

Water Flux Induced Reorientation of Liquid Crystals

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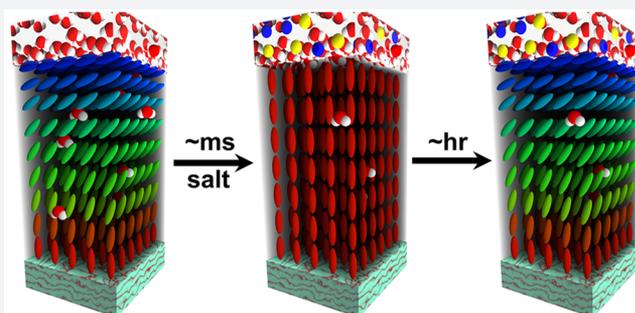
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Supporting Information

ABSTRACT: It is well understood that the adsorption of solutes at the interface between a bulk liquid crystal phase and an aqueous phase can lead to orientational or anchoring transitions. A different principle is introduced here, whereby a transient reorientation of a thermotropic liquid crystal is triggered by a spontaneous flux of water across the interface. A critical water flux can be generated by the addition of an electrolyte to the bulk aqueous phase, leading to a change in the solvent activity; water is then transported through the liquid crystal phase and across the interface. The magnitude of the spontaneous water flux can be controlled by the concentration and type of solutes, as well as the rate of salt addition. These results present new, previously unappreciated fundamental principles that could potentially be used for the design of materials involving transient gating mechanisms, including biological sensors, drug delivery systems, separation media, and molecular machines.



INTRODUCTION

The reorganization of liquid crystals (LCs) at aqueous interfaces induced by the adsorption of molecular and ionic species offers a rich avenue for the design of biological sensors and drug delivery devices.^{1–8} Common approaches for controlling the reorientation of liquid crystals at planar aqueous interfaces involve monolayers decorated with charged and neutral surfactants^{1–3,9} and addition of simple electrolytes to the aqueous phase.^{10,11} The molecular mechanisms responsible for triggering the long-range reorientation of the LC upon the addition of various solutes have commonly been attributed to the specific interactions with the liquid crystal molecules at the LC–aqueous interface.^{12,13} Yet, the physical principles that lead to the collective reorientation of the LC upon the addition of even simple electrolytes remain poorly understood. While the interface itself has attracted much attention in past studies of interfacial transitions, the critical role of dissolved water in the LC phase (Figure 1A) has been largely overlooked. In particular, it is especially important to understand how changes in the thermodynamic properties of the bulk phase upon addition of ionic surfactants and simple electrolytes are expected to affect the dissolved water in the LC phase. In this work, we report that a substantial burst of water transport across a planar LC–water interface introduces a reorienting torque on the liquid crystal molecules that is sufficiently strong to trigger a rapid transition to a uniform geometry, a state that enables release of stored elastic energy (Figure 1B). This physical phenomenon could be exploited to enable low-power,

rational manipulation of molecular alignment and transport at the LC–aqueous interfaces. Because these effects can be coupled with surfactant-induced reorientation of the LC, the principles presented here may also serve as the basis for the detection of chemicals, proteins, or biological toxins.

RESULTS AND DISCUSSION

To understand molecular reorientation near the LC–aqueous interface at a detailed level, we turn to atomistic molecular dynamics simulations of thin films of 4-cyano-4'-pentylbiphenyl (5CB) confined between vacuum (with perpendicular anchoring, similar to that of the treated glass substrates commonly used in experiments)^{14,15} and 2 M solutions of sodium iodide (NaI) and sodium chloride (NaCl) (Figure 1A). Our results show that 5CB molecules assume a parallel orientation at the LC–aqueous interface, analogous to that observed in the vicinity of pure water (Figure 1A and Figures S1–S7).¹⁵ Analysis of the probability of finding ions at a given position across the simulation system shows that the ions remain in the aqueous phase and tend to localize near the interfaces to form cation-rich and anion-rich regions (Figures S8 and S9). This specific arrangement of ions modulates the average orientation and the polarization density of water molecules at the LC–aqueous and aqueous–vacuum interfaces (Figures S8 and S9).¹⁵ The ions remain fully hydrated at room temperature and

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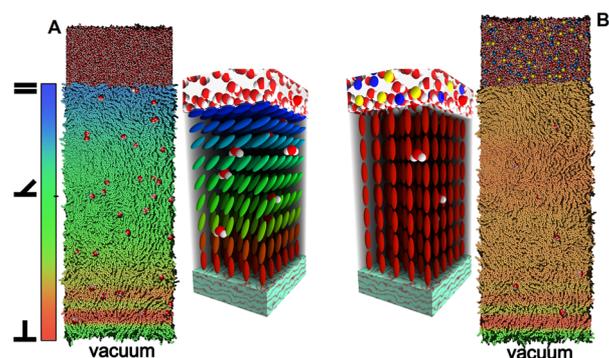


Figure 1. Schematic representations showing the orientation of 5CB before addition of salts and shortly after injection of salts to the aqueous phase. In experiments, a thin film of liquid crystal (LC) is deposited on a treated glass substrate to induce perpendicular alignment of the LC at the surface. In our simulations, a thin film of 5CB is confined between vacuum (with perpendicular anchoring, similar to that of the treated glass substrate) and a water phase. The water in the LC phase is shown in red and white, and the ions in the aqueous phase are shown in blue and yellow. (A) Molecular orientations of 5CB before addition of salt, and setup for molecular dynamics simulations. (B) Schematic representation of the molecular orientations shortly after addition of NaI salt. 2 M solutions of NaI and NaCl are added to the aqueous medium. The color-bar serves to quantify the average orientation of LC molecules, from perpendicular (\perp) to parallel (\parallel). Please see Figures S1–S7 for the analysis of molecular orientations within the liquid crystal phase.

at 40 °C (in the isotropic phase of 5CB) due to the prohibitively high free energy cost for dragging a solvated ion from the bulk solvent to the LC phase (Figures S8 and S9). The anchoring strength of 5CB at the aqueous phase decreases very slightly upon addition of NaI and NaCl (Figure S10).

The 5CB molecule consists of a hydrophilic polar head and a hydrophobic nonpolar tail. In the nematic phase, the dielectric constant of 5CB is relatively large and it is anisotropic, with $\epsilon_{\parallel} = 19$ along the optical axis and $\epsilon_{\perp} = 6$ in the direction perpendicular to the optical axis.^{16–18} Accordingly, one may expect some water to diffuse through the LC–aqueous interface and partition in the bulk LC phase (Figure 1A).¹⁹ The potential of mean force (PMF) for the transfer of a single water molecule from the bulk water phase to the LC phase yields a free energy cost of approximately 4 kcal/mol (Figure 2A). This free energy difference in fact corresponds to a significant (~ 57 mM) concentration of water in the LC phase (see Supporting Information for details), which suggests that approximately 5.5×10^{13} water molecules reside in the LC phase of a single $283 \times 283 \times 20 \mu\text{m}^3$ cell, the size that is typically used in experiments with TEM grids.^{10,11} The PMF profile (Figure 2A) shows that the concentration of water within the LC phase remains much higher in the immediate vicinity of the interface (the ~ 10 – 15 Å region near the interface where the PMF varies continuously).

A mechanism that has been invoked to explain the salt-induced anchoring transitions at the water–LC interfaces is the formation of an ionic double layer on the LC side of the interface able to generate an electric field that affects the orientation of the 5CB molecules.¹⁰ To examine the feasibility of this mechanism in our system, one can compute the free energy cost associated with the transfer of a single ion from the bulk aqueous phase into the bulk LC phase. Ions transferring to the nonpolar phase tend to remain surrounded by a first solvation shell of water at all times due to the prohibitively large

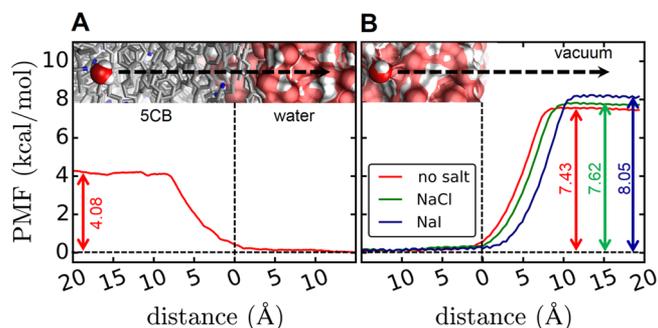


Figure 2. Potential of mean force (PMF) for translocation of a single water molecule across the LC–water and the water–vacuum interfaces. (A) PMF profile corresponding to relocation of a single water molecule from the bulk 5CB phase to the bulk water phase. (B) Free energy profiles for the transfer of a single water molecule from the bulk water to vacuum (red), from a 2 M solution of NaI to vacuum (navy), and from a 2 M solution of NaCl to vacuum (green). The differences in the free energy costs are due to the change in water activity upon addition of salts.

hydration free energy. The free energy cost for translocation of a partially hydrated chloride ion into the LC phase is approximately 12 kcal/mol, which corresponds to nanomolar concentrations of ions in the LC phase (Figure S11). These considerations strongly suggest that the formation of a *bona fide* electrical double layer affecting the reorientation of the LC phase at the aqueous interface is very unlikely. Here we note that alternative mechanisms based on the anion-specific interactions have been proposed to explain salt-induced anchoring transitions at the water–LC interfaces.¹¹ While it is difficult to assess the importance of the anion-specific effects with certainty, the present analysis shows that a simple water flux mechanism can account for the experimentally observed anchoring transitions.

The free energy difference that must be overcome by a single water molecule in order to leave the water phase and reach a vacuum is ~ 7.4 kcal/mol (Figure 2B). The lower free energy cost (~ 3.3 kcal/mol lower) that must be overcome by a water molecule to reach the LC phase is due to its favorable electrostatic and van der Waals interactions with 5CB molecules. Upon addition of salts, the water activity of the electrolyte solution decreases from unity, leading to higher free energy costs for transfer of water molecules into the LC phase or into vacuum (Figure 2B). The reduced water activity causes the LC phase to lose water. The adjusted average concentration of water in the LC phase is a fraction of that initial concentration; it is approximately equal to $a_w C_0$, where a_w is the activity of water in the electrolyte solution, and C_0 is the initial concentration of water in the LC phase. Several factors, including the concentration and type of solutes, as well as the temperature, determine the equilibrium water content of the LC phase.²⁰ The water activity of NaI and NaCl solutions in simulations can be estimated from the expression $a_w = e^{\Delta\mu_{\text{ex}}/k_B T}$, where $\Delta\mu_{\text{ex}}$ is the excess chemical potential difference of pure water and water in the electrolyte solution; k_B is Boltzmann's constant, and T is the temperature. The computed water activity of NaI and NaCl solutions is 0.35 and 0.72, respectively, in qualitative agreement with tabulated data (see Supporting Information).²⁰ These values indicate that the equilibrium concentration of water in the LC phase drops considerably upon addition of salts, particularly for the NaI electrolyte.

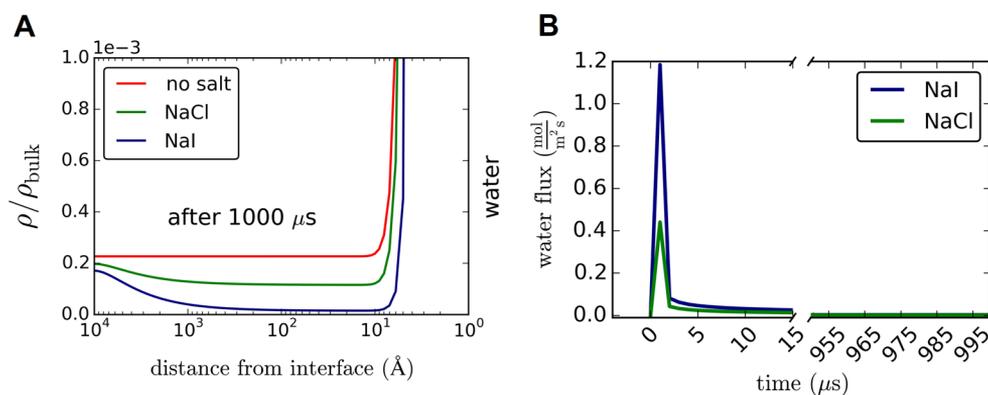


Figure 3. Continuum simulations of water flux according to the Smoluchowski (drift–diffusion) equation. (A) Water density profile prior to addition of salts (red), and 1 ms after addition of NaCl (green) and NaI (blue). (B) Time-dependent flux of water through the LC–aqueous interface after addition of 2 M concentration of NaI and NaCl electrolytes.

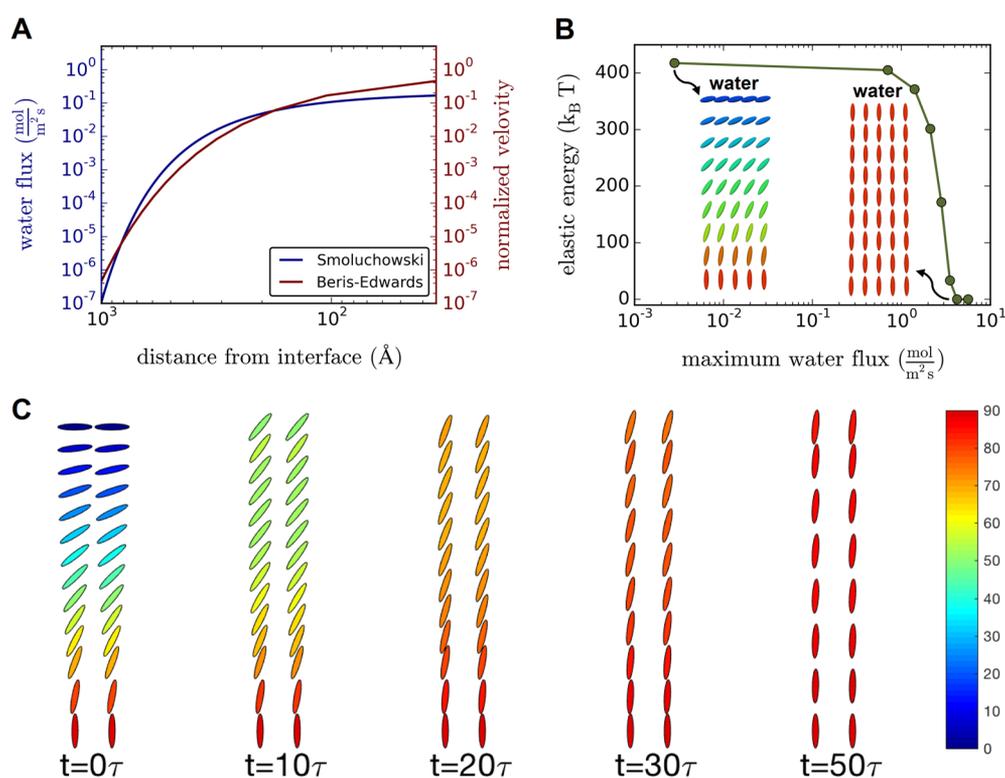


Figure 4. Continuum-level simulations of water flux induced anchoring transitions according to the Beris–Edwards equation. (A) Water flux profile as a function of distance from the LC–water interface 1 μ s after addition of NaI electrolyte (navy blue) computed using the Smoluchowski equation, and the shape of the prescribed velocity profile used to solve the Beris–Edwards model (brown). (B) Stored elastic energy in the liquid crystal film as a function of maximum water flux through the LC–aqueous interface. The LC film transitions from a hybrid geometry onto a uniform configuration above a critical water flux in order to release the stored elastic energy. (C) Time-dependent transition of the hybrid LC film into a uniform configuration using the maximum water flux of 4.22 mol/(m² s). The color bar shows the angle between the nematic director and the surface, and τ is 0.27 ms here.

Because the concentration of water in the region near the LC–water interface is relatively high and the concentration gradients are large, equilibration of the water concentration in that region occurs almost immediately (within microseconds of immersion of the LC phase under an electrolyte solution) (Movie S1). This rapid adjustment of the density leads to a significant burst of water across the interface, whose magnitude depends on the type and concentration of salts. To describe the time-dependent evolution of the density profile and the water flux through the interface, one can solve the Smoluchowski (drift–diffusion) equation, $\frac{\partial \rho}{\partial t} = \nabla \cdot (D \nabla \rho) - \nabla \cdot (\zeta^{-1} \vec{F} \rho)$,

where ρ is the water density, D is the diffusion constant, $\zeta^{-1} = D/k_B T$ is the mobility, and $\vec{F} = -\nabla W$ is the mean force (see Supporting Information, Figure 3, and Movie S1).²¹ Whereas the equilibrium density of water near the interface converges within 1 μ s of the addition of salt, complete equilibration of the density profile throughout the entire LC film requires several hours. For the systems considered here, we estimate a time to equilibrium of approximately 4 h (see Figure S12 and Supporting Information for details). The time-dependent profile of water flux reveals a significant peak within the first microsecond after electrolyte addition. The flux peak reaches

nearly 1.2 mol/(m² s) after addition of NaI, approximately three times larger than the maximum flux produced by addition of NaCl. In our atomistic simulations, this water flux corresponds to the diffusion of ~0.1 water molecule per nanosecond through the LC–aqueous interface, and cannot be quantified in a statistically significant manner by atomistic simulations at that high level of spatial resolution.

By assuming a complete transfer of momentum from the diffusing water molecules to the 5CB molecules, one can assign a velocity profile to the LC phase (Figure 4A) and solve the Beris–Edwards equation ($\partial_t + \mathbf{u} \cdot \nabla$) $\mathbf{Q} - \mathbf{R}(\mathbf{W}, \mathbf{Q}) = \Gamma \mathbf{H}$, which couples the local, time-dependent structure of the LC material to the transfer of momentum across the system.^{22,23} Here, \mathbf{Q} is the tensorial order parameter, \mathbf{W} is the gradient of the velocity, Γ is a parameter related to the rotational viscosity, and \mathbf{H} is the molecular field related to the free energy of the system (see Supporting Information for details). The results of these calculations show that, above a critical threshold of water flux through the LC–water interface, a hybrid liquid crystal cell that exhibits perpendicular alignment on one side and parallel anchoring on the other transforms into a uniform cell with perpendicular alignment throughout the channel (Figure 4B,C). The transition from a hybrid to a uniform configuration is facilitated by the release of the stored elastic energy of the liquid crystalline cell (Figure 4B,C). The system remains in this metastable state as a consequence of the water flux, but begins to return to the original hybrid configuration after a short period of time. Note that past studies of interfacial transitions of LCs using simple electrolytes have been limited to short or intermediate observation times, and longer observation times would be required to characterize the “transient” behavior of these reorientations.^{10,11}

The water flux induced reorientation of the LC combines the concept of osmotic-pressure induced transport to reorientation of LCs for design of responsive materials. For instance, we could exploit the direct relationship between the electrolyte concentration and the magnitude of the water flux to prevent the amplified reorientation of the LC films. To illustrate this concept, one could increase the concentration of salts (NaI for example) in one step, up to an intermediate value (~0.2 M for instance) without triggering an anchoring transition. One could then allow for a full relaxation of the system to ensure complete equilibration of water molecules in the LC phase. Next, the salt concentration could be increased in a stepwise manner, followed by full relaxation of the LC–aqueous interface to arrive at a high concentration of salts without ever inducing a significant change in the orientation of the LC at the aqueous interface. In contrast, a sudden addition of salt to the water phase would trigger the transient behavior proposed here on the basis of theoretical arguments.

Because the orientational transition of a liquid crystal at the aqueous interfaces is mainly triggered by a rapid adjustment of the bulk properties of the water phase, as opposed to explicit solute–LC interactions, other solutions with low water activity are likely to cause similar effects. One could use, for example, lithium chloride (LiCl), because the activity of water in LiCl solutions approaches 0.1 near the saturation limit.²⁰ Additional exploration of these general principles might provide an opportunity to develop a rich library of solutes involving simple salts and other organic molecules that are able to trigger reorientation of LCs at aqueous interfaces (Table S1).^{20,24–26} Future experiments will seek to further characterize the mechanism of solvent flux induced reorientation of LCs. We

note that the minimum solute concentration necessary to drive a water flux induced anchoring transition of the LC depends on several factors, including the type of solutes (ions), the local concentration of the ions near the interface, the temperature, and other design parameters such as LC film thickness.

CONCLUSIONS

The coupling of the bulk properties of the aqueous phase to the orientational transition of a liquid crystal reported here provides a fundamental basis for the design of responsive materials in biological or synthetic environments alike. These principles may offer new approaches for salt-assisted detection of targeted biological species at low concentrations. They may also enable design of selective membranes that open or shut selectively in response to osmotic stresses. Because the water flux induced orientational transition of liquid crystals is a transient phenomenon, these temporary reorientations could be exploited to tailor the interactions between surfactants and liquid crystalline phases. Since the anchoring transition occurs through collective reorientation, these collective motions could potentially be useful for design of drug delivery devices and molecular machines.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.7b00495.

Materials and Methods, Figures S1 to S12, Table S1, and supporting references (PDF)

Movie S1 (AVI)

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Notes

The authors declare no competing financial interest.

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