-ion, ion-dipole), which are the strongest of all the intermolecular interactions in ionic solutions, rather than other effects involving the ion-induced dipole interaction between water molecules and 5CB molecules and the dipole-dipole interactions between water molecules, certainly play a major role in the LC reorientation at aqueous phase.

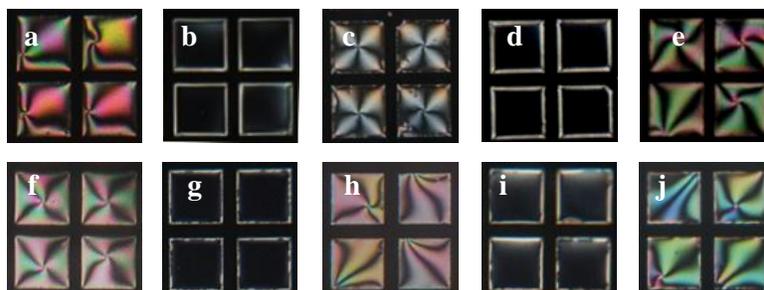


Figure 6. LC response under varying conditions: LC appearance in the absence of OTAB when in contact with pure water (a), 0.5 M NaSCN solution (b), 5 mM NaSCN (c), 0.5 M Na₂SO₄ (d) and 5 mM Na₂SO₄ (e) solution for 5 min, respectively. And LC appearance at the 10 μM OTAB-laden aqueous-LC interface after in contact with pure water (f), 0.5 M NaSCN solution (g), 5 mM NaSCN (h), 0.5 M Na₂SO₄ (i) and 5 mM Na₂SO₄ (j) solution for 5 min, respectively.

CONCLUSIONS

We have systematically explored the influence of chaotropic and kosmotropic ions on the LC ordering transitions at aqueous-LC interface. Both chaotropes and kosmotropes can induce 5CB anchoring transition from planar to homeotropic at aqueous phase with a concentration over its individual critical concentration, yet the critical concentrations of chaotropes are universally lower than those of kosmotropes. The pH effects on the ordering of the LC films were also considered. Most importantly, the experimental evidence supported our hypothesis that the ordering transitions of LC are triggered by the homeotropic electrical double layers formed at the aqueous-LC interface due to the weak hydration of chaotropes or strong hydration of kosmotropes. The ion-induced dipole interaction between chaotropic ions and the nitrile group of 5CB also explained that chaotropic ions induced the homeotropic orientation of 5CB with lower critical concentrations compared with kosmotropic ions. In general, the proposed mechanism not only provides insight into the driving forces behind the LC reorientation in contact with ions solutions at aqueous-LC interface but also guides the design of aqueous-LC interface for detecting chemical and biological interactions involving ions.

Reference

1. **D. S. Miller, R. J. Carlton, P. C. Mushenheim, and N. L. Abbott**, "Introduction to optical methods for characterizing liquid crystals at interfaces," in *Langmuir* **29**(10), pp. 3154–3169 (2013).
2. **K. Iwabata, U. Sugai, Y. Seki, H. Furue, and K. Sakaguchi**, "Applications of

- biomaterials to liquid crystals,” in *Molecules* **18**(4), pp. 4703–4717 (2013).
3. **V. K. Gupta and N. L. Abbott**, “Design of surfaces for patterned alignment of liquid crystals on planar and curved substrates,” *Science* (80-.). **276**(5318), 1533–1536 (1997).
 4. **J. S. Park, C. H. Jang, M. L. Tingey, A. M. Lowe, and N. L. Abbott**, “Influence of 4-cyano-4'-biphenylcarboxylic acid on the orientational ordering of cyanobiphenyl liquid crystals at chemically functionalized surfaces,” *J. Colloid Interface Sci.* **304**(2), 459–473 (2006).
 5. **B. H. Clare, K. Efimenko, D. A. Fischer, J. Genzer, and N. L. Abbott**, “Orientations of liquid crystals in contact with surfaces that present continuous gradients of chemical functionality,” *Chem. Mater.* **18**(9), 2357–2363 (2006).
 6. **V. K. Gupta, W. J. Miller, C. L. Pike, and N. L. Abbott**, “Using Isotropic, Nematic, and Smectic Fluids for the Study of Self-Assembled Monolayers Formed from Alkanethiols on Gold,” *Chem. Mater.* **8**(7), 1366–1369 (1996).
 7. **B. H. Clare and N. L. Abbott**, “Orientations of nematic liquid crystals on surfaces presenting controlled densities of peptides: Amplification of protein-peptide binding events,” *Langmuir* **21**(14), 6451–6461 (2005).
 8. **J. M. Brake and N. L. Abbott**, “Coupling of the orientations of thermotropic liquid crystals to protein binding events at lipid-decorated interfaces,” *Langmuir* **23**(16), 8497–8507 (2007).
 9. **Y. Bai and N. L. Abbott**, “Enantiomeric interactions between liquid crystals and organized monolayers of tyrosine-containing dipeptides,” *J. Am. Chem. Soc.* **134**(1), 548–558 (2012).
 10. **J. S. Park, S. Teren, W. H. Tepp, D. J. Beebe, et al.**, “Formation of oligopeptide-based polymeric membranes at interfaces between aqueous phases and thermotropic liquid crystals,” *Chem. Mater.* **18**(26), 6147–6151 (2006).
 11. **C. Binet, S. Ferrère, A. Lattes, E. Laurent, et al.**, “Benefit of liquid crystal moieties in the MIP technique,” *Anal. Chim. Acta* **591**(1 SPEC. ISS.), 1–6 (2007).
 12. **F. Zuo, Z. Liao, C. Zhao, Z. Qin, et al.**, “An air-supported liquid crystal system for real-time reporting of host-guest inclusion events,” *Chem. Commun. (Camb)*. **50**(15), 1857–1860 (2014).
 13. **S. Zhong and C. H. Jang**, “Highly sensitive and selective glucose sensor based on ultraviolet-treated nematic liquid crystals,” *Biosens. Bioelectron.* **59**, 293–299 (2014).
 14. **N. A. Lockwood, J. K. Gupta, and N. L. Abbott**, “Self-assembly of amphiphiles, polymers and proteins at interfaces between thermotropic liquid crystals and aqueous phases,” in *Surface Science Reports* **63**(6), pp. 255–293 (2008).
 15. **L. N. Tan and N. L. Abbott**, “Dynamic anchoring transitions at aqueous-liquid crystal interfaces induced by specific and non-specific binding of vesicles to proteins,” *J. Colloid Interface Sci.* **449**, 452–461 (2015).
 16. **A. D. Price and D. K. Schwartz**, “DNA hybridization-induced reorientation of liquid

- crystal anchoring at the nematic liquid crystal/aqueous interface,” *J. Am. Chem. Soc.* **130**(26), 8188–8194 (2008).
17. **P. S. Noonan, R. H. Roberts, and D. K. Schwartz**, “Liquid crystal reorientation induced by aptamer conformational changes,” *J. Am. Chem. Soc.* **135**(13), 5183–5189 (2013).
 18. **A. C. McUmbler, P. S. Noonan, and D. K. Schwartz**, “Surfactant–DNA interactions at the liquid crystal–aqueous interface,” *Soft Matter* **8**(16), 4335 (2012).
 19. **S. M. Malone and D. K. Schwartz**, “Macroscopic liquid crystal response to isolated DNA helices,” *Langmuir* **27**(19), 11767–11772 (2011).
 20. **K. M. Macri, P. S. Noonan, and D. K. Schwartz**, “Receptor-mediated liposome fusion kinetics at aqueous/liquid crystal interfaces,” *ACS Appl. Mater. Interfaces* **7**(36), 20400–20409 (2015).
 21. **W. Iglesias, N. L. Abbott, E. K. Mann, and A. Jákli**, “Improving liquid-crystal-based biosensing in aqueous phases,” *ACS Appl. Mater. Interfaces* **4**(12), 6884–6890 (2012).
 22. **P. Lo Nostro and B. W. Ninham**, “Hofmeister Phenomena: An Update on Ion Specificity in Biology,” *Chem. Rev.* **112**(4), 2286–2322 (2012).
 23. **S. Zhai and H. Zhao**, “Enhancement of Sensitivity of the Solution-Phase Localized Surface Plasmon by a Nanostructured Substrate,” *MRS Adv.* **1**(28), 2059–2064 (2016).
 24. **W. Kunz**, “Specific ion effects in liquids, in biological systems, and at interfaces,” *Pure Appl. Chem.* **78**(8), 1611–1617 (2006).
 25. **W. Kunz**, “Specific ion effects in colloidal and biological systems,” in *Current Opinion in Colloid and Interface Science* **15**(1–2), pp. 34–39 (2010).
 26. **K. D. Collins**, “Ions from the Hofmeister series and osmolytes: Effects on proteins in solution and in the crystallization process,” *Methods* **34**(3), 300–311 (2004).
 27. **P. K. Weissenborn and R. J. Pugh**, “Surface tension of aqueous solutions of electrolytes: Relationship with ion hydration, oxygen solubility, and bubble coalescence,” *J. Colloid Interface Sci.* **184**(2), 550–563 (1996).
 28. **P. K. Weissenborn and R. J. Pugh**, “Surface Tension and Bubble Coalescence Phenomena of Aqueous Solutions of Electrolytes,” *Langmuir* **11**(5), 1422–1426 (1995).
 29. **L. M. Pegram and M. T. Record**, “Hofmeister salt effects on surface tension arise from partitioning of anions and cations between bulk water and the air-water interface,” *J. Phys. Chem. B* **111**(19), 5411–5417 (2007).
 30. **W. L. Guest and W. C. M. Lewis**, “The Effect of Electrolytes upon the Interfacial Tension between Water and Dekalin (Trans-Decahydronaphthalene),” *Proc. R. Soc. A Math. Phys. Eng. Sci.* **170**(943), 501–513 (1939).
 31. **H. H. Girault and D. J. Schiffrin**, “Thermodynamic Surface Excess of Water and Ionic Solvation at the Interface Between Immiscible Liquids,” *J. Electroanal. Chem.* **150**(1–2), 43–49 (1983).
 32. **R. Aveyard and S. M. Saleem**, “Interfacial tensions at alkane-aqueous electrolyte

- interfaces,” J. Chem. Soc. Faraday Trans. 1 **72**(9), 1609 (1976).
33. **R. J. Carlton, J. K. Gupta, C. L. Swift, and N. L. Abbott**, “Influence of simple electrolytes on the orientational ordering of thermotropic liquid crystals at aqueous interfaces,” *Langmuir* **28**(1), 31–36 (2012).
34. **A. Covington**, “Thermodynamics of Solvation - Solution and Dissolution - Ions and Solvents - Structure and Energetics, by G.A. Krestov,” in *NATURE* **351**(6327), p. 534 (1991).

Supporting Information

Table S1. Jonse-Dole viscosity B coefficients

Anions	B	radius/pm	Cations	B	radius/pm
SO ₄ ²⁻	0.208	240	Al ³⁺	0.744	53
CH ₃ CO ₂ ⁻	0.250	190	Mg ²⁺	0.385	72
Cl ⁻	-0.007	181	Ca ²⁺	0.285	100
ClO ₄ ⁻	-0.061	250	Na ⁺	0.086	102
SCN ⁻	-0.103	209	K ⁺	-0.007	138
H ₂ PO ₄ ⁻	*	213			

Phosphate and thiocyanate from Krestov et al^[34], all others from K.D.Collins^[26].

Table S2. The Critical concentration of ion solutions inducing LCs homeotropic alignment at aqueous-LC interface

Salts(anions)	C _m [M]	C[mM]	Salts(cations)	C _m [M]	C[mM]
Na ₂ SO ₄	2	75	KCl	4.59	25
NaH ₂ PO ₄	0.75	*	AlCl ₃	3.44	*
CH ₃ COONa	3.98	20	--	--	--
NaCl	6.14	100	--	--	--
NaClO ₄	9	50	--	--	--
NaSCN	17.14	15	--	--	--

Notation: C_m, the maximum solubility at 25 °C; C, the critical concentration; ‘*’, the critical concentration was not found within its solubility.

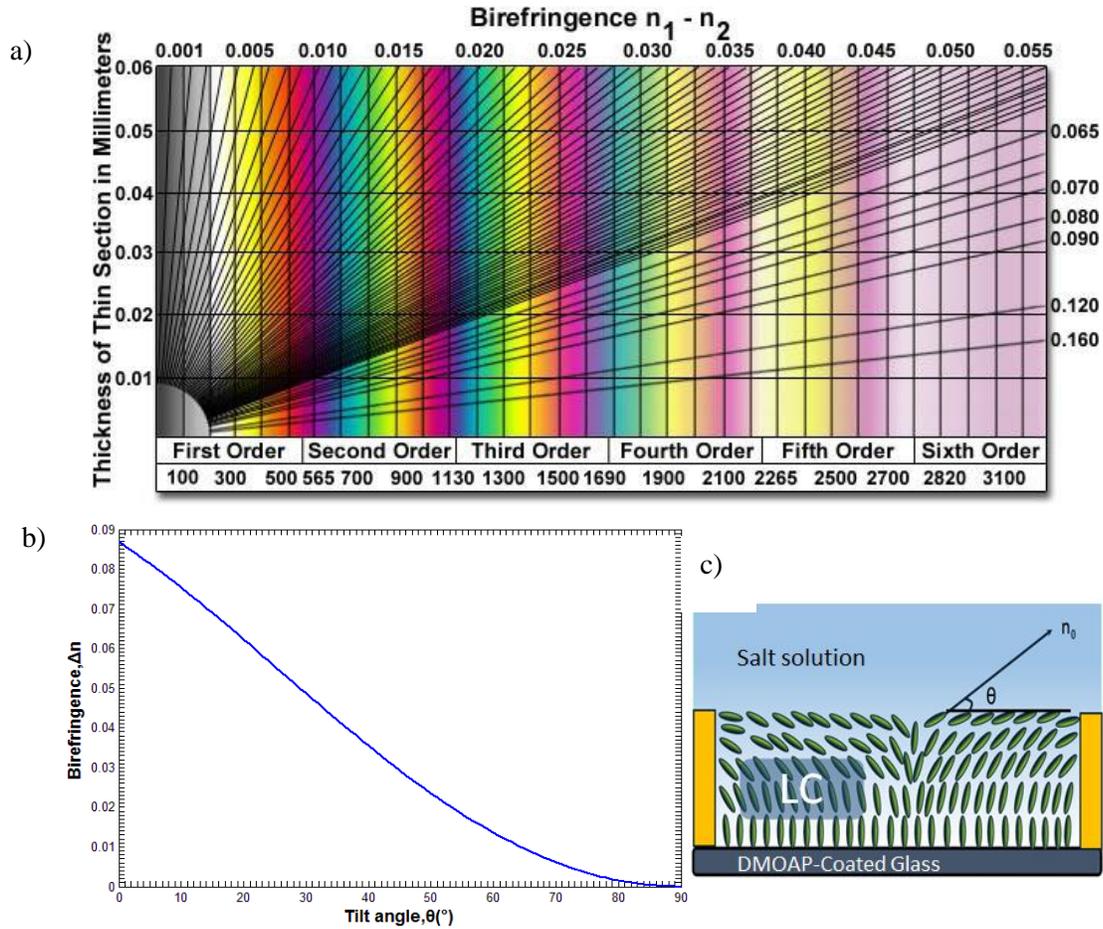


Figure S1. The Michel-Levy color chart(a). The chart is associated with the sample thickness, optical retardance, and the effective birefringence of optically anisotropic materials to colors observed using crossed polarizers and white light illumination. The optical retardance (in nm) is given at the bottom of the chart [2]. Relation between tilt angle of the LC at the aqueous interface and the effective birefringence of a 5CB film with homeotropic anchoring at the lower interface(b). Schematic of a LC film with a tilted ordering at the aqueous interface and perpendicular anchoring at the bottom interface (DMOAP-functionalized), θ is the tilt angle with respect to the planar interface.

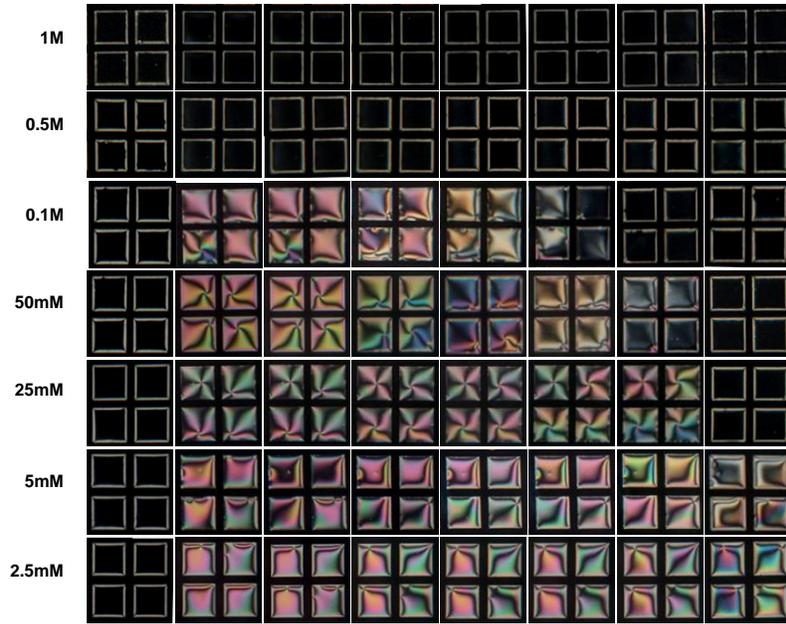


Figure S2. Results of addition of potassium ions (chaotropic cation): Time-lapse polarized light microscopy images of 5CB after contacting aqueous solutions of potassium chloride (KCl) with 1 M, 0.5 M, 0.1 M, 50 mM, 25 mM, 5 mM, and 2.5 mM, respectively. Obviously, its critical concentration is approximately 2.5 mM. When the concentration was above the critical concentration, it caused homeotropic alignment in LC over a period of time. While the concentration was under the critical concentration, it caused tilted orientation in LC similar to the behavior of addition of pure water.

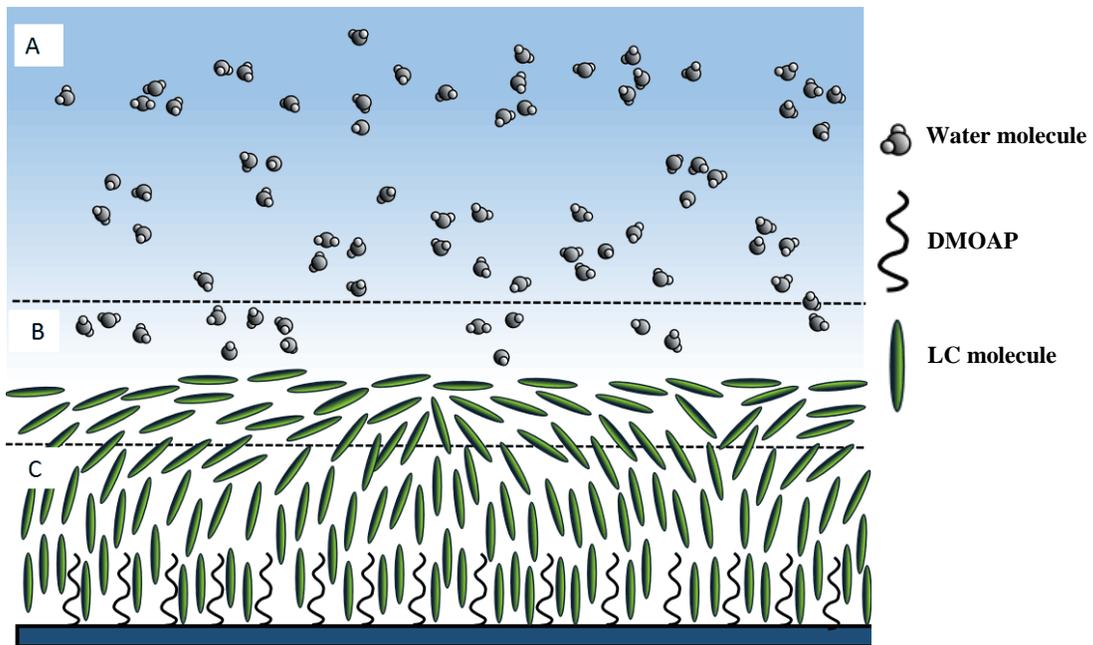


Figure S3. Schematic illustration of the mechanism for a LC reorientation in contact with pure water: The system is divided into three layers: the bulk solution phase (A), the aqueous-LC interface (B), the bulk LC phase (C). There are no specific interactions between water molecules and LC molecules at the aqueous-LC interface so that the LC films were anchored parallel to the aqueous interface for accommodating the hybrid boundary conditions.

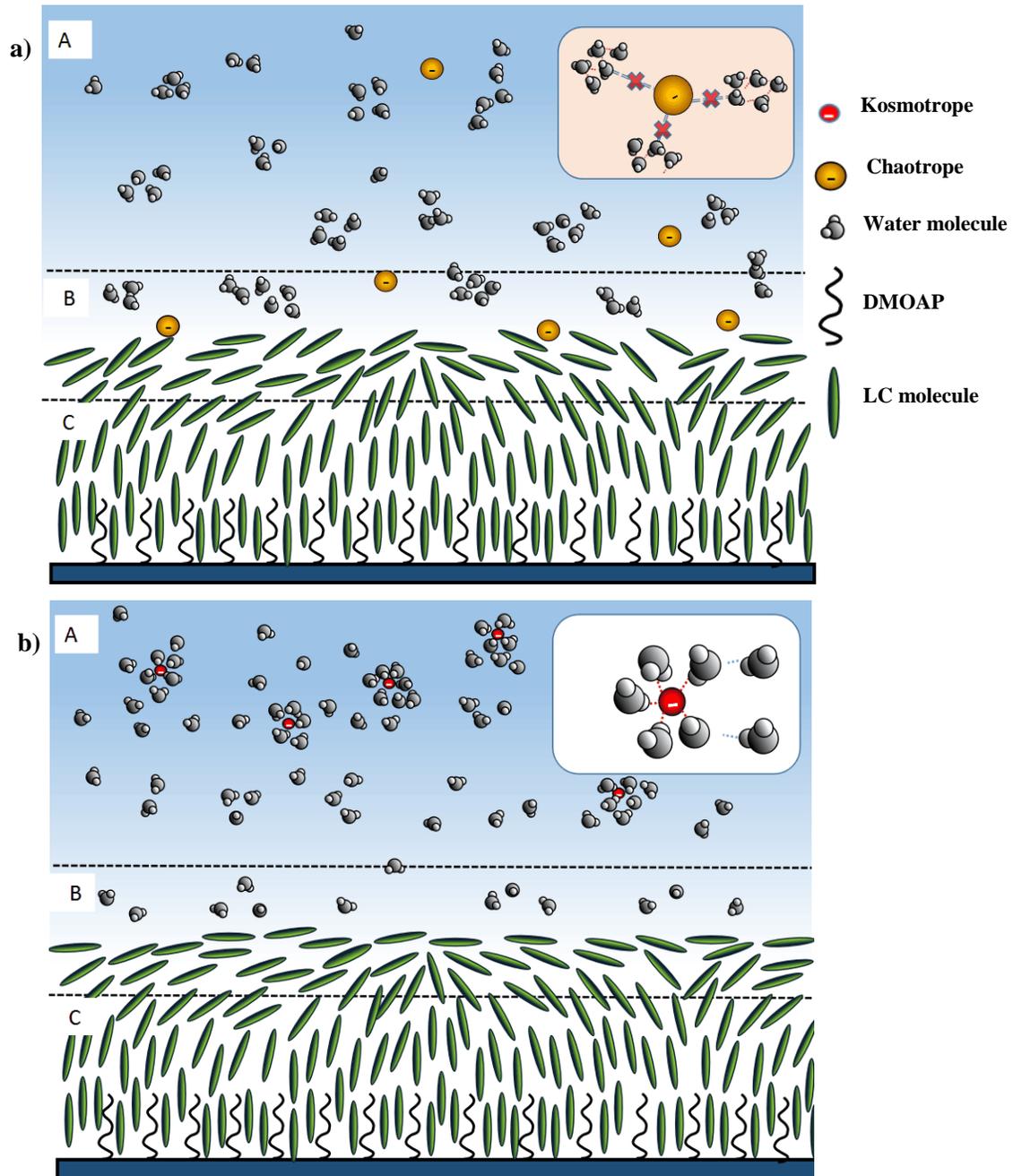


Figure S4. Schematic illustration of the mechanism for a LC reorientation in contact with a) low concentration (lower than the critical concentration) of aqueous chaotropic ions, b) low concentration of aqueous kosmotropic ions. The system is divided into three layers: the bulk solution phase (A), the aqueous-LC interface (B), the bulk LC phase (C). Upon addition of low concentration of either chaotropes or kosmotropes, the number of ions at the aqueous-LC interface is relatively few such that the tilted orientations of LC films were unchanged.

Supplemental Reference:

1. **A. Covington**, “Thermodynamics of Solvation - Solution and Dissolution - Ions and Solvents - Structure and Energetics, by G.A. Krestov,” in NATURE **351**(6327), p. 534 (1991).
2. **K. D. Collins**, “Ions from the Hofmeister series and osmolytes: Effects on proteins in solution and in the crystallization process,” Methods **34**(3), 300–311 (2004).