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Surfactant-induced nematic wetting layer at a thermotropic liquid crystal/water interface

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An ellipsometric study of the interface between a thermotropic liquid crystal and water near the nematic–isotropic phase transition of the liquid crystal is presented. At temperatures above the transition, a nematic wetting layer appears at the interface if the water phase contains a surfactant inducing a homeotropic alignment of the nematic phase. The detailed behavior is significantly influenced by the concentration of the surfactant. The results can be described by a Landau model of nematic wetting in which the surfactant concentration tunes the magnitude of an ordering interface potential.

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Heterogeneous systems consisting of a thermotropic liquid crystal (LC) and a second nonmiscible liquid are becoming increasingly important in both fundamental and applied research. Investigated topics range from novel colloidal interactions between isotropic droplets in a nematic matrix [1,2] over pressure-induced layering transitions in smectic Langmuir films [3,4] and electro-optic properties of nematic emulsions [5,6], to monitoring of phospholipid layer assembly at nematic LC/water interfaces [7].

LCs show quite often at interfaces, in the temperature range of some K above their phase transitions, the formation of a thin layer possessing the structure of the low-temperature phase; in many cases, the thickness of this layer diverges at the bulk transition temperature, i.e., the interface is completely wetted by the low-temperature LC phase. Although this behavior is well known at LC/air [8,9] and LC/solid interfaces [10–12], it has so far not been demonstrated for LC/liquid interfaces. A few studies are concerned with the behavior of the tension γ of the interface between nematic LCs and different isotropic liquids [13–15]. From the unusual temperature dependence (positive slope) of γ near the nematic–isotropic transition, the presence of a residual nematic order at the interface above the transition was inferred. However, the temperature dependence of γ is primarily related to the excess surface entropy and does not provide direct information about the structure of the interface.

We present here an ellipsometric study which directly probes the structure of the interface between an aqueous phase and a LC near the nematic–isotropic phase transition. The nematic phase is a liquid in which the rodlike molecules of the LC compound tend to align along a common direction, specified by a unit vector (“director”), which also corresponds to the optical axis of this uniaxial birefringent phase. Our results show that at temperatures above the nematic–isotropic phase transition a birefringent uniaxial, probably nematic, layer is present at the interface. The layer thickness strongly increases and possibly diverges when the bulk transition to the nematic phase is approached. An essential requirement for this behavior is the presence of a surfactant in the aqueous phase, which induces a homeotropic alignment (director perpendicular to the interface) of the LC at the interface. By comparing our results with the predictions of Landau theory of nematic wetting, we show that the surfactant concentration may be used as a tuning parameter for the ordering interface field.

The compound under investigation is 8CB (4-octyl-4′-cyanobiphenyl), which undergoes a nematic–isotropic phase transition at $T_{NI}=41\ ^\circ\mathrm{C}$. About 200 mg of the sample are filled into a teflon tube (diameter 7 mm), which dips into a reservoir with either pure water or an aqueous solution of the surfactant CTAB (hexadecyltrimethylammonium bromide). By adjusting the immersion depth of the tube, a plane interface between the LC and the aqueous phase can be obtained. The interface is located in the center of a spherical glass container, which is placed in a copper oven allowing for optical access of the incident and reflected laser beam of the ellipsometer. The temperature of the sample is controlled with a resolution of ≈ 0.02 K. A phase-modulated ellipsometer is used to determine the magnitude $\tan\Psi$ and the argument Δ of the complex amplitude ratio $r_p/r_s=\tan\Psi\exp(i\Delta)$ of the p- and s-polarized components of the laser beam ($\lambda=633$ nm), which is reflected from the LC/water interface. Since the adsorption of the surfactant at the interface needs some time, the sample is allowed to equilibrate for a certain period before a measurement of the temperature dependence is started. This period ranges from several hours at larger CTAB concentrations to several days at very low CTAB concentrations; the equilibration is monitored by measuring the ellipsometric parameters at a fixed temperature just above the nematic–isotropic bulk transition until the values stay constant.

For the measurements of the temperature dependence, data are continuously collected while the temperature is changed at a slow constant rate (typically 0.02 K/min). The angle of incidence θ_i is permanently adjusted so that the value of Δ is between 85° and 95°. Under this condition, θ_i is a good approximation of the Brewster angle θ_B, and the value of $\tan\Psi$, then designated as ellipticity coefficient $\bar{\rho}$, is most sensitive to the presence of an interface layer that differs in its optical properties from the two bulk media. For very thin layers, ellipsometry cannot in some cases, e.g., surfactant monolayers at water/air interfaces, provide detailed structural information [16,17]. However, in the present case,

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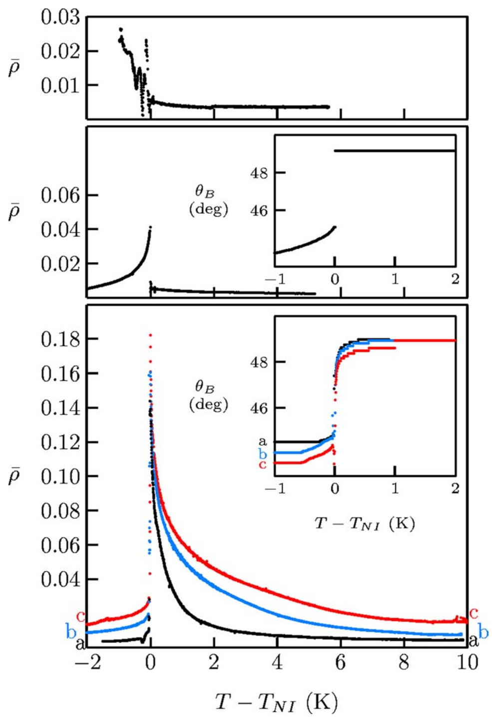

FIG. 1. (Color online) Temperature dependence of the ellipticity coefficient $\bar{\rho}$ near the nematic–isotropic transition of 8CB. Top: interface to pure water. Middle: interface to an aqueous CTAB solution with concentration $c_a=4\times10^{-4}$ mM. Bottom: interface to aqueous CTAB solutions with (a) $c_a=8\times10^{-4}$ mM, (b) 3×10^{-3} mM, and (c) 3×10^{-2} mM. The two insets give the temperature dependence of the Brewster angle θ_B near T_{NI}.

the thickness of the interface layer becomes large near the transition to the nematic phase and $\bar{\rho}$, as well as θ_B, show a characteristic temperature dependence that enables unequivocal conclusions about the interface structure.

Figure 1 shows $\bar{\rho}$ as a function of temperature for the interface to pure water and various aqueous phases with different CTAB concentrations. CTAB is known [18] to induce a homeotropic alignment of nematic LCs at interfaces to aqueous phases. In a recent study [19] it was shown that CTAB induces a surface freezing transition at an alkane/water interface. As is shown below, CTAB possesses a pronounced ordering effect also at a LC/water interface.

For the interface to pure water, we obtain above T_{NI} small and temperature-independent values of $\bar{\rho}$ corresponding to a simple interface between two isotropic liquids. Below T_{NI}, the $\bar{\rho}$ values (and also the θ_B values, not shown in the figure) show a fluctuating behavior that is consistent with the random planar alignment that pure water interfaces impose on nematic LCs [20]; the fluctuations of the $\bar{\rho}$ values reflect the in-plane fluctuations of the orientation of the nematic director.

Already at a CTAB concentration in the aqueous phase, c_a, as small as 4×10^{-4} mM, the behavior changes significantly: whereas the behavior above T_{NI} is the same as for pure water, the fluctuations below T_{NI} are replaced by temperature-dependent but well-reproducible values. As will be discussed below, the jump of θ_B at T_{NI} to lower values by ≈4° (cf. inset of Fig. 1, middle) indicates that the nematic phase now is homeotropically aligned at the interface.

For $c_a=8\times10^{-4}$ mM, again a significantly different behavior is observed: the $\bar{\rho}$ values show now a pronounced increase when T_{NI} is approached from above, whereas the values are small and only little temperature dependent below T_{NI}. At larger c_a values the increase of $\bar{\rho}$ on approaching T_{NI} from above starts at larger temperature distances to T_{NI}. The increase of $\bar{\rho}$ is accompanied by a decrease of θ_B (cf. inset of Fig. 1, bottom). If the c_a value is increased above 3×10^{-2} mM, the behavior does not change significantly and the same results as shown for curve (c) in Fig. 1 are obtained.

The pronounced increase of $\bar{\rho}$, accompanied by a decrease of θ_B, on approaching T_{NI} from above suggests that we observe the wetting of the interface between the isotropic LC and the aqueous surfactant solution by a nematic layer. The simplest refractive index profile of a nematic layer between two isotropic liquids is a slab model with constant index values n_{aq} for the aqueous phase, n_{iso} for the isotropic LC phase, and n_o and n_e for the ordinary and extraordinary index of the nematic phase. If we calculate $\bar{\rho}$ and θ_B as a function of the thickness of such a model nematic layer ($n_o=1.5$, $n_e=1.6$) for three different cases of director orientation (homeotropic, planar and perpendicular to the plane of incidence, planar and parallel to the plane of incidence), we obtain only for the homeotropic case the observed combination of increasing $\bar{\rho}$ and decreasing θ_B values. Concerning the data for $c_a=4\times10^{-4}$ mM (Fig. 1, middle), which do not show any pretransitional change above T_{NI}, the observed decrease of θ_B by 4° at T_{NI} is again obtained only for a model in which the isotropic LC transforms into a homeotropically aligned nematic phase. Moreover, because of the random nature (absence of any preferred in-plane direction) of the planar aligning effect of the water interface, we would expect a fluctuation of the ellipsometric data if the director contains above or below T_{NI} a nonzero in-plane component (i.e., for planar or tilted alignment). Thus, our data confirm the homeotropic alignment effect of CTAB that was already observed below T_{NI} by polarization microscopy [18].

Nematic wetting at LC/air and LC/solid interfaces has been described by a mean-field model [21] in which the Landau–de Gennes theory of the nematic–isotropic bulk transition is extended by a coupling of the nematic order parameter S to a short-range interface potential. We applied this model to our experiments and could achieve an almost quantitative description of the measured data. The free-energy density f reads [21]

$$f=\frac{a}{2}(T-T^{*})S^{2}-\frac{B}{3}S^{3}+\frac{C}{4}S^{4}+\frac{L}{2}\left(\frac{dS}{dz}\right)^{2}-V\delta(z)S. \quad (1)$$

The first three terms are the usual Landau expansion in powers of S with T^{*} being the stability limit of the isotropic phase, the last term describes the coupling to the interface potential V, and the term with coefficient L gives the elastic energy associated with a spatial variation of S; z is the distance to the interface along the interface normal.

By minimization of $f(S,T)$ [21] one can obtain for a given temperature an order parameter profile $S(z)$, which can be transformed into refractive index profiles $n_o(z)$ and $n_e(z)$ as

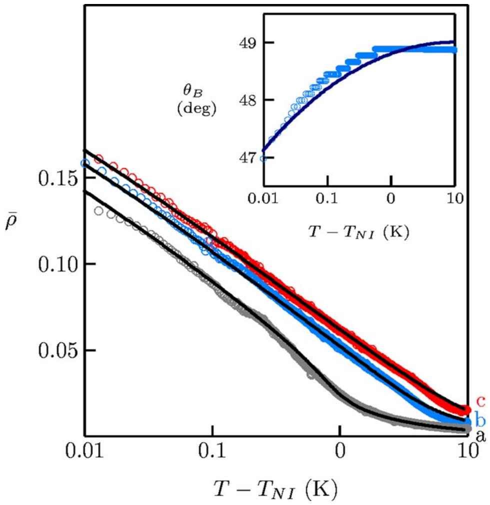

FIG. 2. (Color online) Comparison of measured (∘ symbols) and calculated (solid lines) values of the ellipticity coefficient $\bar{\rho}$ and Brewster angle θ_B. (Inset) The calculated values are based on the free-energy density of Eq. (1), the experimental data are the same as shown in Fig. 1. CTAB concentrations are $c_a = 8 \times 10^{-4}$ (a), 3×10^{-3} (b), and 3×10^{-2} mM (c). The values of the interface potential V used for the three calculated data sets are 1.1×10^{-3} (a), 2.4×10^{-3} (b), and 4.8×10^{-3} Jm^{-2} (c). For θ_B, data for only one concentration are shown, since there are only small differences between the data sets of different concentrations.

described in [9,22]. For the calculation of $\bar{\rho}(T)$ and $\theta_B(T)$, the index profiles are divided into several hundred uniaxial layers; in each layer the optical axis is taken parallel to z and the index values are set to constant values corresponding to averages along z. The ellipsometric parameters of such multilayer systems can be calculated using the recursive formalism by Crook [23] or the 4×4 matrix method [24].

Figure 2 shows the experimental data, which were already presented in Fig. 1 (bottom), together with calculated values of $\bar{\rho}$ and θ_B resulting from the Landau free-energy density given in Eq. (1). Remarkably, all experimental data sets with $c_a \geq 8 \times 10^{-4}$ mM can be reproduced by adjusting just one parameter, the interface potential V, while all other parameters in Eq. (1) can be left unchanged [25]. The value of V increases with increasing concentration c_a; as shown in Fig. 3, the relation between V and c_a is nonlinear, with the V values tending to saturate at larger c_a values.

The amount Γ of surfactant adsorbed at the interface is related to the bulk concentration c_a via an adsorption isotherm that is in the simplest case of the Langmuir type. If we assume a simple proportionality between V and Γ, V should depend on c_a as

$$V = \kappa\Gamma = \kappa \frac{Kc_a}{1 + Kc_a}, \tag{2}$$

with K denoting the adsorption/desorption equilibrium constant and κ being a coefficient relating V and Γ. In fact, our V vs c_a data are well described by this Langmuir-like fitting function (cf. Fig. 3). This result is a strong indication that the magnitude of V, or the ordering field of the interface, is indeed linearly related to the amount of adsorbed surfactant. The value of K obtained from the data of Fig. 2 is ≈ 310 m^3 mol^{-1}. This value is larger than expected since for CTAB at a hexadecane–water interface a value of $K = 18$ m^3 mol^{-1} was determined [26]. The larger value at the LC/water interface might be due to the nematic order of 8CB, which could facilitate, compared to the isotropic hexadecane, a strong adsorption of CTAB.

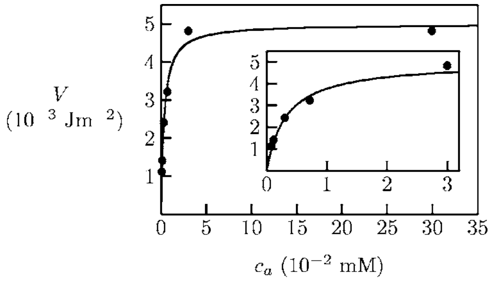

FIG. 3. Values of the interface potential V as function of the CTAB concentration in the aqueous phase c_a. The solid line is a fit corresponding to a Langmuir adsorption isotherm [cf. Eq. (2)]. The inset shows an expansion of the low concentration range.

Furthermore, we should note that the behavior at very low c_a values is more complex than represented by Eq. (2). Our data for $c_a = 4 \times 10^{-4}$ mM show clearly that for this concentration a pretransitional nematic wetting layer above T_{NI} does not occur (as is indicated by the constant $\bar{\rho}$ and θ_B data). Instead we observe an increase of $\bar{\rho}$ when T_{NI} is approached from below. Such an increase is obtained with model profiles in which the nematic order parameter at the interface is *smaller* than in the bulk which would correspond to a negative interface potential V, i.e., V becomes zero at finite c_a. Our data for $c_a = 4 \times 10^{-4}$ mM also show that a homeotropic aligning effect of a surfactant is not necessarily accompanied by an interface-enhanced order parameter.

For $c_a \geq 8 \times 10^{-4}$ mM, we could describe all experimental data sets with parameter values in Eq. (1) that predict complete wetting of the isotropic LC/aqueous phase interface by the nematic phase. It would be worthwhile to study the transition from complete to partial wetting which should occur at $c_a < 8 \times 10^{-4}$ mM. Because of the very long equilibration times (longer than one week) in this low concentration regime, we plan detailed studies with a more suitable surfactant, which would induce a less strong ordering effect at the interface so that the same behavior would occur at higher surfactant concentrations; CTAB analogs with shorter alkyl chains might be good candidates.

In conclusion, we have shown that the interface between a thermotropic LC and an aqueous surfactant solution is at temperatures above the nematic–isotropic transition covered by a nematic wetting layer. The surfactant concentration can be used to change the magnitude of the ordering interface potential so that experimental model systems of wetting with continuously tunable ordering fields can be designed. A similar situation occurs at solid surfaces coated with surfactants or self-assembled monolayers, where it is possible to fine tune the wetting and anchoring behavior by small structural modifications of the monolayer molecules [11,27]. The LC/liquid interface of our study possesses the additional feature of the dynamic equilibrium between the surfactant molecules adsorbed at the interface and those in the aqueous bulk phase. In principle, we could change the properties of the surfactant layer (by changing the bulk concentration c_a) while it is in contact with the LC. This might enable the study of the dynamics of nematic (or smectic) wetting. Our results are also of relevance for recent theoretical studies of nematic wetting layers on colloidal particles in isotropic LCs [28], since small water droplets suspended in isotropic LCs would provide a corresponding experimental system.

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