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Influence of Specific Anions on the Orientational Ordering of Thermotropic Liquid Crystals at Aqueous Interfaces

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Abstract

We report that specific anions (of sodium salts) added to aqueous phases at molar concentrations can trigger rapid, orientational ordering transitions in water-immiscible, thermotropic liquid crystals (LCs; e.g., nematic phase of 4'-pentyl-4-cyanobiphenyl, 5CB) contacting the aqueous phases. Anions classified as chaotropic, specifically iodide, perchlorate and thiocyanate, cause 5CB to undergo continuous, concentration-dependent transitions from planar to homeotropic (perpendicular) orientations at LC-aqueous interfaces within 20 s of addition of the anions. In contrast, anions classified as relatively more kosmotropic in nature (fluoride, sulfate, phosphate, acetate, chloride, nitrate, bromide, and chlorate) do not perturb the LC orientation from that observed without added salts (i.e., planar orientation). Surface pressure-area isotherms of Langmuir films of 5CB supported on aqueous salt solutions reveal ion-specific effects ranking in a manner similar to the LC ordering transitions. Specifically, chaotropic salts stabilized monolayers of 5CB to higher surface pressures and areal densities (12.6 mN/m at 27 Å²/molec. for NaClO₄) and thus smaller molecular tilt angles (30° from the surface normal for NaClO₄) than kosmotropic salts (5.0 mN/m at 38 Å²/molec. with a corresponding tilt angle of 53° for NaCl). These results and others reported herein suggest that anion-specific interactions with 5CB monolayers lead to bulk LC ordering transitions. Support for the proposition that these ion-specific interactions involve the nitrile group was obtained by using a second LC with nitrile groups (E7; ion-specific effects similar to 5CB were observed) and a third LC with fluorine-substituted aromatic groups (TL205; weak dipole and no ion-specific effects were measured). Finally, we also establish that anion-induced orientational transitions in micrometer-thick LC films involve a change in the easy axis of the LC. Overall, these results provide new insights into ionic phenomena occurring at LC-aqueous interfaces, and reveal that the long-range ordering of LC oils can amplify ion-specific interactions at these interfaces into macroscopic ordering transitions.

Keywords

oil-water interfaces; liquid crystals; ordering transitions; specific anion effects; electrolytes; Hofmeister series; Langmuir films

Introduction

Ion-specific phenomena in colloidal and macromolecular systems have been reported for over 120 years (the original work of Franz Hofmeister from 1888 is translated into English in reference 1).¹ At elevated concentrations, in particular, ion-specific effects are evident in

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Supporting Information Available. Experimental procedures. Calculation of tilt angles of LCs from measurements of optical retardance. Table S1, S2. Figures S1, S2, S3, S4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

a wide variety of biological and physiochemical phenomena^{2–6} including measurements of protein stability,^{1, 7–10} micelle formation,^{10–13} polymer behavior,^{14–16} and colloidal aggregation.^{17–20} In early studies, salts were ranked and classified according to their tendency to stabilize or destabilize the native structure of proteins, leading to the naming of some ions as kosmotropes (generally small and strongly hydrated ions) and others as chaotropes (large and weakly hydrated ions).⁵ Of relevance to the study reported in this paper, ion-specific effects are also evident in measurements of the surface tensions of aqueous salt solutions^{21–25} and interfacial tensions of oil-water interfaces.^{26–28} In particular, Jones and Ray reported the surface tensions of aqueous solutions to *decrease* upon addition of low concentrations of salts, a result that is noteworthy because it indicates a positive surface excess of ions according to the Gibbs adsorption equation.^{21, 22} Although characterization of the effects of salts on oil-water interfaces (free of surfactants and other stabilizing agents) is not as complete as that of the surface of water, past reports do describe (i) an increase in the oil-water interfacial tension for aqueous solutions containing kosmotropic anions and (ii) a pronounced decrease in interfacial tension for aqueous solutions containing chaotropic anions (iodide and thiocyanate, up to 0.8 M).^{26–28} Overall, the above-described measurements of surface and interfacial tensions highlight two key specific ion effects that are not yet fully understood: (i) the origin of the positive surface excess concentration of ions that can form at an interface between water and a second phase with a low dielectric constant (as indicated by a decrease in surface/interfacial tension), and (ii) the dependence of changes in surface/interfacial tension, in general, on ion-type.

Past efforts to provide insight into the above-described interfacial ionic phenomena include additional experiments^{23–25, 29–38} as well as simulations^{37–42} and theories.^{43–51} In particular, several theoretical descriptions have been reported in which the potential of an ion within an electrical double layer was modified to account for long-range screened image forces, changes in local Born energy of ions near interfaces (with the interfacial region described as possessing a continuously changing dielectric constant), dispersion forces, and other effects.^{43–51} Here we draw attention to two investigations of particular relevance to the current study, as each predicts the accumulation of ions at oil-water interfaces. Wang and coworkers modeled the interface between two dielectric phases using solution thermodynamics to calculate the solvent composition across the slightly miscible interfacial region. Their evaluation of the chemical potential of the ions included a contribution due to a local Born energy, which established a Galvani potential between the two phases due to the difference in ionic sizes.⁵⁰ Although this model predicts a positive surface excess of ions based on charge separation at the interface due to differences in Born energy of the ions, the values of the dielectric constants of the oils ($\epsilon_{\text{oil}} = 20$ or 40) that were used in the calculations were higher than most experimental values. More recently, dos Santos and Levin reported a model that shows good agreement with experimental measurements of the effects of salts on surface tensions *and* oil-water interfacial tensions.^{45–47} Their approach involved modification of the Poisson-Boltzmann equation at a sharp interface to account for long-range screened image forces, ionic polarizability, position-dependent Born self energies, a hydrophobic cavitation energy (i.e., the entropic energy penalty to create a cavity the size of the ion), and dispersion interactions.^{45–47}

Whereas the experimental studies and theories reported above deal with isotropic oils, the investigation reported in this paper moves to consider ionic phenomena at interfaces formed between *anisotropic* oils (i.e., thermotropic liquid crystals (LCs)) and aqueous phases. We show that the orientational ordering of micrometer-thick films of LCs equilibrated against aqueous solutions of sodium salts can be used to report specific ion effects at LC-water interfaces. The LC-aqueous interface is a particularly interesting type of oil-water interface with which to study interfacial ionic phenomena because past studies have demonstrated that the ordering of LCs at interfaces can report changes in the surface energy of the LC that are

on the order of $1\text{--}10\text{ }\mu\text{J}/\text{m}^2$.⁵² Of particular relevance to the study reported in this paper, we recently described the existence of ordering transitions triggered at the LC-aqueous interface caused by ions that form an electrical double layer on the LC-side of the interface.⁵³ This effect was seen when the interface was highly charged, which was achieved by equilibrating the LC films against aqueous solutions at high pH (ordering transitions were observed to begin at pH values greater than 9.4, with completely homeotropic orientations induced above pH 12.8).⁵³ In contrast to these past observations, the experimental observations reported in this paper were obtained at values of pH that were below pH 9 (in the aqueous phase). Our observations are, instead, generally consistent with the conclusions of past studies that have used infrared reflection-absorption spectroscopy to characterize ionic phenomena at lipid monolayers⁵⁴ and vibrational sum frequency spectroscopy to investigate surfactant-laden aqueous interfaces.⁵⁵ These studies have concluded that chaotropic anions but not kosmotropic anions accumulate and perturb the ordering of amphiphilic molecules at these interfaces. We end this introduction by noting that the interactions of LCs with aqueous electrolyte solutions, as investigated in the study reported in this paper, is of relevance to the broad topic of oil-water interfacial phenomena. It is also significant in guiding the design of dynamic and responsive LC interfaces for the sensing of chemical and biological molecules and interactions.^{52, 56–68}

Experimental Section

In a typical experiment, a film of nematic LC with an approximately flat interface was prepared by filling the pores ($283\text{ }\mu\text{m} \times 283\text{ }\mu\text{m}$) of a $20\text{ }\mu\text{m}$ -thick gold-coated specimen grid supported on a chemically functionalized glass slide (Figure 1a), as detailed elsewhere.^{69, 70} Briefly, glass microscope slides were cleaned according to published procedures⁶⁹ and coated with octadecyltrichlorosilane (OTS) to anchor the LC in an orientation that was perpendicular (homeotropic) to the LC-glass interface (Figure 1b).⁵⁷ Immersion of the supported LC-filled grid under ultrapure Milli-Q water ($18.2\text{ M}\Omega\cdot\text{cm}$) led to the formation of a stable interface between the aqueous phase and LC. In the experiments reported below, LC interfaces thus obtained were equilibrated against aqueous solutions of sodium salts. To quantify the orientation of the LC at the aqueous interface, the optical retardance of each LC film was measured using a Berek U-CTB compensator. The orientation of the LC at the aqueous interface was calculated from the measured retardance using methods described in Supporting Information (SI). Experimental information regarding the measurement of surface pressure-area isotherms of Langmuir monolayers of LC can also be found in SI. In some of the experiments described below, a 5CB-filled specimen grid was supported on a gold-coated glass microscope slide on which a monolayer was formed from hexadecanethiol (HSC16). The gold film was formed by physical vapor deposition at an oblique angle of incidence (64° measured from normal), which has been reported previously to lead to a uniform azimuthal orientation of the LC.⁷¹ As also reported previously, the HSC16 monolayer causes nematic 5CB to assume an orientation that is parallel to the surface (planar anchoring).⁷² Additional experimental details are presented in the SI.

Results and Discussion

In our first experiments, we contacted nematic phases of the nitrile-containing mesogen 5CB (Scheme 1a) with pure water or aqueous solutions containing either 2 M NaCl or 2 M NaClO_4 ($T=25\text{ }^\circ\text{C}$; with pH values of 6.4 ± 0.6 and 7.3 ± 0.8 , respectively, $n = 4$). Here we note in advance that the origin of trends in the orientations of LCs described below is not related to variations in pH. We comment also that we avoided the addition of buffering salts to the aqueous phase in order to minimize the number of ion types in our experimental system. Under white light illumination (crossed polars), the 5CB in contact with the pure

water exhibited interference colors (Figure 1a) consistent with an LC film that was anchored parallel to the aqueous interface (so-called planar anchoring) and perpendicular to the OTS-treated glass (homeotropic anchoring). The bulk of the LC film is thus splayed and bent to accommodate the hybrid boundary conditions (Figure 1b).⁵⁷ Upon contact with aqueous 2 M NaCl, the parallel orientation of 5CB at the aqueous interface was unchanged (Figure 1c–d). However, upon equilibration with 2 M NaClO₄, we observed the 5CB film to undergo an *immediate* transition (within 10–20 seconds) in optical appearance to a dark state (Figure 1e) that corresponded to homeotropic ordering at the aqueous interface (Figure 1f). Conoscopic imaging (inset in Figure 1e) was used to confirm the homeotropic alignment (see SI for details). Confirmation that the bulk phase behavior of the 5CB was not significantly affected by contact with the aqueous solutions containing molar concentrations of salts was obtained through measurements of the clearing temperature of the 5CB, i.e. the temperature at which 5CB becomes isotropic oil. The clearing temperature of pure 5CB was measured to be 35.1 ± 0.1 °C; the clearing temperature of 5CB equilibrated overnight with either pure water, aqueous 2 M NaCl, or aqueous 2 M NaClO₄ was 35.0 ± 0.1 °C, 35.0 ± 0.1 °C, and 34.9 ± 0.1 °C, respectively. Overall, the results in Figure 1 indicate that the presence of perchlorate anions in the aqueous phase can trigger an ordering transition in the LC whereas chloride ions do not measurably perturb the orientation of the LC.

We explored further the dependence of the ordering of the nematic 5CB on the identity of the anions by contacting aqueous solutions of other sodium salts with concentrations of 2 M (or less if limited by solubility) at 25 °C with nematic films of 5CB. We selected the salts according to a previously reported Hofmeister series of anions (Table 1).^{3, 5} We note here that there exist a number of Hofmeister series in the literature and that the order of the anions is dependent on the phenomenon studied.^{5, 11, 54} The salts listed in Table 1 are organized with kosmotropic anions at the top and chaotropic anions at the bottom. Inspection of Table 1 (Column 5) reveals the orientation of 5CB observed after 10 mins of equilibration of 5CB against each salt solution (the orientations did not change further after an additional hour of equilibration) to correlate with a Hofmeister series.¹¹ Specifically, contact of nematic 5CB with aqueous solutions of kosmotropic anions resulted in planar orientations of the LC whereas chaotropic anions caused tilted or homeotropic orientations. Here we note that an aqueous 2 M NaSCN solution led to a tilted orientation of 5CB, but that a concentration of 6 M caused homeotropic ordering in 5CB. In contrast to the behavior of NaSCN, kosmotropic salts that caused planar LC orientations at 2 M concentrations *still* caused planar orientations in LC films at much higher concentrations (see Table S1 in SI).

Figure 2 shows the effect of the concentration of a chaotropic anion (perchlorate) on the orientation of nematic 5CB (Figure 2, diamonds), determined via measurement of the optical retardance of the thin LC films. The observation of a continuous, concentration-dependent change in the tilt of the LC was common to all chaotropic anions in Table 1. In contrast, quantification of the tilt angle (measured relative to the surface normal) of the LC in contact with 0 – 2 M NaCl (Figure 2, squares) revealed no evidence of a change in orientation with increasing salt concentration. Here we emphasize again that the origins of the trends in orientations of the LC evident in Table 1 or Figure 2 are not variation in pH (for the data set reported in Table 1, the pH varied randomly between 6.1 and 8.9). As noted in the Introduction, in our past studies⁵³ we demonstrated that pH can impact the orientations of LC films through a mechanism that involves formation of an electrical double layer at the LC-aqueous interface (the LC is poled by the internal electric field generated in the diffuse part of the double layer extending into the LC). However, in those studies, pH values in excess of 12.8 were required to achieve sufficient charging of the interface to trigger a homeotropic orientation of the LC. In contrast, inspection of Table 1 reveals that solutions of chaotropic anions can trigger ordering transitions from solutions with pH values below 7 (e.g., pH 6.6 for NaSCN and pH 6.4 for NaI). At the solution conditions shown in Table 1,

therefore, we conclude that the influence of the ions on the ordering of the nematic LC is not due to an internal electric field associated with formation of an electrical double layer, a conclusion that is supported further by measurements reported below. Instead, our observations of the effects of specific ions on ordering transitions in the LC correlate directly with past measurements of interfacial tensions of isotropic oil-water systems^{26–28} that have revealed the formation of a positive surface excess concentration of chaotropic anions at oil-water interfaces. This close correlation with past measurements of oil-water interfacial tensions led us to hypothesize that the LC ordering transitions reported in Table 1 are triggered by interactions associated with a positive surface excess concentration of chaotropic anions in the interfacial region of the LC. In further support for this hypothesis, and as noted above, recent spectroscopic studies of amphiphile-decorated aqueous interfaces have reported that the accumulation of chaotropic anions at lipid- or surfactant-decorated interfaces can perturb the packing of the hydrocarbon tails of the amphiphiles.^{54, 55}

To provide further insight into the origins of the LC ordering transitions summarized in Table 1, we characterized the dynamics of the changes in orientation of nematic 5CB. Figure 3 shows a series of time-lapse images that reveal the dynamics of the LC orientation following the addition of 2 M NaClO₄ to an aqueous phase. Inspection of the interference colors of the LC in Figure 3 reveals the LC to undergo a continuous tilting transition to a uniformly dark (homeotropic) state within ~10 seconds of addition of the salt solution. Here we contrast these dynamics to those observed when LC ordering transitions are caused by formation of electrical double layers at the LC-aqueous interface (as described above). Specifically, in our previous study, the ordering transitions induced by 1 M NaCl solutions at pH 12.8 occurred with characteristic times that ranged from 5 mins to 60 mins.⁵³ In contrast, for the salts and conditions reported in Table 1, we consistently observed all ordering transitions to occur within 20 s. These relatively fast dynamics are consistent with our hypothesis that the ordering transitions are triggered by interactions of the chaotropic anions with an interfacial layer of mesogens in contact with the aqueous phase. That is, the chaotropic anions do not have to diffuse across the interface and into the bulk of the LC film to trigger the ordering transition, as is the case with orientational transitions triggered by the formation of electrical double layers on the LC side of the interface (see our past study for details).⁵³

As a further test of the hypothesis that the ordering transitions reported in Table 1 are triggered by the interactions of chaotropic ions with the interfacial region of the LC, we measured the surface pressure-area isotherms of *monolayers* of 5CB formed on the surface of aqueous sub-phases containing a range of salts. Nitrile-containing LCs are known to form stable monolayers at aqueous interfaces.^{73–77} In particular, past reports have described monolayers of 5CB and 8CB that form over sub-phases of pure water and inferred that the mesogens are oriented such that their polar nitrile groups ($-\text{C}\equiv\text{N}$) are pointing towards the water (see schematic in Figure 4a⁷⁴). These studies have reported an increase in surface pressure at an areal density of $44 \pm 3 \text{ \AA}^2/\text{molecule}$ (due to coalescence of liquid-phase domains). The subsequent compression of a homogeneous monolayer resulted in measurement of a plateau of the surface pressure, characteristic of the formation of trilayers (Figure 4b), at surface pressures of about $5.0 \pm 0.1 \text{ mN/m}$ and at an areal density of about $34 \pm 3 \text{ \AA}^2/\text{molecule}$ (measured at 22–23.5 °C).^{77–79} In our experiments, the temperature of the sub-phase was maintained at $25.0 \pm 0.1 \text{ °C}$ by circulating water at a constant temperature beneath the trough. Figure 5a shows representative surface pressure-area isotherms that we measured for a 5CB monolayer spread on water, or aqueous sub-phases containing a kosmotropic salt or a chaotropic salt (see Figure S3 in SI for data obtained with 8CB). Due to the large volume of solution needed to form the sub-phase, the salt concentration (0.5 M) used in our monolayer studies was lower than that used in the experiments with bulk LCs shown in Figure 1 (typically 2 M). We did, however, perform monolayer isotherm

measurements for two salts at a concentration of 2 M (NaCl and NaSCN) to confirm that the difference in salt concentration does not change the conclusions reported below (see SI for details, Figure S4 and Table S2). Our measurements of the isotherm of a 5CB monolayer over pure water, as shown in Figure 5a, agree closely with these previous reports. Specifically, the surface pressure began to rise ($\pi = 0.25$ mN/m) at an areal density of $43 \text{ \AA}^2/\text{molecule}$, and multilayer formation was indicated by a plateau in surface pressure at 4.3 mN/m at an area of $34 \text{ \AA}^2/\text{molecule}$ (numerical averages for isotherm data are summarized in Table 2). A principal effect of addition of the kosmotropic salts (see Figure 5a, and Figure 5b for a comparison of NaF, NaCl and NaBr) was to cause the initial rise in surface pressure to occur at a larger molecular area ($51\text{--}55 \text{ \AA}^2/\text{molecule}$, as compared to $43 \text{ \AA}^2/\text{molecule}$ measured on pure water). Similar results were found with other kosmotropic salts (not shown). In contrast, we measured the initial rise in surface pressure of monolayers of 5CB over aqueous solutions of chaotropic salts to occur at molecular areas that were comparable to that measured on pure water, with the exception of SCN^- (Figure 5c). Additionally, we measured monolayers of 5CB to be stable to much higher surface pressures (10.7 mN/m or more), and correspondingly, much smaller molecular areas ($24\text{--}28 \text{ \AA}^2/\text{molecule}$) in the presence of the chaotropic anions as compared to kosmotropic anions. As shown in Figure 5c, the effect of the anion type on molecular area and surface pressure at collapse of the monolayer followed the series $\text{NaSCN} < \text{NaClO}_4 < \text{NaI}$. Here we note also that NaI isotherms reproducibly showed a gradual change in surface pressure with decrease in area at the mono- to multi-layer transition. In contrast, all other salts showed an abrupt change in the isotherm. We do not yet fully understand why NaI differed from the other salts in this respect. Finally, the two-dimensional elasticity of the monolayers, calculated as $-A \cdot d\pi/dA$,^{80, 81} reveals that chaotropic anions cause significantly greater monolayer elasticity than do kosmotropic ions (Figure 6, Table 2).

The influence of the anions on the minimum molecular area at which monolayers of 5CB are stable is interesting to consider in light of past studies that have estimated the molecular tilt angle of 5CB within monolayers assuming a molecular cross sectional area of approximately $23 \text{ \AA}^2/\text{molecule}$.^{75, 79} From these measurements, we calculate, just prior to multilayer formation, the tilt angle of the 5CB molecules at the surface of the aqueous sub-phase to be 27° (relative to the interface normal) for NaClO_4 and 53° for NaCl (Figure 6, Table 2). While it is well-established that molecular tilt angles in monolayers do not generally predict the bulk tilt angles of LCs,⁸² we do note the qualitative correlation between the effects of the anions on the tilt angles of 5CB in monolayers at the surface of water and bulk LC orientations, as reported in this paper. Additionally, we note that NaSCN causes a change in the 5CB isotherm that is intermediate between NaClO_4 and NaCl (A_{mono} and elasticity similar to the kosmotropic anions and maximum surface pressure resembling the other chaotropic anions). Such intermediate behavior correlates with the observation reported in Table 1 that the effect of NaSCN on the tilt of the micrometer-thick 5CB films is intermediate between that of ClO_4^- and Cl^- (Table 1).

While spectroscopic studies are underway to provide additional insight into the intermolecular interactions underlying the influence of chaotropic anions on the surface pressure-area isotherms of 5CB reported in Figure 5, we comment here that formation of a multilayer of 5CB (upon monolayer collapse) involves the transfer of 5CB molecules from an environment in which the nitrile group is available for interaction with ions and water in the aqueous phase to an environment in which the nitrile group is sequestered within a bilayer of 5CB removed from the aqueous phase (Figure 4). This observation hints that the stabilizing influence of the chaotropic anions on the monolayer of 5CB (as determined by π_c (pressure at collapse) and elasticity) may be a consequence of an effective attraction between the chaotropic anions and the nitrile group of the 5CB. While speculative, support for the proposition regarding the possible role of the nitrile group in mediating interactions

with the anions was obtained by performing additional experiments with two additional nematic LCs; E7 (a mixture of nitrile-containing mesogens) and TL205 (a mixture containing a fluoro-phenyl functional group) (Scheme 1). We note that E7 has chemical functionality and a dipole moment similar to 5CB ($\mu_{\text{avg}} = 4.96$ D for 5CB at 25 °C),⁸³ whereas TL205 does not possess a nitrile group and has a smaller dipole moment (similar to 1,2-difluorobenzene: $\mu = 2.6$ D).⁸⁴ Using the procedures described above to characterize the effects of salts on micrometer-thick films of 5CB, we measured the orientations of E7 and TL205 following contact with aqueous solutions of sodium salts (Table 1). Inspection of Table 1 reveals that E7 responds to specific anions in a manner identical to 5CB, with chaotropes inducing tilted or homeotropic ordering (E7 displayed homeotropic anchoring when contacted with 8 M NaSCN). In contrast, TL205 differed from the two nitrile-containing LCs in its response to salts in that a planar orientation of the nematic phase was observed for all salts. The absence of a measurable effect of the chaotropic salts on the ordering of TL205 is consistent with our proposal that the nitrile group of 5CB plays a key role in mediating the effects of specific anions on the LC ordering transitions. The nitrile group could, for example, participate in a dipole (nitrile)-induced dipole (chaotropic anion) interaction because the nitrile group of 5CB possesses a relatively large dipole moment and the chaotropic anions are relatively large and polarizable.

We make four additional comments regarding the results described above. First, we note that our interpretation of these results is generally consistent with prior studies (see above for details) that have reported the accumulation of chaotropic anions at lipid- or surfactant-decorated interfaces and perturbation of the hydrocarbon tails of the amphiphiles.^{54, 55} Second, the results also appear to fit within the conceptual framework of the theory reported by dos Santos and Levin, to the extent that the theory includes consideration of the role of the polarizability of ions in mediating the accumulation of the ions at fluid interfaces.^{45–47} The development of a full understanding of the cause of the ordering transitions in LC films that are triggered by chaotropic anions may, however, also require consideration of the dielectric, flexoelectric and ordoelectric properties of the LCs.^{85, 86} Third, we note that the orientation of the LC is expected to modulate the adsorption of ions since the LC orientation will determine the dielectric environment experienced by an ion as it approaches the interface (and thus influence the Born energy of the ion). In this context, we comment that past reports have described how the orientational ordering of LCs can influence the adsorption of amphiphiles at LC interfaces.⁸⁷ The influence of the orientational order of the LC on adsorption of ions will be the subject of a future study. Finally, we end these comments by noting that Langmuir monolayer experiments described above could not be performed with TL205 because it did not spread into stable monolayers (presumably due to the relatively weak dipole moment of the mesogen).

The final experiment that we report in this paper addresses the influence of the salts on the anisotropic surface energy (γ_{aniso}) of the LC. Specifically, we sought to determine if the influence of the specific anions on the orientational ordering of LCs, as reported in Figure 1 and Table 1, was caused by a change in the orientation of the LC corresponding to the lowest interfacial free energy (the so-called easy axis, φ_e) or a change in the depth of the free energy minimum corresponding to the easy axis (so-called anchoring strength, W , as defined by Eq. (1)).⁸⁶

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

where θ characterizes the orientation of the LC director at the interface. Relevant to this question, as shown in Figure 1b, the initial state of the LC contacting pure water is

elastically strained by the hybrid boundary conditions. Under these conditions, a decrease in anchoring strength at the aqueous-LC interface will permit the anchoring at the OTS-treated surface to dictate the orientation of the LC across the entire film (via the effects of the elasticity of the LC; Figure 1f). To probe the origin of the ordering transitions observed in our experiments, we quantified the orientation of 5CB in contact with aqueous solutions of either NaCl, NaSCN, NaI, or NaClO₄, when the LC film was supported on an obliquely deposited gold film treated with hexadecanethiol (HSC16; HSC16-treated gold surfaces cause the LC to align parallel to the surface). In this experiment, the oblique deposition of the gold, when combined with the effect of the monolayer formed from HSC16 on the LC, leads to a preferred azimuthal direction (i.e. parallel to the direction of gold deposition),⁷¹ which propagates to the aqueous interface since this interface has degenerate planar anchoring (i.e. no preferred azimuthal orientation). Because the initial state of the HSC16-supported LC film that contacts pure water is not strained (Figure 7b), any change in the LC orientation at the aqueous interface caused by addition of salt would necessarily strain the LC (and cannot, therefore, be driven solely by a decrease in W). Polarized light micrographs of the 5CB films used in these measurements revealed that addition of NaCl to the aqueous phase resulted in no measureable change in the ordering (easy axis) of 5CB at the aqueous-LC interface (Figure 7a versus Figure 7c, with corresponding schematics in Figures 7b and 7d respectively). In contrast, addition of NaClO₄ resulted in a clearly observed change in the LC ordering (Figure 7a versus Figure 7e, with corresponding schematics in Figures 7b and 7f, respectively). Quantitation of the optical retardance of these 5CB films after 5–10 minutes of contact with the salt solutions allowed us to calculate the tilt angle of the director at the aqueous interface (with respect to the surface normal). From these measurements, we determined that contact of the nematic 5CB with 2 M NaClO₄ caused nearly homeotropic ordering of the LC at the aqueous interface (Figure 7c), with a tilt angle of $4 \pm 3^\circ$ (measured from the surface normal). In contrast, when contacted with aqueous phases containing 2 M of either NaI, NaSCN or NaCl, the 5CB films supported on HSC16 exhibited tilt angles of $30 \pm 9^\circ$, $44 \pm 6^\circ$, and $90 \pm 13^\circ$, respectively, at the aqueous interface. From these observations, we conclude that the ordering transition induced by the chaotropic anions in Table 1 is due to a change in the easy axis of the LC, and not solely a decrease in the anchoring energy.

Conclusions

The key result reported in this paper is that thermotropic LCs containing nitrile groups undergo anion-specific ordering transitions at interfaces to aqueous salt solutions. Only chaotropic anions, which have been reported previously to exhibit positive surface excess concentrations at isotropic oil-water interfaces,^{26, 27} trigger the ordering transitions in the two nitrile-containing LCs. Kosmotropic anions do not trigger orientational transitions in the three LCs investigated in our study. Inspired by previous spectroscopic studies of monolayers at the surface of water that have revealed chaotropic anions to perturb the packing of the aliphatic tails of amphiphiles,^{54, 55} our results support the hypothesis that chaotropic anions penetrate into the interfacial layer of the LC in contact with the aqueous phase, interact with the relatively large dipole of the nitrile group to perturb the organization of the mesogens at the interface, and thereby change the easy axis of the LC. Support for this proposition is found in three key experiments reported in this paper. First, measurements of pressure-area isotherms of 5CB monolayers supported on chaotropic salt solutions revealed that chaotropic anions stabilize monolayers of 5CB (against collapse into trilayers) at smaller area/molecule values as compared to pure water or kosmotropic salt solutions. This result can be interpreted in terms of an effective attraction between the nitrile-containing mesogens and the aqueous solution of chaotropic anions. Second, ordering transitions induced by specific anions were observed for nitrile-containing LCs (nematic 5CB and E7) but not for TL205. This result is consistent with our proposition, as TL205 possesses a weak

dipole moment, and thus interacts weakly with polarizable anions. Third, consistent with the proposal that the interaction of the salt and the LC occurs at the interface of the two phases and does not require diffusion of the salt into the bulk of the LC, the dynamics of the transitions induced by chaotropic anions are much faster (< 20 s) than previously reported salt-induced ordering transitions that are associated with partitioning of salts into the LC (tens of mins to ~ 1 hour). The measurements reported in this paper also reveal that the LC ordering transitions triggered by contact with chaotropic salt solutions are due to an anion-induced change in the easy axis of the LC and not just a decrease in the strength of the anchoring. Overall, we note that the LC-ion interactions unmasked in this paper are significant in light of past and ongoing studies using LC-aqueous interfaces for amplification of molecular interactions.^{52, 56–68} Further investigation of the specific ion effects revealed in this study may also lead to an experimental system that can be used to report positive surface excess ion concentrations and thus test model predictions regarding specific ion phenomena at oil-water interfaces. Finally, we note that application of an external electric field, which would be expected to influence ion adsorption, might provide additional insights into the ionic phenomena reported in this paper.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References

1. Kunz W, Henle J, Ninham BW. 'Zur Lehre von der Wirkung der Salze' (about the science of the effect of salts): Franz Hofmeister's historical papers. *Curr Opin Colloid Interface Sci.* 2004; 9:19–37.
2. Cacace MG, Landau EM, Ramsden JJ. The Hofmeister Series: Salt and Solvent Effects on Interfacial Phenomena. *Q Rev Biophys.* 1997; 30:241–277. [PubMed: 9394422]
3. Zhang Y, Cremer P. Interactions between Macromolecules and Ions: The Hofmeister Series. *Curr Opin Chem Bio.* 2006; 10:658–663. [PubMed: 17035073]
4. Kunz W. Specific Ion Effects in Liquids, in Biological Systems, and at Interfaces. *Pure Appl Chem.* 2006; 78:1611–1617.
5. Kunz W. Specific Ion Effects in Colloidal and Biological Systems. *Curr Opin Colloid Interface Sci.* 2010; 15:34–39.
6. Lo Nostro P, Ninham BW. Hofmeister Phenomena: An Update on Ion Specificity in Biology. *Chem Rev.* 2012; 112:2286–2322. [PubMed: 22251403]
7. Collins KD. Ions from the Hofmeister Series and Osmolytes: Effects on Proteins in Solution and in the Crystallization Process. *Methods.* 2004; 34:300–311. [PubMed: 15325648]
8. von Hippel PH, Wong KY. On the Conformational Stability of Globular Proteins. *J Biol Chem.* 1965; 240:3909–3923. [PubMed: 5842063]
9. Rembert KB, Paterova J, Heyda J, Hilty C, Jungwirth P, Cremer PS. Molecular Mechanisms of Ion-Specific Effects on Proteins. *J Am Chem Soc.* 2012; 134:10039–10046. [PubMed: 22687192]
10. Pegram LM, Record MT. Thermodynamic Origin of Hofmeister Ion Effects. *J Phys Chem B.* 2008; 112:9428–9436. [PubMed: 18630860]
11. Anacker EW, Ghose HM. Counterions and Micelle Size. I. Light Scattering by Solutions of Dodecyltrimethylammonium Salts. *J Phys Chem.* 1963; 67:1713–1716.
12. Zemb T, Belloni L, Dubois M, Aroti A, Leontidis E. Can We Use Area per Surfactant as a Quantitative Test Model of Specific Ion Effects? *Curr Opin Colloid Interface Sci.* 2004; 9:74–80.

13. Sun W, Shen Y, Hao J. Phase Behavior and Rheological Properties of Salt-Free Catanionic TTAOH/DA/H₂O System in the Presence of Hydrophilic and Hydrophobic Salts. *Langmuir*. 2011; 27:1675–1682. [PubMed: 21192689]
14. Deyerle BA, Zhang YJ. Effects of Hofmeister Anions on the Aggregation Behavior of PEO-PPO-PEO Triblock Copolymers. *Langmuir*. 2011; 27:9203–9210. [PubMed: 21688819]
15. Patra L, Vidyasagar A, Toomey R. The Effect of the Hofmeister Series on the Deswelling Isotherms of Poly(N-isopropylacrylamide) and Poly(N,N-diethylacrylamide). *Soft Matter*. 2011; 7:6061–6067.
16. Ren, C-l; Tian, W-d; Szleifer, I.; Ma, Y-q. Specific Salt Effects on Poly(ethylene oxide) Electrolyte Solutions. *Macromolecules*. 2011; 44:1719–1727.
17. Lyklema J. Lyotropic Sequences in Colloid Stability Revisited. *Adv Colloid Interface Sci*. 2003; 100:1–12.
18. López-León T, Santander-Ortega MJ, Ortega-Vinuesa JL, Bastos-González D. Hofmeister Effects in Colloidal Systems: Influence of the Surface Nature. *J Phys Chem C*. 2008; 112:16060–16069.
19. Peula-García JM, Ortega-Vinuesa JL, Bastos-González D. Inversion of Hofmeister Series by Changing the Surface of Colloidal Particles from Hydrophobic to Hydrophilic. *J Phys Chem C*. 2010; 114:11133–11139.
20. Calero C, Faraudo J, Bastos-González D. Interaction of Monovalent Ions with Hydrophobic and Hydrophilic Colloids: Charge Inversion and Ionic Specificity. *J Am Chem Soc*. 2011; 133:15025–15035. [PubMed: 21823608]
21. Jones G, Ray WA. The Surface Tension of Solutions of Electrolytes as a Function of the Concentration. I. A Differential Method for Measuring Relative Surface Tension. *J Am Chem Soc*. 1937; 59:187–198.
22. Jones G, Ray WA. The Surface Tension of Solutions of Electrolytes as a Function of the Concentration II. *J Am Chem Soc*. 1941; 63:288–294.
23. Weissenborn PK, Pugh RJ. Surface-Tension and Bubble Coalescence Phenomena of Aqueous-Solutions of Electrolytes. *Langmuir*. 1995; 11:1422–1426.
24. Weissenborn PK, Pugh RJ. Surface Tension of Aqueous Solutions of Electrolytes: Relationship with Ion Hydration, Oxygen Solubility, and Bubble Coalescence. *J Colloid Interface Sci*. 1996; 184:550–563. [PubMed: 8978559]
25. Pegram LM, Record MT Jr. Hofmeister Salt Effects on Surface Tension Arise from Partitioning of Anions Cations between Bulk Water and the Air-Water Interface. *J Phys Chem B*. 2007; 111:5411–5417. [PubMed: 17432897]
26. Guest WL, Lewis WCM. The Effect of Electrolytes upon the Interfacial Tension between Water and Dekalin (Trans-Decahydronaphthalene). *Proc R Soc Lond A*. 1939; 170:501–513.
27. Aveyard R, Saleem SM. Interfacial Tensions at Alkane-Aqueous Electrolyte Interfaces. *J Chem Soc, Faraday Trans 1*. 1976; 72:1609–1617.
28. Girault HH, Schiffrin DJ. Thermodynamic Surface Excess of Water and Ionic Solvation at the Interface between Immiscible Liquids. *J Electroanal Chem*. 1983; 150:43–49.
29. Ghosal S, Hemminger JC, Bluhm H, Mun BS, Hebenstreit ELD, Ketteler G, Ogletree DF, Requejo FG, Salmeron M. Electron Spectroscopy of Aqueous Solution Interfaces Reveals Surface Enhancement of Halides. *Science*. 2005; 307:563–566. [PubMed: 15681380]
30. Maheshwari R, Sreeram KJ, Dhathathreyan A. Surface Energy of Aqueous Solutions of Hofmeister Electrolytes at Air/Liquid and Solid/Liquid Interface. *Chem Phys Lett*. 2003; 375:157–161.
31. Pegram LM, Record MT. Quantifying Accumulation or Exclusion of H(+), HO(–), and Hofmeister Salt Ions near Interfaces. *Chem Phys Lett*. 2008; 467:1–8.
32. Liu DF, Ma G, Levering LM, Allen HC. Vibrational Spectroscopy of Aqueous Sodium Halide Solutions and Air-Liquid Interfaces: Observation of Increased Interfacial Depth. *J Phys Chem B*. 2004; 108:2252–2260.
33. Petersen PB, Saykally RJ. Probing the Interfacial Structure of Aqueous Electrolytes with Femtosecond Second Harmonic Generation Spectroscopy. *J Phys Chem B*. 2006; 110:14060–14073. [PubMed: 16854101]

34. Fernandes GE, Bevan MA. Equivalent Temperature and Specific Ion Effects in Macromolecule-Coated Colloid Interactions. *Langmuir*. 2007; 23:1500–1506. [PubMed: 17241080]
35. Wendorf JR, Radke CJ, Blanch HW. The Role of Electrolytes on Protein Adsorption at a Hydrophilic Solid-Water Interface. *Colloids Surf B*. 2010; 75:100–106.
36. Flores SC, Kherb J, Cremer PS. Direct and Reverse Hofmeister Effects on Interfacial Water Structure. *J Phys Chem C*. 2012; 116:14408–14413.
37. Petersen PB, Saykally RJ, Mucha M, Jungwirth P. Enhanced Concentration of Polarizable Anions at the Liquid Water Surface: SHG Spectroscopy and MD Simulations of Sodium Thiocyanide. *J Phys Chem B*. 2005; 109:10915–10921. [PubMed: 16852329]
38. Mucha M, Frigato T, Levering LM, Allen HC, Tobias DJ, Dang LX, Jungwirth P. Unified Molecular Picture of the Surfaces of Aqueous Acid, Base, and Salt Solutions. *J Phys Chem B*. 2005; 109:7617–7623. [PubMed: 16851882]
39. Jungwirth P, Tobias DJ. Molecular Structure of Salt Solutions: A New View of the Interface with Implications for Heterogeneous Atmospheric Chemistry. *J Phys Chem B*. 2001; 105:10468–10472.
40. Bhatt D, Chee R, Newman J, Radke CJ. Molecular Simulation of the Surface Tension of Simple Aqueous Electrolytes and the Gibbs Adsorption Equation. *Curr Opin Colloid Interface Sci*. 2004; 9:145–148.
41. Huang DM, Cottin-Bizonne C, Ybert C, Bocquet L. Aqueous Electrolytes near Hydrophobic Surfaces: Dynamic Effects of Ion Specificity and Hydrodynamic Slip. *Langmuir*. 2008; 24:1442–1450. [PubMed: 18052395]
42. Netz RR, Horinek D. Progress in Modeling of Ion Effects at the Vapor/Water Interface. *Annu Rev Phys Chem*. 2012; 63:401–18. [PubMed: 22404593]
43. Bier M, Zwanikken J, van Roij R. Liquid-Liquid Interfacial Tension of Electrolyte Solutions. *Phys Rev Lett*. 2008; 101:046104. [PubMed: 18764343]
44. Boström M, Kunz W, Ninham BW. Hofmeister Effects in Surface Tension of Aqueous Electrolyte Solution. *Langmuir*. 2005; 21:2619–2623. [PubMed: 15752061]
45. dos Santos AP, Levin Y. Ions at the Water-Oil Interface: Interfacial Tension of Electrolyte Solutions. *Langmuir*. 2012; 28:1304–1308. [PubMed: 22166104]
46. Levin Y. Polarizable Ions at Interfaces. *Phys Rev Lett*. 2009; 102:147803. [PubMed: 19392484]
47. Levin Y, dos Santos AP, Diehl A. Ions at the Air-Water Interface: An End to a Hundred-Year-Old Mystery? *Phys Rev Lett*. 2009; 103:257802. [PubMed: 20366288]
48. Manciu M, Ruckenstein E. On the Interactions of Ions with the Air/Water Interface. *Langmuir*. 2005; 21:11312–11319. [PubMed: 16285805]
49. Manciu M, Ruckenstein E. Ions at the Air/Water Interface. *J Colloid Interface Sci*. 2006; 304:541–544. [PubMed: 17045284]
50. Wang R, Wang ZG. Effects of Ion Solvation on Phase Equilibrium and Interfacial Tension of Liquid Mixtures. *J Chem Phys*. 2011; 135:014707. [PubMed: 21744914]
51. López-García JJ, Horno J, Grosse C. Poisson-Boltzmann Description of the Electrical Double Layer Including Ion Size Effects. *Langmuir*. 2011; 27:13970–13974. [PubMed: 22035520]
52. Lin IH, Miller DS, Bertics PJ, Murphy CJ, de Pablo JJ, Abbott NL. Endotoxin-Induced Structural Transformations in Liquid Crystalline Droplets. *Science*. 2011; 332:1297–1300. [PubMed: 21596951]
53. Carlton RJ, Gupta JK, Swift CL, Abbott NL. Influence of Simple Electrolytes on the Orientational Ordering of Thermotropic Liquid Crystals at Aqueous Interfaces. *Langmuir*. 2012; 28:31–36. [PubMed: 22106820]
54. Aroti A, Leontidis E, Maltseva E, Brezesinski G. Effects of Hofmeister Anions on DPPC Langmuir Monolayers at the Air-Water Interface. *J Phys Chem B*. 2004; 108:15238–15245.
55. Gurau MC, Lim SM, Castellana ET, Albertorio F, Kataoka S, Cremer PS. On the Mechanism of the Hofmeister Effect. *J Am Chem Soc*. 2004; 126:10522–10523. [PubMed: 15327293]
56. Bai Y, Abbott NL. Recent Advances in Colloidal and Interfacial Phenomena Involving Liquid Crystals. *Langmuir*. 2011; 27:5719–5738. [PubMed: 21090596]

57. Lockwood NA, Gupta JK, Abbott NL. Self-Assembly of Amphiphiles, Polymers and Proteins at Interfaces between Thermotropic Liquid Crystals and Aqueous Phases. *Surf Sci Rep.* 2008; 63:255–293.
58. Bahr C. Surfactant-Induced Nematic Wetting Layer at a Thermotropic Liquid Crystal/Water Interface. *Phys Rev E.* 2006; 73:030702.
59. Feng XD, Bahr C. Surface Order at Surfactant-Laden Interfaces between Isotropic Liquid Crystals and Liquid Phases with Different Polarity. *Phys Rev E.* 2011; 84:031701.
60. Kinsinger ML, Sun B, Abbott NL, Lynn DM. Reversible Control of Ordering Transitions at Aqueous/Liquid Crystal Interfaces Using Functional Amphiphilic Polymers. *Adv Mater.* 2007; 19:4208–4212.
61. Brake JM, Abbott NL. Coupling of the Orientations of Thermotropic Liquid Crystals to Protein Binding Events at Lipid-Decorated Interfaces. *Langmuir.* 2007; 23:8497–8507. [PubMed: 17595119]
62. Price A, Schwartz D. Fatty-Acid Monolayers at the Nematic/Water Interface: Phases and Liquid-Crystal Alignment. *J Phys Chem B.* 2007; 111:1007–1015. [PubMed: 17266255]
63. Price AD, Schwartz DK. DNA Hybridization-Induced Reorientation of Liquid Crystal Anchoring at the Nematic Liquid Crystal/Aqueous Interface. *J Am Chem Soc.* 2008; 130:8188–8194. [PubMed: 18528984]
64. Bi XY, Hartono D, Yang KL. Real-Time Liquid Crystal pH Sensor for Monitoring Enzymatic Activities of Penicillinase. *Adv Funct Mater.* 2009; 19:3760–3765.
65. Hartono D, Bi X, Yang K, Yung L. An Air-Supported Liquid Crystal System for Real-Time and Label-Free Characterization of Phospholipases and Their Inhibitors. *Adv Funct Mater.* 2008; 18:2938–2945.
66. Fletcher PDI, Kang NG, Paunov VN. UV Polymerisation of Surfactants Adsorbed at the Nematic Liquid Crystal-Water Interface Produces an Optical Response. *Chem Phys Chem.* 2009; 10:3046–3053. [PubMed: 19780096]
67. Zou J, Bera T, Davis AA, Liang W, Fang J. Director Configuration Transitions of Polyelectrolyte Coated Liquid-Crystal Droplets. *J Phys Chem B.* 2011; 115:8970–8974. [PubMed: 21667976]
68. Rey AD. Thermodynamic Model of Surfactant Adsorption on Soft Liquid Crystal Interfaces. *Langmuir.* 2004; 20:11473–11479. [PubMed: 15595772]
69. Brake JM, Abbott NL. An Experimental System for Imaging the Reversible Adsorption of Amphiphiles at Aqueous-Liquid Crystal Interfaces. *Langmuir.* 2002; 18:6101–6109.
70. Brake JM, Daschner MK, Luk YY, Abbott NL. Biomolecular Interactions at Phospholipid-Decorated Surfaces of Liquid Crystals. *Science.* 2003; 302:2094–2097. [PubMed: 14684814]
71. Luk YY, Yang KL, Cadwell K, Abbott NL. Deciphering the Interactions between Liquid Crystals and Chemically Functionalized Surfaces: Role of Hydrogen Bonding on Orientations of Liquid Crystals. *Surf Sci.* 2004; 570:43–56.
72. Gupta VK, Abbott NL. Azimuthal Anchoring Transition of Nematic Liquid Crystals on Self-Assembled Monolayers Formed from Odd and Even Alkanethiols. *Phys Rev E.* 1996; 54:R4540–R4543.
73. de Mul MNG, Mann JA. Determination of the Thickness and Optical Properties of a Langmuir Film from the Domain Morphology by Brewster Angle Microscopy. *Langmuir.* 1998; 14:2455–2466.
74. de Mul MNG, Mann JA. Multilayer Formation in Thin-Films of Thermotropic Liquid-Crystals at the Air-Water-Interface. *Langmuir.* 1994; 10:2311–2316.
75. Xue JZ, Jung CS, Kim MW. Phase-Transitions of Liquid-Crystal Films on an Air-Water-Interface. *Phys Rev Lett.* 1992; 69:474–477. [PubMed: 10046948]
76. Zou L, Wang J, Basnet P, Mann EK. Line Tension and Structure of Smectic Liquid-Crystal Multilayers at the Air-Water Interface. *Phys Rev E.* 2007; 76:031602.
77. Zhang Z, Zheng DS, Guo Y, Wang HF. Water Penetration/Accommodation and Phase Behaviour of the Neutral Langmuir Monolayer at the Air/Water Interface Probed with Sum Frequency Generation Vibrational Spectroscopy (SFG-VS). *Phys Chem Chem Phys.* 2009; 11:991–1002. [PubMed: 19177218]

78. Delabre U, Richard C, Cazabat AM. Some Specificities of Wetting by Cyanobiphenyl Liquid Crystals. *J Phys: Condes Matter*. 2009; 21:464129.
79. Inglot K, Martynski T, Bauman D. Influence of the Alkyl Chain Length of Some Mesogenic Molecules on Their Langmuir Film Formation Ability. *Liq Cryst*. 2006; 33:855–864.
80. Ariga K, Yuki H, Kikuchi J, Dannemuller O, Albrecht-Gary AM, Nakatani Y, Ourisson G. Monolayer Studies of Single-Chain Polyprenyl Phosphates. *Langmuir*. 2005; 21:4578–4583. [PubMed: 16032875]
81. Giner I, Pera G, Lafuente C, López MC, Cea P. Influence of the Hofmeister Series of Anions on the Molecular Organization of Positively Ionized Monolayers of a Viologen Derivative. *J Colloid Interface Sci*. 2007; 315:588–596. [PubMed: 17692865]
82. Jerome B. Surface Effects and Anchoring in Liquid-Crystals. *Rep Prog Phys*. 1991; 54:391–451.
83. Gueu KP, Megnassan E, Proutiere A. Dipole-Moments of 4-N Alkyl-4'-Cyanobiphenyl Molecules (from OCB to 12CB) Measurement in 4 Solvents and Theoretical Calculations. *Mol Cryst Liq Cryst*. 1986; 132:303–323.
84. Nygaard L, Hansen ER, Hansen RL, Rastrup-Andersen J, Sørensen GO. Microwave Spectra and Dipole Moments of 1,2-Difluorobenzene and 1,3-Difluorobenzene. *Spectrochim Acta*. 1967; 23:2813–2819.
85. Barbero, G.; Durand, G. Surface Anchoring of Nematic Liquid Crystals. In: Crawford, GP.; Zumer, S., editors. *Liquid Crystals in Complex Geometries*. Taylor and Francis; London: 1996. p. 21-52.
86. de Gennes, PG.; Prost, J. *The Physics of Liquid Crystals*. 2. Clarendon Press; Oxford University Press; Oxford New York: 1993.
87. Gupta JK, Meli MV, Teren S, Abbott NL. Elastic Energy-Driven Phase Separation of Phospholipid Monolayers at the Nematic Liquid-Crystal-Aqueous Interface. *Phys Rev Lett*. 2008; 100:048301. [PubMed: 18352339]

Figure 1.

(a–f) Polarized micrographs (crossed polars) and schematic illustrations of nematic films of 5CB in contact with aqueous solutions of (a, b) ultrapure MilliQ water, (c, d) 2 M NaCl, or (e, f) 2 M NaClO₄. Inset in (e) is a conoscopic image confirming homeotropic alignment. In a–f the 5CB is supported on an OTS-treated glass surface. Each square is ~300 μm on a side.

Figure 2. The tilt angles of nematic 5CB (angle from normal at the aqueous interface) after ~20 minutes of equilibration against aqueous solutions of either NaCl (squares) or NaClO₄ (diamonds) plotted as a function of the salt concentration.

Figure 3.

Time-lapse polarized light micrographs showing an ordering transition in a 5CB film triggered by contact with 2 M NaClO_4 (at $t = 0$ s). Images taken between 1–3 s are blurred due to the addition and mixing of the salt solution, which caused variation in the refractive index of the aqueous phase. The inset at 20s is a conoscopic image confirming homeotropic orientation. Each square is $\sim 300 \mu\text{m}$ on a side.

Figure 4. Schematic illustration of a 5CB monolayer (a) supported on an aqueous sub-phase, which forms a trilayer structure (b) upon compression. Figure adapted from de Mul and Mann.⁷⁴

Figure 5.

Surface pressure (π) – area isotherms of 5CB monolayers supported on aqueous sub-phases containing either (a) water (solid line), 0.5 M NaCl (dotted line), or 0.5 M NaClO₄ (dashed line); (b) water or 0.5 M halide salts that span the Hofmeister series listed in Table 1; and (c) water or 0.5 M chaotropic salts.

Figure 6. Calculated values of the molecular tilt angle (black diamonds, left axis) and 2-dimensional elasticity (grey squares, right axis) of monolayers of 5CB supported on aqueous sub-phases containing the indicated salts (isotherms shown in Figure 5).

Figure 7.

Polarized light micrographs and schematic illustration of 5CB films supported on a gold-coated glass slide functionalized with HSC16: Nematic 5CB in contact with (a, b) water, (c, d) aqueous 2 M NaCl for 10 minutes, or (e, f) aqueous 2 M NaClO₄ for 10 minutes. The bright interference colors of 5CB in contact with 2 M chaotropic salts indicates that the easy axis of 5CB at the aqueous interface is influenced by the introduction of chaotropic anions in water.

Scheme 1.

Molecular structures of the LCs used in this study. (a) 5CB; (b) E7 and (c) TL205.

Table 1

Orientations of LCs at interfaces of aqueous salt solutions. Notation: P: planar orientation; H: homeotropic (perpendicular) orientation; T: tilted orientation; C₀: maximum solubility at 25°C; C: concentration used. The LCs were supported on OTS-treated glass surfaces (see text for details).

Salts	pH	C ₀ [M]	C [M]	5CB	E7	TL205
NaF	7.11	0.98	0.75	P	P	P
Na ₂ SO ₄	6.73	2	1.5	P	P	P
Na ₂ HPO ₄	8.86	0.54	0.5	P	P	P
NaC ₂ O ₂ H ₃	8.11	5.67	2	P	P	P
NaCl	6.36	6.14	2	P	P	P
NaNO ₃	6.08	10.83	2	P	P	P
NaBr	6.31	7.12	2	P	P	P
NaClO ₃	7.37	9.49	2	P	P	P
NaSCN	6.62	17.14	2	T	T	P
NaClO ₄	7.29	9	2	H	H	P
NaI	6.41	12	2	H	H	P

Table 2

Properties of the Langmuir isotherms shown in Figure 5. With the exception of water, the aqueous sub-phase contained 0.5 M of the indicated salt. Notation: A_{mono} is the mean molecular area at which the surface pressure rose to 0.25 mN/m. A_c and π_c are the mean molecular area and surface pressure at collapse (multilayer formation), respectively. The fifth column is the interfacial tilt angle of 5CB molecules within the monolayer calculated from A_c (see text for details). The sixth column reports the maximum elasticity of the 5CB monolayer on the indicated sub-phase. Averages and errors are reported from multiple experiments, $n = 3$.

Aqueous Sub-phase	A_{mono} ($\text{\AA}^2/\text{molec.}$)	A_c ($\text{\AA}^2/\text{molec.}$)	π_c (mN/m)	Interfacial Tilt Angle ($^\circ$)	Elasticity (mN/m)
Water	40 ± 2	32 ± 2	4.1 ± 0.2	44 ± 3	23 ± 2
NaF	51 ± 6	38 ± 4	4.6 ± 0.1	52 ± 6	18 ± 3
NaCl	55 ± 2	38 ± 1	5.0 ± 0.1	53 ± 1	20 ± 2
NaBr	52 ± 5	36 ± 3	5.5 ± 0.1	49 ± 4	22 ± 4
NaSCN	54 ± 6	28 ± 4	10.3 ± 0.4	37 ± 6	35 ± 2
NaClO ₄	50 ± 8	27 ± 3	12.6 ± 0.4	30 ± 12	51 ± 12
NaI	42 ± 6	24 ± 2	17.7 ± 1.6	13 ± 9	81 ± 25