Published in final edited form as:

Langmuir. 2009 February 17; 25(4): 2026–2033. doi:10.1021/la803475c.

Principles for Manipulation of the Lateral Organization of Aqueous-Soluble Surface-Active Molecules at the Liquid Crystal-Aqueous Interface

Jugal K. Gupta and Nicholas L. Abbott*

Department of Chemical & Biological Engineering, University of Wisconsin-Madison 1415 Engineering Drive, Madison, Wisconsin 53706, USA

Abstract

We report an investigation of the lateral organization of water-soluble, surface-active molecules within monolayers formed spontaneously at interfaces between aqueous phases and immiscible, micrometer-thick films of nematic liquid crystals (LCs; 4'-pentyl-4-cyanobiphenyl and TL205, a mixture of cyclohexanefluorinated biphenyls and fluorinated terphenyls). Using both anionic (sodium dodecylsulfate) and cationic surfactants (dodecyltrimethylammonium bromide), we demonstrate that the nematic order of the LCs can direct monolayers of surfactant in dynamic equilibria with bulk aqueous solutions to phase separate and assume lateral organizations at the interfaces of the LCs that are not seen in the absence of the nematic order. The lateral organization of the surfactants is readily evidenced by the patterned orientations assumed by the LCs, and can be manipulated reversibly by changes in the bulk concentrations of the surfactants. Experimental observations of the effects of bulk surfactant concentration, thickness of the film of LC, nematic order, and aqueous electrolyte concentration are placed within the framework of a simple thermodynamic model. The model incorporates the dynamic equilibration of surfactant between the bulk and interface as well as the coupling between the elasticity of nematic LCs and the lateral organization of the water-soluble surfactants within the monolayers. Qualitative agreement is found between the model predictions and experimental observations, thus supporting our conclusion that LCs offer the basis of general and facile methods to direct the lateral organization of interfacial molecular assemblies.

Introduction

Recent studies have revealed that a diverse range of dynamic and equilibrium phenomena can occur when molecular self-assembly and specific biomolecular recognition events take place at interfaces formed between nematic liquid crystals (LCs) and immiscible aqueous phases (see¹ for a recent review). It has been shown, for example, that the organization of surfactants,^{2–5} phospholipids,^{6–10} proteins,^{6, 11} and synthetic polymers^{12–16} adsorbed at these interfaces strongly influences the orientational ordering of the LCs. Past studies have exploited this coupling to report enzymatic reactions,^{6, 11} the interaction of cells with extracellular protein matrices,¹⁷ protein binding events,⁶ DNA hybridization¹⁸ and reorganization of polymeric complexes.^{13, 15} More recently, however, in the context of a study of insoluble monolayers of phospholipids,⁹ we reported that the phospholipids assume lateral organizations at the interface of LCs that are not observed when using isotropic oils. These observations led us to demonstrate that the elasticity of LCs can play an important role in directing the interfacial organization and phase behavior of water-insoluble phospholipids at the aqueous-LC interface.⁹

*Correspondence should be addressed to Nicholas L. Abbott (abbott@engr.wisc.edu, Fax: 1+608-262-5434).

In the study described in this paper, we build on our recent communication⁹ to provide evidence that the influence of LC order on the organization of species assembled at aqueous-LC interfaces is not limited to water-insoluble phospholipids,⁹ but that it includes the broad class of water-soluble amphiphilic species that form monolayers when in dynamic equilibrium with their bulk solutions. We emphasize here that the prior observation of phase-separation of monolayers of phospholipids adsorbed irreversibly at the aqueous-LC interface does not obviously lead to the conclusion that water-soluble amphiphiles in dynamic equilibrium with a bulk solution will also phase separate at the aqueous-LC interface. Indeed a past study by Folkers and co-workers¹⁹ demonstrates that the presence of a dynamic equilibrium between a monolayer-decorated interface and a bulk solution can abolish phase-separation within a monolayer that occurs in the absence of the dynamic equilibrium. This difference in phase behavior arises because the chemical potential of surface-active molecules within a monolayer in dynamic equilibrium with a bulk solution is set by the thermodynamic state of the surfactant in the bulk. We also note here that the dynamic equilibrium with the bulk solution, as described above, enables reversible control over interfacial density of amphiphiles more easily than can be achieved when using water-soluble amphiphiles.

The study reported herein employs dodecyltrimethylammonium bromide (DTAB) and sodium dodecylsulfate (SDS) as model systems to investigate the lateral organization of water-soluble, surface-active molecules at interfaces between nematic phases and LCs. We selected one cationic surfactant and one anionic surfactant in order to explore the generality of the phenomena. Similarly, two different nematic liquid crystals were selected for investigation (5CB and TL205). Our choice of experimental systems was influenced in part by the large number of past studies^{2, 18, 20–23} that have employed surfactants to control the orientations of LCs at aqueous-LC interfaces. These studies have generally designed and interpreted their experiments assuming the lateral distribution of surfactants to be homogeneous at the interfaces of the LCs, an assumption that, on the basis of the results reported herein, does not appear to be generally valid. Our results reveal that interactions of the LCs with the surfactants can lead to inhomogeneous distributions of the surfactants at LC interfaces and consequently inhomogeneous (patterned) ordering of the LCs. Our results also suggest that the elastic energy stored in distorted states of LCs plays a central role in directing the non-uniform distribution of surfactant at the LC interface. These results, when combined with the results of our past study obtained using insoluble amphiphiles,⁹ suggest that LCs offer the basis of broadly applicable principles for manipulation of the interfacial organization of molecules. Because weak fields can be used to manipulate LC order with high spatial (micrometer) and temporal (tens of millisecond) resolution, these results suggest principles leading to methods for active control of the interfacial organization of molecules and thus their functionality.

Materials and Methods

Materials

Dodecyltrimethylammonium bromide (DTAB) and sodium bromide (NaBr) were obtained from Sigma-Aldrich (St. Louis, MO). Deionization of a distilled water source was performed using a Milli-Q system (Millipore, Bedford, MA) to give water with a resistivity of 18.2 M Ω cm. Octadecyltrichlorosilane (OTS), hydrogen peroxide (30% w/v) and sulfuric acid were all obtained from Fisher Scientific (Pittsburgh, PA). 4'-pentyl-4-cyanobiphenyl (5CB) and TL205 (a mixture of cyclohexanefluorinated biphenyls and fluorinated terphenyls) were obtained from EM Sciences (New York, NY). DTAB was recrystallized three times in acetone/ethanol mixture²⁴ before use while all other chemicals were used as obtained without further purification. The glass microscope slides were Fisher's Finest Premium Grade obtained from Fisher. Gold specimen grids (5–40 μ m thickness, 292 μ m

grid spacing, and 55 μm bar width) were obtained from Electron Microscopy Sciences (Fort Washington, PA).

Preparation of Optical Cells containing LC

Details regarding the preparation and examination of the optical cells filled with LC can be found in one of our past publications.² Briefly, glass microscope slides were cleaned according to published procedures² and coated with octadecyltrichlorosilane (OTS). The quality of the OTS layer was assessed by checking the alignment of nematic 5CB confined between two OTS-treated glass slides. Gold specimen grids (rinsed three times each in ethanol, methanol and dichloromethane and dried) were then placed onto the surface of a piece of OTS-treated glass (5mm $\times$ 5mm). 1 μL of 5CB was dispensed onto each grid and the excess LC was removed by using a 10 μL syringe (Fisher) in order to obtain a uniformly filled grid. The OTS-treated glass supporting the gold specimen grid was placed into the chamber (volume of 0.5 ml) of a flow cell prepared by sandwiching a PDMS gasket (2mm thick) between two glass slides. The flow cell possessed an inlet and outlet for exchanging the solution within the flow cell. To obtain a desired concentration of surfactant inside the chamber of the flow cell, 10 ml of surfactant solution was flowed through it.

Optical Characterization of LC Ordering

The orientation of 5CB within each specimen grid was determined by using plane-polarized light in transmission mode on an Olympus BX60 microscope with crossed polarizers. The optical cells were placed on a rotating stage located between the polarizers. Orthoscopic examinations were performed with the source light intensity set to 50% of full illumination and the aperture set to 10% in order to collimate the incident light. Homeotropic alignments of the LCs were determined by first observing the absence of transmitted light during a 360° rotation of the sample. Insertion of a condenser below the stage and a Bertrand lens above the stage allowed conoscopic examination of the optical cell. An interference pattern consisting of two crossed isogyres indicated homeotropic alignment. In-plane birefringence was indicated by the presence of brush textures, typically four-brush textures emanating from a line defect, when the sample was viewed between crossed polarizers.^{9,10} All images were captured using a digital camera (Olympus C-2040 Zoom) mounted on the microscope and set to an f-stop of 2.6 and a shutter speed of 1/320 sec. All images shown in this paper correspond to the equilibrium alignment of the LC.

Measurement of Optical Retardance

In order to precisely quantify the orientations of LCs anchored at aqueous-LC interfaces, we measured the optical retardance of LC hosted within the specimen grids using a CRI PolScope (CRI, Woburn, MA) (a retardance mapping instrument), which can measure optical retardance with a precision of $\pm 0.2\text{nm}$. The retardance values reported in this paper are the average obtained within four squares of the gold specimen grid used to host the LC. For a thin film of nematic LC with strong homeotropic anchoring ($\theta_1 = 0^\circ$) at the OTS-treated glass interface and a tilt of angle of θ_2 away from the surface normal at the aqueous-LC interface, the tilt of LC across the film varies linearly with position so as to minimize the elastic energy of the LC film (assuming splay and bend elastic constants of the LC to be equal²⁵). This result permits the establishment of a relationship between optical retardance (Δr) of the film of LC and the tilt of the director at the aqueous-LC interface (θ_s), namely 3

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

where n_o and n_e are the indices of refraction parallel (so-called extraordinary refractive index) and perpendicular (ordinary refractive index) to the optical axis of the LC, respectively, and θ_S is the tilt angle of LC measured relative to the surface normal. The retardance values measured using the PolScope were used to calculate the tilt angle of LC at the aqueous-LC interface by numerically solving equation (1). The indices of refraction of 5CB were taken to be $n_o = 1.711$ and $n_e = 1.5296$ ($\lambda = 632$ nm at 25°C).⁴

Image Analysis

Using Adobe Photoshop, each polarized light micrograph of LC was cropped to avoid analysis of the region of LC within $10\mu\text{m}$ of the gold grid. Image J (<http://rsb.info.nih.gov/ij/>) was used to convert the cropped color images into black and white contrast. The fraction of the LC interfacial area corresponding to homeotropic anchoring was calculated by evaluation of the area that appeared black in each image.

Results and Discussion

We first sought to determine the phase behavior of monolayers of DTAB at the aqueous-LC interface that were in equilibrium with a bulk aqueous solution of DTAB. In a typical experiment described in this paper, a thin film of nematic 5CB or TL205 with an approximately flat interface was obtained by hosting the LC in the pores ($283\mu\text{m} \times 283\mu\text{m}$) of a $20\mu\text{m}$ -thick gold electron microscopy grid (Figure 1A). The LC-filled grids were supported on a glass microscope slide treated with octadecyltrichlorosilane (OTS). The OTS anchors both nematic 5CB and TL205 phases in an orientation that is perpendicular (homeotropic) to the LC-glass interface.² 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, the aqueous-LC interface thus obtained was equilibrated with various concentrations of the cationic surfactant DTAB dissolved in the bulk of an aqueous electrolyte solution (see Methods section for details). The resulting alignment of the LC at the aqueous interface was quantified by measurement of the optical retardance of the LC (detailed below).

Figure 1B–F shows polarized light micrographs of nematic 5CB equilibrated against increasing concentrations of the surfactant DTAB in presence of 1M NaBr. The system was equilibrated for at least 12hrs at each bulk concentration of surfactant prior to capturing the images. In these initial experiments, we dissolved 1M NaBr in the bulk aqueous solution as we sought to screen electrostatic interactions arising from the presence of the charged head groups of DTAB at the interface (see below for results and a discussion of the effects of electrolyte concentration). Prior to surfactant adsorption, the optical appearance of 5CB in contact with the aqueous electrolyte solution was observed to be bright, with pale green and pink interference colors (Figure 1B). As reported previously,² these interference colors are indicative of planar anchoring (aligned parallel or very close to parallel to the interface) of LC in contact with the aqueous electrolyte solution. Planar anchoring of 5CB at the aqueous-LC interface and perpendicular (or, so-called homeotropic) anchoring at the OTS-coated glass interface induces a splay and bend distortion into the film of LC (see cartoon in Figure 1A). We note that elastic energy stored in this distorted initial state of the LC plays an important role in directing the interfacial behavior of the surfactants. We also note that all conclusions regarding the orientations of the LCs reported here are supported by quantitative measurements of optical retardance of the LC, which we report towards the end of this paper (see Figure 7 and associated discussion). When low concentrations of DTAB (0.01mM) were introduced into the bulk aqueous phase, no significant change in the optical appearance of the LC was observed (Figure 1C) relative to that documented in the absence of surfactant (Figure 1B). However, at a bulk concentration of DTAB of 0.04mM, bright domains surrounded by contiguous dark regions were observed to form at the aqueous-LC interface

(Figure 1D). These bright domains were found to be stable for at least a week. The dark regions were determined to correspond to homeotropic anchoring of the LC at the aqueous-LC interface. A past study⁹ of the assembly of fluorescently labeled phospholipid at the aqueous-LC interface observed that domains of LC with a parallel orientation at the interface corresponded to lipid-lean regions whereas the surrounding homeotropic region corresponded to lipid-rich areas of the interface. Furthermore, previous studies^{1, 2, 26} of surfactant adsorption at the aqueous-LC interface have demonstrated that surfactant-saturated interfaces cause homeotropic anchoring of 5CB. These prior observations, when combined with the results in Figure 1, in which we show a decrease in the number and size of bright (planar) domains with increase in bulk phase surfactant concentration (Figure 1E), lead us to conclude that the black (homeotropic) regions correspond to high interfacial concentrations of DTAB whereas the bright regions correspond to low interfacial concentrations of DTAB (with planar alignment of the LC). We note that these domains of DTAB formed at the aqueous-LC interface are in equilibrium with the surfactant present in the bulk aqueous phase. At a bulk surfactant concentration of 0.1mM, the interface of the LC appeared uniformly dark (homeotropic, Figure 1F). The formation of domains, as shown in Figure 1D and E, was found to be a reversible phenomenon. As the concentration of DTAB was decreased from 0.1mM to 0mM, an anchoring transition from homeotropic to planar, with domains at intermediate concentrations, was observed. Qualitatively similar DTAB domains were observed to form at the interface between nematic TL205 and an aqueous phase of DTAB in the presence of 1M NaBr, and also when using the anionic surfactant sodium dodecyl sulfate (SDS, for both LCs). In summary, the results above when combined, reveal that amphiphilic molecules adsorbed at the aqueous-LC interface can phase separate to form domains while in dynamic equilibrium with a coexisting bulk aqueous solution of the amphiphiles.

In order to provide insight into the factors that control the formation of surfactant domains at the interfaces of the 5CB and TL205, we next performed an experiment to determine if nematic ordering of the LCs plays a role in the phenomenon. To this end, we investigated the temperature-dependence of the interfacial phase behavior of the surfactant monolayers reported in Figure 1. In these experiments, we exploited the relatively low temperature at which nematic 5CB undergoes a bulk phase transition to an isotropic oil ($T_{NI} = 33^{\circ}\text{C}$)⁹ and our observation that the patterned orientational domains of LC of the type evident in Figure 2A and 2B are long-lived. In particular, we observed the LC domains corresponding to surfactant-lean regions of the interface of 5CB at 32°C to be invariant over periods of at least 12 hrs. We hypothesized that if surfactant domains persisted during a transient (~2hr) excursion of temperature into the isotropic phase of 5CB (corresponding to the case where the domains are not caused by the nematic order of the LC), the initial orientational pattern of the LC would be recovered upon cooling into the nematic phase. Inspection of Figure 2, however, reveals that upon heating of the nematic 5CB (Figure 2A and B) into the isotropic phase (Figure 2C & D) at 34°C for 2 hrs, and subsequent cooling into the nematic phase, although patterned domains of LC reform, the patterns are different from those observed prior to heating into the isotropic phase (Figure 2E & F). These observations suggest that the surfactant domains disappear upon heating 5CB above T_{IN} . Although temperature can, in general, influence the phase behavior of surfactant monolayers and solubility of surfactant within the bulk LC,^{27, 28} the close coincidence of the temperature of the bulk nematic-to-isotropic phase transition of the 5CB and the change in surfactant domain structure suggests that the two are closely coupled. This conclusion is further supported by our observation that DTAB domains formed at the aqueous-TL205 interface did not disappear upon heating of the system to 34°C (T_{IN} of TL205 = 86°C). We make two additional comments regarding this experiment. First, these results are consistent with our prior observations in which we observed domains of a fluorescently-labeled phospholipid adsorbed irreversibly at the aqueous-LC interface to disappear upon heating of 5CB approximately 2°C above its T_{IN} .⁹

The absence of straightforward methods to fluorescently label DTAB (and likely changes in properties associated with labeling of small molecules such as DTAB) prevents the use of fluorescence microscopy to directly observe the loss interfacial domains of surfactant upon heating of the 5CB into the isotropic phase. Second, we note that recent studies by Bahr^{29, 30} have demonstrated that near-surface, nematic ordering can persist at surfactant-laden interfaces of 8CB when it is heated above the bulk T_{IN} . Although this type of near-surface interfacial ordering might influence the surface phase behavior of surfactants, experiments reported below suggest that, if this phenomenon is present in our experimental system, it does not drive the interfacial phase separation of the surfactants reported in this paper.

To provide further insight into the origin of the phase-separated domains of surfactant presented in Figure 1 and Figure 2, we have developed a simple thermodynamic model that incorporates two possible mechanisms that couple the order of the LC to the lateral organization of surfactants at the interface of the LC. The first mechanism involves the influence of the nematic order of the LC on effective attractive interactions between the surfactant tails, similar to the well-known lower solubility of alkanes in nematic phases as compared to isotropic phases.^{31, 32} This physical phenomenon will promote segregation of DTAB molecules at the aqueous-LC interface, and it is incorporated in our thermodynamic model through the use of an interaction parameter (defined below in Eq. 5). The second mechanism promoting formation of interfacial domains of surfactant in our model considers the influence of the nematic elasticity of the film of LC that supports the surfactant monolayer. This mechanism captures the tendency of the LC (being an elastic material) to minimize its distortion. In brief, a film of LC with an initial state that contains a distortion will promote a lateral interfacial distribution of surfactant that leads to the anchoring of the LC in a manner that minimizes the distortion and thus elastic energy stored in the LC. As shown below, when certain conditions are met, the elastic energy stored in a film of LC can be minimized by distributing the surfactant non-uniformly across the interface of the LC (i.e., through formation of domains). Below we describe the simple thermodynamic model that captures the potential influence of both of the above-described mechanisms on the phase behavior of DTAB at the aqueous-LC interface, and then we compare the predictions of the model to additional experimental observations. Because DTAB is soluble in the bulk aqueous phase, within the framework of our model, we calculate the interfacial concentration of DTAB by equating the chemical potential of DTAB in the bulk aqueous phase to the chemical potential of DTAB adsorbed at the aqueous-LC interface.

$$\mu_{DTAB}^{Sol} = \mu_{DTAB}^{Interface} \quad (2)$$

The chemical potential of DTAB dissolved in aqueous electrolyte (1M NaBr) at concentrations less than CMC is described as,³³

$$\mu_{DTAB}^{Sol} = \mu_0^{Sol} + RT \ln y \quad (3)$$

where μ_0^{Sol} is the standard state chemical potential of DTAB at infinite dilution and y is the mole fraction of DTAB in the bulk aqueous solution. In order to relate the chemical potential of DTAB at the aqueous-LC interface to the interfacial state of the DTAB, we write the free energy of the system to include the entropy and enthalpy of mixing of DTAB at the interface and the free energy of the film of LC, namely

$$\Delta G_{\text{Total}} = \Delta S_{\text{Mixing}} + \Delta H_{\text{Mixing}} + \Delta G_{\text{LC}} \quad (4)$$

where ΔG_{LC} is the free energy of the film of LC, which includes the elastic energy due to distortion in the LC ($\Delta G_{\text{elastic}}$) as well as the surface anchoring energy arising from a possible deviation of the director of the LC from the easy axis ($\Delta G_{\text{anchoring}}$). This model differs from classical models of phase separation of surfactant monolayers formed at the interfaces of isotropic materials by the incorporation of ΔG_{LC} ³⁴. For a film of LC supported on an OTS-treated glass slide that causes strong perpendicular anchoring of the director, the total free energy given in Eq. 4 can be written as,⁹

$$\Delta G_{\text{Total}} = \underbrace{[n_1 \ln x + (N - n_1) \ln(1 - x)]}_{\Delta S_{\text{mixing}}} + \underbrace{\chi N x(1 - x)}_{\Delta H_{\text{mixing}}} * K_B T + \left[\underbrace{\frac{1}{2} \frac{K(T)}{D} \theta_s^2}_{\Delta G_{\text{elastic}}} + \underbrace{\frac{1}{2} W \sin^2(\theta_s - \varphi(x))}_{\Delta G_{\text{anchoring}}} \right] NA^* \quad (5)$$

where n_1 is the number of molecules of surfactant at the interface, x is the fraction of saturation monolayer coverage, N is the number of surfactants on the interface at saturation, θ_s is the tilt angle of the LC at the interface, φ is the easy angle of the LC (both θ_s and φ being measured from the surface normal), A^* is the area per surfactant molecule at saturation coverage, χ is a pair-wise interaction parameter for surfactant molecules at the interface, $K(T)$ is the temperature-dependent elastic constant of the LC (assuming splay and bend elastic constants to be equal), W is the anchoring strength coefficient and D is the thickness of the film of LC. For simplicity, we evaluate the model in this paper by assuming that (1) the surfactant-decorated interface of the LC provides strong anchoring to the LC ($\theta = \varphi$) and (2) that there is an abrupt change in the easy angle (φ) of the LC from 90° to 0° when a critical monolayer coverage of the surfactant (x_c) at the interface is achieved. The abrupt nature of the orientational transition is supported by experimental measurements discussed below in the context of Figure 7. For convenience, the change in the easy angle is specified by a sigmoidal function

$$\varphi = \frac{\pi}{2} \left[1 - \frac{1}{1 + \exp(-1000(x - x_c))} \right] \quad (6)$$

The parameter x_c sets the interfacial surfactant concentration at which the LC assumes homeotropic alignment. Because past studies have (i) established that the interaction of LCs with surfactant tails largely dictates the orientations of LC at surfactant-laden interfaces of the type reported on in this paper,^{4, 26} (ii) determined that dilaurylphosphatidylcholine (L-DLPC)¹⁰ causes homeotropic orientations of 5CB at an average density of $50 \text{ \AA}^2/\text{molecule}$, and (iii) established that the saturation coverage of DTAB at oil-water interfaces is $\sim 40 \text{ \AA}^2/\text{molecule}$,³⁵ we estimate x_c for DTAB to be ~ 0.8 . We note that the qualitative predictions of our model do not rely heavily on the exact value of x_c . By equating the chemical potential of DTAB in the aqueous phase (Eq. 3) to the chemical potential of DTAB at the aqueous-LC interface (derived from Eq. 5), a relationship is obtained that relates the normalized bulk

surfactant mole fraction (y/y_o) and the surface fraction of surfactant at the aqueous-LC interface (x), namely,

$$\ln(y/y_o) = \ln x + \chi(1-x)^2 + \frac{\pi^2 K(T) A^*}{8 D k_B T} \left(\left\{ \frac{\exp(-1000(x-x_c))}{1 + \exp(-1000(x-x_c))} \right\}^2 - 2000(1-x) \frac{\exp^2(-1000(x-x_c))}{(1 + \exp(-1000(x-x_c)))^3} \right) \quad (10)$$

where $y_o = (\mu_0^{\text{Interface}} - \mu_0^{\text{Sol}})/K_B T$. The prefactor $\frac{\pi^2 K A^*}{8 D k_B T}$ in Eq. (10) is the dimensionless elastic energy²⁵. For a 20 μm -thick (D) film of nematic LC with elastic constant $K = 10\text{pN}$ ³⁶ (assuming splay and bend elastic constants to be equal) at room temperature (298 $^\circ\text{K}$) and $A^* = 40 \text{ \AA}^2/\text{molecule}$ ¹⁰, we estimated the dimensionless elastic energy to be $\sim 0.6 \times 10^{-4}$.

In Figure 3, we report predictions of the above described model. Figure 3A shows a plot of surface fraction of surfactant (x) as a function of the normalized bulk surfactant concentration ($\ln(y/y_o)$), as given by equation (10), for different LC film thicknesses and $\chi = 2$. We choose $\chi = 2$ because this value of χ does not induce phase separation when ΔG_{LC} is set to zero. By choosing $\chi = 2$, we test whether nematic elasticity can induce phase separation in adsorbed surfactant monolayers in the absence of other mechanisms leading to phase separation.

As shown in Figure 3A, when $\Delta G_{\text{LC}} = 0$, there exists only one surface concentration of surfactant for each bulk phase surfactant concentration. However, when ΔG_{LC} is non-zero (for the three LC film thicknesses in Fig 3A), we calculate that more than one concentration of surfactant can co-exist on the interface of the LC for a given bulk phase surfactant concentration (see arrows on line 1 for the 5 μm -thick LC film in Figure 3A). These results demonstrate that the elastic energy stored in the film of LC can drive lateral phase separation in Gibbs monolayers of surfactants under conditions that do not lead to phase separation in absence of nematic elasticity. Figure 3B shows the phase diagram for the adsorbed surfactant as a function of normalized bulk phase surfactant concentration ($\ln(y/y_o)$) for the 20 μm -thick film of LC. The phase diagram shows that for low surfactant concentrations in the aqueous phase, there exists a unique surface concentration of surfactant and that the corresponding orientation of LC is parallel to the interface (planar anchoring). Similarly, at high values of surfactant concentration in the bulk aqueous phase, there also exists a unique value for the surface concentration of surfactant; the orientation of the LC corresponding to that surface concentration of surfactant, however, is homeotropic. At intermediate concentrations of surfactant in the bulk solution, there exists a range within which more than one surface concentration of surfactant coexists with each bulk solution concentration, and thus phase-separated domains of surfactant are predicted. We emphasize that the key prediction that emerges from our model is that phase separation in Gibbs monolayers of surfactant at the aqueous-LC interface can be induced by nematic elasticity of LC. We caution, however, that the model is a simple one and it is not expected to provide quantitative descriptions of the behavior of the experimental system reported in this paper. Despite the simple nature of the model, it does provide a number of qualitative predictions that we compare to experimental observations below.

The experiments that we performed to test the qualitative predictions of the model revolved around the predicted effects of thickness of the LC film on the interfacial phase behavior of

the surfactants. Because the contribution of the interaction parameter χ to the phase behavior of the surfactant-laden interface is independent of thickness of the film of LC, we designed experiments to selectively manipulate the elastic energy stored in the LC by varying the LC film thickness. In these experiments, we also sought to demonstrate the generality of the phenomenon by using the second nematic LC, TL205. As shown in Figure 4, DTAB was adsorbed from bulk aqueous solutions onto the aqueous-TL205 interface of 5, 20 and 40 μm -thick films of the LC at room temperature. The system was equilibrated for at least 12hrs at each concentration of DTAB, and then the optical micrographs were recorded. Below we discuss the interfacial phase behavior evident in Figure 4 in light of the predictions of our model.

The first prediction of the model that is tested by the experiments in Figure 4 relates to the effects of the thickness of the LC film on the onset of phase separation of the surfactant monolayer. The model predicts that phase separated domains of surfactants will be observed at a lower bulk concentrations of surfactant for thinner films of LC (see lines marked 1, 2 and 3 in Figure 3A). Inspection of Figure 4 reveals that when the LC films were equilibrated with aqueous 1M NaBr (with no DTAB), all three LC films with different thicknesses appeared bright, although with different interference colors. The different interference colors observed for the three films are due to the increase in optical retardance with film thickness. When LC films that differed in thickness were contacted with a solution of 30 μM DTAB, domains were observed to form on the 5 μm -thick LC film but not on the 20 and 40 μm -thick LC films, even after 12hrs of equilibration. With an increase in DTAB concentration, domains did form on the thicker LC films (see Figure 4 corresponding to 35 μM and 40 μM DTAB concentrations). These experimental observations are consistent with the first prediction of our model: the higher elastic energy stored in thin films of LC will drive the interfacial phase separation of the surfactant at lower bulk surfactant concentrations.

A second prediction of our model is that coexistence of phase separated domains of surfactant at the interface of the LC will persist over a wider window of bulk surfactant concentration when using thinner LC films. Inspection of Figure 4 reveals this prediction to also be realized in our experimental measurements. For 5 and 20 μm -thick films of LC, we observe the domains to coexist over a concentration window of 10 μM (between 30 to 40 μM and 35 to 45 μM , respectively) whereas for a 40 μm -thick film of LC domains exist only for a concentration window of 5 μM (between 40 to 45 μM). This trend in the experimental data is further illustrated in Figure 5 where the fraction of the LC interfacial area corresponding to homeotropic orientation is plotted as a function of the surfactant concentration in the bulk of the aqueous solution. With reference to the two phase region shown in Figure 3A, we also point out that, for the same bulk phase concentration, the surface concentration of surfactants in the surfactant-rich domains increases with increase in elastic energy (see arrows on line 2 in Figure 3A).

A third prediction of our model is that uniform homeotropic orientation across the entire interfacial area of the LC will be observed at lower bulk phase surfactant concentrations when using thinner films of LC (line 3 in Figure 3A shows that 5 and 20 μm -thick films of LC have turned homeotropic, whereas the 40 μm -thick film still has domains for the same bulk phase surfactant concentration). Inspection of Figure 4 reveals that as the concentration of DTAB was increased to 45 μM , we observed the 5 μm -thick film of LC to turn completely homeotropic, whereas domains still persisted on the 20 and 40 μm -thick films of LC. At a DTAB concentration of 50 μM , all three films turned completely homeotropic. These experimental observations are, therefore, also qualitatively consistent with the model predictions.

In summary, our experimental observations and model predictions, when combined, provide strong evidence that the elastic energy stored in a film of LC can direct the formation of domains of soluble amphiphiles at the aqueous-LC interface. Because the soluble amphiphiles used in our study are ionic surfactants, and because past studies have shown the electrostatic repulsion amongst ionic amphiphiles with like-charges can suppress phase separation at interfaces³⁷, we predicted that a reduction in the electrolyte concentration in the bulk aqueous phase would introduce electrostatic interactions between adsorbed DTAB molecules that would suppress phase separation induced by the LC. Figure 6 shows polarized light micrographs of 5CB in contact with aqueous solutions of DTAB in the absence of electrolyte added to the aqueous phase. We make two observations regarding these measurements. First, it is evident that patterned orientational domains of LC are not observed in the absence of added electrolyte. Second, we observed a continuous progression of interference colors toward low order (according to a Michel-Levy chart³⁸) with increase in DTAB concentration. We quantified the orientation of the LC corresponding to the continuous orientational transition observed in the absence of added electrolyte by measurement of the retardance of the LC films at each surfactant concentration (Figure 7). As shown in Figure 7, a continuous change in tilt angle was observed for DTAB solutions containing no added electrolyte or 100mM NaBr. Only in the case of DTAB solutions containing 1M NaBr was a discontinuous orientation of the LC, corresponding to interfacial phase separation, observed. As noted above, the abrupt change in orientation of the LC observed in these experimental measurements influenced our choice of the sigmoidal function used in Eq. 6. The observation of interfacial domains when using 1M NaBr but not at lower concentrations of salt (0mM and 100mM) indicates that phase separation of the surfactant monolayers induced by the nematic elasticity of the LC is opposed by electrostatic interactions between the surfactant molecules, thus providing a simple balance of opposing forces by which to design interfaces that permit manipulation of the phase behavior of charged amphiphiles at LC interfaces.

We end this paper by commenting that patterned orientations of LCs at the aqueous-LC interface have been observed in a number of past studies, but that the origins of these observations have not been completely understood.^{4-8, 18} The present study provides insight into the underlying mechanism of lateral patterning of amphiphiles at the aqueous-LC interface for the important case where the amphiphile-laden interfaces are in dynamic equilibrium with a bulk aqueous phase of the amphiphiles. Our results demonstrate that the elasticity of the LC can play an important role in directing the interfacial organization of water-soluble surfactants. Whereas a number of prior studies dealing with adsorbed monolayers of soluble surfactants have assumed a uniform distribution of surfactant across the aqueous-LC interface,^{2, 18, 20-23} the experimental observations reported in this study demonstrate that the elastic energy stored in micrometer-scale LC systems can lead to inhomogeneous distributions of soluble surfactants. In addition, we demonstrate control over the lateral organization of surfactants at the aqueous-LC interface by manipulating the elastic energy stored in a thin film of LC, the bulk phase surfactant and electrolyte concentrations. In a technological context, the present study in combination with our previous study⁹ with insoluble amphiphiles, suggests new principles for the design of interfaces at which the molecular assemblies can be placed under active control. Active control of the lateral organization of molecular assemblies at interfaces is relevant to a range of interfacial phenomena, including cell-receptor interactions where spreading and focal adhesion dynamics of cells are regulated by the lateral organization of binding groups³⁹ and in the context of multivalent ligand-receptor binding⁴⁰ (such as the interaction of carbohydrate moieties of five gangliosides GM₁ with cholera toxin⁴¹). Because past studies²⁵ have shown that the ordering of LCs can be readily tuned by using weak electric and magnetic fields, temperature, stress (flexoelectric effects) and contacting surfaces, and because our studies demonstrate that the organization of molecular assemblies at the

aqueous-LC interfaces are coupled to the ordering of LCs, the results presented in this paper point the way towards methods that will enable the realization of materials that will permit active control of the interfacial organization of molecular assemblies.

Acknowledgments

This research was supported by the National Science Foundation (DMR-0520527, CTS-0553760), and the National Institutes of Health (CA108467).

References

1. Lockwood NA, Gupta JK, Abbott NL. *Surface Science Reports*. 2008; 63:255–293.
2. Brake JM, Abbott NL. *Langmuir*. 2002; 16:6101–6109.
3. Brake JM, Mezera AD, Abbott NL. *Langmuir*. 2003; 21:8629–8637.
4. Lockwood NA, de Pablo JJ, Abbott NL. *Langmuir*. 2005; 21:6805–6814. [PubMed: 16008390]
5. Price AD, Schwartz DK. *Journal of Physical Chemistry B*. 2007; 111:1007–1015.
6. Brake JM, Daschner MK, Luk YY, Abbott NL. *Science*. 2003; 302:2094–2097. [PubMed: 14684814]
7. Brake J, Daschner M, Abbott N. *Langmuir*. 2005; 21:2218–2228. [PubMed: 15752009]
8. Brake JM, Abbott NL. *Langmuir*. 2007; 23:8497–8507. [PubMed: 17595119]
9. Gupta JK, Meli MV, Teren S, Abbott NL. *Physical Review Letters*. 2008; 100:048301–4. [PubMed: 18352339]
10. Meli MV, Lin IH, Abbott NL. *Journal of the American Chemical Society*. 2008; 130:4326–33. [PubMed: 18335929]
11. Park JS, Abbott NL. *Advanced Materials*. 2008; 20:1185–1190.
12. Tjijto E, et al. *Nano Letters*. 2006; 6:2243–2248. [PubMed: 17034091]
13. Kinsinger MI, Sun B, Abbott NL, Lynn DM. *Advanced Materials*. 2007; 19:4208–4212.
14. Lockwood NA, Cadwell KD, Caruso F, Abbott NL. *Advanced Materials*. 2006; 18:850–854.
15. Gupta JK, et al. *Langmuir*. 2008; 24:5534–5542. [PubMed: 18419143]
16. Sivakumar S, Gupta JK, Abbott NL, Caruso F. *Chem Mater*. 2008; 20:2063–2065.
17. Lockwood NA, et al. *Advanced Functional Materials*. 2006; 16:618–624.
18. Price AD, Schwartz DK. *Journal of the American Chemical Society*. 2008; 130:8188–8194. [PubMed: 18528984]
19. Folkers JP, Laibinis PE, Whitesides GM, Deutch J. *Journal of Physical Chemistry*. 1994; 98:563–571.
20. Poulin P, Stark H, Lubensky TC, Weitz DA. *Science*. 1997; 275:1770–1773. [PubMed: 9065396]
21. Khullar S, Zhou CF, Feng JJ. *Physical Review Letters*. 2007; 99:237802–5. [PubMed: 18233413]
22. Poulin P, Bibette J. *Physical Review Letters*. 1997; 79:3290–3293.
23. Mondain-Monval O, Poulin P. *Journal of Physics-Condensed Matter*. 2004; 16:S1873–S1885.
24. Mullally MK, Doyle MJ, Marangoni DG. *Colloid and Polymer Science*. 2004; 283:335–339.
25. de Gennes, PG.; Prost, J. *The Physics of Liquid Crystals*. Oxford University Press; London: 1994.
26. Brake JM, Mezera AD, Abbott NL. *Langmuir*. 2003; 16:6436–6442.
27. Hayami Y, et al. *Journal of Colloid and Interface Science*. 1995; 172:142–146.
28. Uredat S, Findenegg GH. *Langmuir*. 1999; 15:1108–1114.
29. Bahr C. *Physical Review E*. 2006; 73:030702–5.
30. Bahr C. *Physical Review Letters*. 2007; 99:057801–4. [PubMed: 17930793]
31. Chow LC, Martire DE. *Journal of Physical Chemistry*. 1971; 75:2005–2015.
32. Kempe MD, et al. *Nature Materials*. 2004; 3:177–182.
33. Hiemenz, PC.; Rajagopalan, R. *Principles of Colloid and Surface Chemistry*. Marcel Dekker, Inc; New York: 1997.
34. Ferri JK, Stebe KJ. *Journal of Colloid and Interface Science*. 1999; 209:1–9. [PubMed: 9878129]

35. Medrzycka K, Zwierzykowski W. *Journal of Colloid and Interface Science*. 2000; 230:67–72. [PubMed: 10998289]
36. Simoes M, Simeao DS. *Physical Review E*. 2006; 73:062702–6.
37. Kaganer VM, Mohwald H, Dutta P. *Reviews of Modern Physics*. 1999; 71:779–819.
38. Robinson, PC.; Davidson, MW. <http://www.microscopyu.com/articles/polarized/michel-levy.html>
39. Cavalcanti-Adam EA, et al. *Biophysical Journal*. 2007; 92:2964–2974. [PubMed: 17277192]
40. Hlavacek WS, Posner RG, Perelson AS. *Biophysical Journal*. 1999; 76:3031–3043. [PubMed: 10354429]
41. Pukin AV, et al. *Chembiochem*. 2007; 8:1500–1503. [PubMed: 17625801]

Figure 1.

(A) Schematic illustration of the experimental system used to study the adsorption of surfactant at the aqueous-LC interface. The cartoon in (A) also illustrates the lateral distribution of surfactant and patterned orientation of 5CB corresponding to (D) & (E). (B–F) Polarized light micrographs (cross polars) of nematic 5CB hosted in a gold grid and equilibrated with aqueous solutions of 0, 10, 40, 60, 100 μM concentrations of DTAB (each containing 1M NaBr), respectively. Scale bar is 150 μm

Figure 2.

Temperature dependent phase behavior of Gibbs monolayer of DTAB at the aqueous-5CB interface: (A) Polarized light micrograph of DTAB-laden 5CB interface in contact with a 40 μ M DTAB solution at 32°C, (B) is the corresponding phase contrast image. (C) & (D) shows samples in A and B heated to 34°C for 2 hrs. (E) & (F) shows the same sample cooled back to 32°C. Scale bar is 75 μ m.

Figure 3.

(A) Plot of mole fraction of surfactant at the aqueous-LC interface (x) versus normalized bulk phase surfactant concentration $\ln(y/y_0)$ for 5, 20 and 40 μm thick films of LC and for the case when there is no elastic energy present. (B) Phase diagram for DTAB at the aqueous-5CB interface for a film thickness of 20 μm .

Figure 4. Polarized light micrographs (cross polars) of aqueous-TL205 interface equilibrated with various bulk phase concentrations of the surfactant DTAB for three LC film thicknesses: 5, 20 & 40 μm . Scale bar is 75 μm .

Figure 5. Plot of the area fraction of the aqueous-TL205 interface exhibiting a planar orientation, as a function of the bulk phase surfactant concentration for 5, 20 and 40 μm thick films of LC. The surfactant DTAB is adsorbed in presence of 1M NaBr.

Figure 6. Polarized light micrograph (cross polars) of nematic 5CB hosted in a gold grid and equilibrated with solutions containing (A) 0 mM, (B) 1.7 mM, (C) 1.9 mM, (D) 2.1 mM, (E) 2.3 mM, (F) 2.7 mM, (G) 3.0 mM, and (H) 3.2 mM of DTAB in absence of added salt. Scale bar is 150 μm .

Figure 7. Quantification of the tilt angle of 5CB at the aqueous-5CB interface (measured relative to the interface normal) in absence/presence of 100mM and 1M NaBr.