

Layering Transitions at the Free Surface of a Smectic Liquid Crystal

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We present an ellipsometric study of the free surface of the isotropic phase of a liquid-crystal compound possessing an isotropic–smectic-A transition. Approaching the bulk transition from above, a series of at least eight layering transitions is observed, indicating the successive formation of smectic layers at the surface. Although the growth of the surface smectic-A phase can be described by a logarithmic divergence, the current data allows for a better, if not unambiguous, description in terms of a crossover from logarithmic to power law divergence.

Introduction

Smectic-A (Sm-A) liquid crystals are orientationally ordered fluids in which the rodlike molecules tend to align along a common direction and form additionally a weakly defined layer structure. The layer thickness is about one molecular length, and the layer normal is parallel to the mean direction of the long molecular axis. Many compounds show a direct phase transition from the Sm-A phase to the isotropic liquid phase without an intermediate nematic phase.

If the isotropic–Sm-A phase transition is approached from above, theories^{1–4} predict the formation of the Sm-A phase at an interface to a solid wall or to the vapor phase (free surface) already at temperatures above the bulk transition temperature T_{AI} ; i.e., the interface is wetted by the Sm-A phase. The wetting can be partial (finite thickness of the Sm-A surface film at T_{AI}) or complete (divergence of the Sm-A film thickness at T_{AI}). The growth of the wetting film may proceed via a series of discrete layering transitions, similar to that observed in the adsorption of gases on solid substrates.^{5–7} In particular, the following behaviors are predicted: partial wetting without any layering transitions,^{2,3} partial wetting with a finite number of layering transitions,^{1,4} and complete wetting via a series of an infinite number of layering transitions.^{2,4} In the latter case, a finite number of layering transitions may collapse into a single prewetting transition⁴ where the Sm-A film thickness jumps by a multiple of the single molecular layer thickness.

Experimental studies have concentrated almost solely on homologues of the *n*CB and *n*OCB series,⁸ which show isotropic to Sm-A transitions for $n > 9$. The studies, which are mainly based on X-ray reflectivity measurements, concern mainly the behavior at the free surface,^{9–12} but also at the interface to a wall and in cylindrical pores.^{13,14} Compared to theories, the variety of observed behaviors is much smaller. For the free surface of the cyano-substituted compounds described above, only for the partial wetting case in connection with a finite number of layering transitions was unambiguous evidence obtained, namely, for the compound 16OCB, which shows two sharp layering steps.¹⁰ A similar behavior is observed in 12CB

where five layering transitions are observed.^{9,11} For shorter alkyl chain lengths, the layering transitions are smeared out and the distinction between partial and complete wetting is difficult. In a recent ellipsometry study,¹² complete wetting was found for all smectic *n*CB compounds, similar to that observed in earlier studies^{15,16} of the nematic *n*CB compounds ($n \leq 9$). The layering transitions of 12CB were apparently not seen in ref 12.

While at a planar wall interface basically the same behavior is observed¹³ as for a free surface, the confinement in cylindrical pores is found to increase the number of layering steps (up to eight) in 12CB.¹⁴ Finite volume effects, however, then make a conclusion on the macroscopic wetting behavior more difficult.

We have recently studied^{17–19} the free surface of several nonpolar Sm-A compounds (possessing a second alkyl chain instead of the cyano group) and found a larger variety of wetting behaviors, e.g., complete wetting without any layering transitions but accompanied by a single prewetting transition,¹⁷ partial wetting (or nonwetting) without any pretransitional increase of surface order,¹⁸ and a prewetting critical point in binary mixtures of two liquid crystal compounds.¹⁹ A series of subsequent layering transitions, however, was not observed for the nonpolar smectic compounds.

The different behavior of polar and nonpolar compounds may have several reasons: It is well-known that *n*CB and *n*OCB compounds form a partial bilayer Sm-A phase different from the monolayer Sm-A phase of nonpolar compounds; it is also known that the layering transitions in the *n*CB and *n*OCB series are considerably sharpened with increasing alkyl chain length. The present study addresses the questions whether the same alkyl chain length dependence exists in nonpolar compounds and whether the occurrence of surface layering is connected to the structure of the Sm-A phase. We report ellipsometric measurements on a nonpolar compound (“18.O.6”, hexyl oxyphenyl ester of octadecyloxybenzoic acid) possessing a long alkyl chain; 18.O.6 is a longer homologue of the compound 12.O.6 which was studied earlier by us¹⁷ and did not show a layer-by-layer growth but rather a continuous growth of the surface phase. In contrast, we observe for 18.O.6 a series of at least eight layering transitions. We believe that our study represents the

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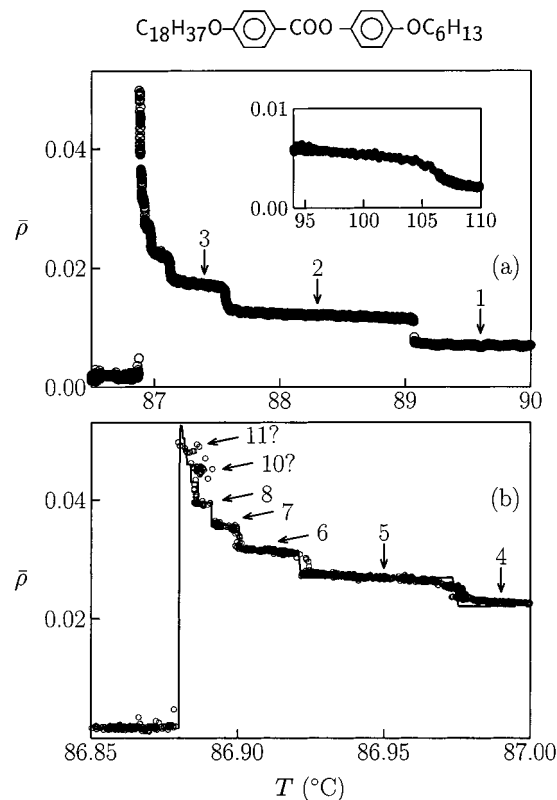


Figure 1. Temperature dependence of ellipticity coefficient $\bar{\rho}$ at the free surface of 18.O.6 in a temperature interval of 3 K (a) and 0.1 K (b) above the bulk isotropic–Sm-A transition temperature $T_{AI} = 86.88$ °C. The numbers indicate the numbers of smectic layers present in the temperature interval of each “plateau”. The inset in (a) shows the “step” where the first smectic layer is formed at the surface. The solid line in (b) represents calculated $\bar{\rho}$ values from a simple slab model (see text).

first example of complete wetting of the liquid/vapor interface by a Sm-A phase via a series of discrete layering transitions, although, as will be described below, definite proof of complete wetting is difficult to obtain by ellipsometric measurements.

Experimental Section

The 18.O.6 compound (the molecular structure is shown on top of Figure 1) was prepared by standard organic chemistry procedures and thoroughly purified by chromatography and multiple recrystallization. The bulk Sm-A–isotropic transition temperature T_{AI} is 87 °C. A 1 mm thick film (area ≈ 2 cm²) is prepared on a rough glass substrate and maintained in a temperature-controlled oven possessing a temperature stability of 10 mK. The temperature is measured by a 100 k Ω thermistor providing a resolution better than 5 mK. The structure of the free surface is studied by reflection ellipsometry as described in refs 17 and 18. The quantities $\tan \Psi$ and Δ are measured, which correspond to the magnitude and the argument of the complex amplitude ratio $r_p/r_s = \tan \Psi \exp(i\Delta)$ of the p- and s-polarized components of the reflected laser light ($\lambda = 633$ nm). The growth of the surface layer is monitored by measuring the ellipticity coefficient $\bar{\rho}$, which is the value of $\tan \Psi$ when the angle of incidence θ_i equals the Brewster angle θ_B , where $\Delta = 90^\circ$. In practice, the values of $\tan \Psi$ and Δ are continuously collected while θ_i is permanently aligned so that $85^\circ < \Delta < 95^\circ$ and the temperature is changed at a constant rate (between 0.5 and 0.1 K/h).

The free surface induces a homeotropic alignment^{9–12,15,16} of the molecules; we have thus to consider a uniaxial surface

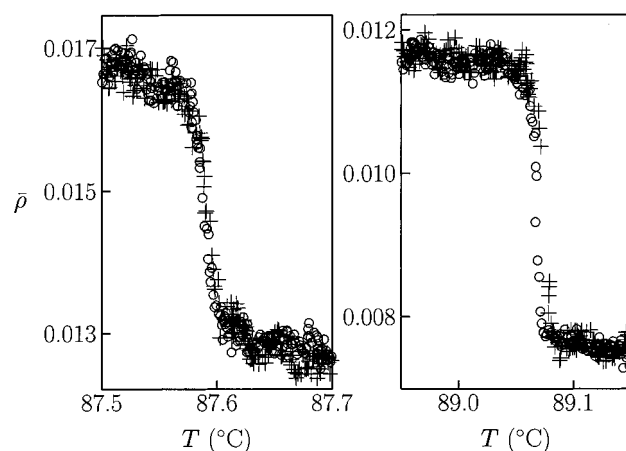


Figure 2. Temperature dependence of the ellipticity coefficient $\bar{\rho}$ in the vicinity of the layering transitions from 1 to 2 (right) and from 2 to 3 (left) layers: +, heating run; O, cooling run; temperature rate 0.4 K/h.

layer with ordinary and extraordinary refractive indices n_o and n_e and its optical axis along the surface normal. The measured value of $\bar{\rho}$ then contains two contributions: $\bar{\rho} = \bar{\rho}_0 + \bar{\rho}_\Gamma$ where $\bar{\rho}_0$ is determined by the roughness or width of the surface ($\bar{\rho}_0 = 0$ for an ideal surface) and $\bar{\rho}_\Gamma$ is in first approximation proportional to the coverage $\Gamma = \int (n_e^2 - n_o^2) dz$ (z being the direction along the surface normal).²⁰ As will be described below, the proportionality between $\bar{\rho}_\Gamma$ and Γ holds only for small surface layer thicknesses. In the limit of n_o and n_e being independent of z , Γ is equivalent to the thickness l of the surface wetting layer.

Results and Discussion

Figure 1 shows the temperature dependence of $\bar{\rho}$ near the bulk isotropic–Sm-A transition temperature T_{AI} . The stepwise growth of $\bar{\rho}$ on approaching T_{AI} is obvious. The first “step”, which occurs with decreasing temperature around 105 °C, is smeared out over a T interval of several K [inset of Figure 1a]. In contrast, all following steps have a very sharp appearance and temperature widths considerably smaller than 0.1 K. Figure 2 shows heating and cooling runs for the second (at 89.1 °C) and third (at 87.6 °C) step. At least at the second step thermal hysteresis is present, indicating that we observe a real first-order transition.

In the following we will argue, by comparison of our measured $\bar{\rho}$ data with calculated $\bar{\rho}$ values resulting from a simple model profile, that each step corresponds to the formation of a single Sm-A layer at the surface. The simplest possible model consists of a uniaxial dielectric slab of thickness l with constant indices n_e and n_o between two isotropic bulk media with indices $n_v = 1$ (vapor) and n_{iso} (isotropic liquid). The value of n_{iso} is obtained from the Brewster angle of the isotropic liquid surface far above T_{AI} ; we find $n_{iso} = 1.470$. From the Brewster angle of the bulk Sm-A phase below T_{AI} we obtain $n_e = 1.525$ and $n_o = 1.441$ if we assume that these values have to fulfill the equation $3n_{iso}^2 = n_e^2 + 2n_o^2$.

With these values of n_{iso} , n_e , and n_o we calculate $\bar{\rho}$ as a function of l using the standard Fresnel formula. The result is shown as the solid line in Figure 3a. Placing onto this line the experimental $\bar{\rho}$ values measured in the middle of each “plateau”, we get values of l that correspond to the thickness of the uniaxial surface film present in the temperature interval of each plateau. A plot of these l values as a function of the plateau number N (counting the plateau between 89 °C and 105 °C as number 1)

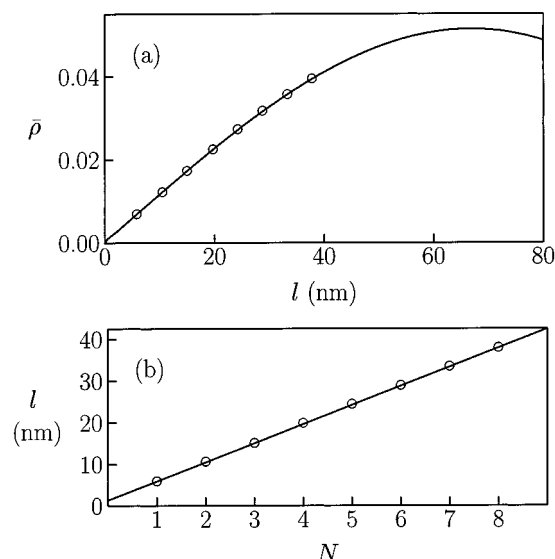


Figure 3. (a) Ellipticity coefficient $\bar{\rho}$ calculated (solid line) as a function of thickness l of a uniaxial layer on top of an isotropic bulk medium with values of n_o , n_e , and n_{iso} as given in the text; the data points are the experimentally measured $\bar{\rho}$ values of each plateau; (b) l values belonging to the experimental $\bar{\rho}$ values as a function of plateau number N ; the solid line corresponds to a linear fit yielding a slope 4.57 nm (the finite l value at $N = 0$ results from a nonzero value of $\bar{\rho}_0$ (contribution of surface roughness), which adds a constant offset to the measured $\bar{\rho}$ values).

can be fitted excellently by a straight line possessing a slope of 4.57 ± 0.01 nm (Figure 3b). Thus, in our simple slab model each step in Figure 1 corresponds to a thickness change of the surface Sm-A film of 4.57 nm, which compares well with the length of the 18.O.6 molecule and the thickness of a single Sm-A layer.

Eight layering steps are clearly resolved. Our present temperature resolution does not permit the observation of further steps in the temperature range of 10 mK above T_{AI} , although we find two accumulations of data points (Figure 1b) that could correspond to the presence of 10 and 11 smectic layers.

Does the Sm-A phase wet the liquid/vapor interface completely? Generally, in the case of complete wetting, theory predicts either a logarithmic divergence of the thickness l of the wetting layer, i.e., $l \propto |\log(T - T_{AI})|$, or a power law divergence, $l \propto (T - T_{AI})^{-1/3}$, depending on the range of the relevant interactions.²¹ For thermotropic liquid crystals mainly van der Waals interactions and thus power law divergence are expected. Figure 4a shows the $\bar{\rho}$ data of Figure 1 on a logarithmic temperature scale. There is a tendency that the distance between two steps (on the logarithmic temperature scale) is not constant but decreases on approaching T_{AI} , indicating that a simple logarithmic divergence is not sufficient to describe the growth of l .

In Figure 4b we have plotted the thickness l of the surface Sm-A phase at the steps vs the step temperatures (on a logarithmic scale), using for the l -axis both a linear and a logarithmic scale. In the following discussion, we do not include the first (smeared out) step around 105 °C since the formation of the first smectic layer at the surface obviously differs from the following steps.²² The interpretation of our data depends on the accuracy of the measured $(T_{\text{step}} - T_{AI})$ values. As can be seen in Figure 1b, T_{AI} can be localized within a temperature interval smaller than 5 mK and the temperature width of the steps is of the order of 10 mK. We assume thus an error interval of 15 mK for each $(T_{\text{step}} - T_{AI})$ value resulting in the

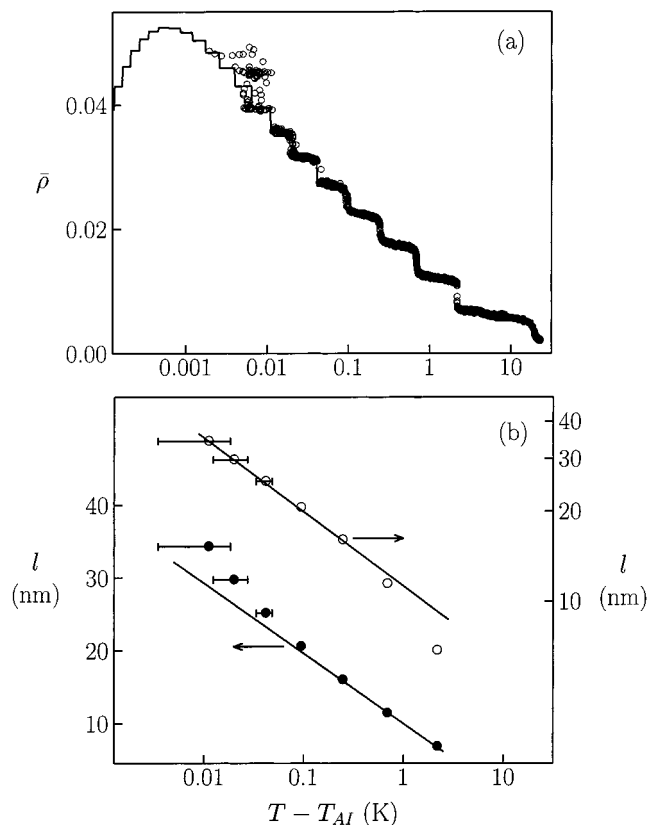


Figure 4. (a) Values of the ellipticity coefficient $\bar{\rho}$ as a function of $T - T_{AI}$ (on a logarithmic scale with $T_{AI} = 86.880$ °C); the solid line represents calculated $\bar{\rho}$ values from a simple slab model (see text). (b) Wetting layer thickness l at each step as a function of step temperature: ●, l vs $\log(T - T_{AI})$; ○, $\log l$ vs $\log(T - T_{AI})$. The values of l were taken at the half-step heights; i.e., for a step where the wetting layer jumps from N to $N + 1$ layers, l was calculated as $l = (N + 0.5) \times 4.57$ nm; the uncertainty in l is smaller than the size of the symbols; the uncertainty in $(T - T_{AI})$ is of the order of 15 mK.

error bars shown in Figure 4b. The l vs $\log(T - T_{AI})$ plot (● data in Figure 4b) seems to deviate close to T_{AI} from a linear behavior; however, a straight line (corresponding to a logarithmic divergence) is still just in accordance with our accuracy. The double-logarithmic plot, $\log l$ vs $\log(T - T_{AI})$ (○ data in Figure 4b), shows linear behavior close to T_{AI} , but there are clear deviations far from T_{AI} . Thus, our data are best described by a crossover from logarithmic growth far from T_{AI} to power law growth close to T_{AI} ; i.e., thin films (four layers and less) are determined by short-range interactions whereas in thicker films long-range (van der Waals) interactions are relevant. A similar crossover from logarithmic to power law growth has been reported for the surface melting of neon films of different thickness.²³

In the case of power law growth, an exponent value of $-1/3$ is expected from the Landau theory of wetting.²¹ Indeed, the value $-1/3$ is experimentally observed in several systems such as gases adsorbed on gold and graphite^{24,25} and freely suspended smectic liquid crystal films.^{26,27} The ○ data shown in Figure 4b indicate a slightly different value ($-1/4$) of the exponent for the present system; at present, we do not have an explanation for this observation.

The data presented in Figure 4 do not yield an indication for a truncation of the wetting layer growth at T_{AI} . Thus, the wetting seems to be complete although this is difficult to prove by ellipsometry. The sharp drop of $\bar{\rho}$ at T_{AI} is not contradictory to a diverging wetting layer thickness l since $\bar{\rho}$ decreases again

when l exceeds a value of ≈ 70 nm (Figure 3a). The solid lines in Figures 1b and 4a give calculated $\bar{\rho}$ values obtained from the simple slab model using the values of n_e , n_o , and single smectic layer thickness given above and extrapolating the power law growth to a temperature less than 1 mK above T_{AI} . For temperatures down to $T_{AI} + 10$ mK, our ellipsometric data are well-described by the slab model. Our present temperature resolution, however, does not allow one to collect data in the temperature range very close to T_{AI} where $\bar{\rho}$ decreases with increasing l .

The tendency to show sharp layering transitions with increasing alkyl chain length has now been established in three different structures: nCB , $nOCB$, and $\bar{n}O.6$. Long alkyl chains increase the smectic (positional) order parameter and suppress the occurrence of a nematic phase. Thus, in smectic compounds with long alkyl chains a sharp interface between well-defined surface Sm-A layers and the isotropic interior can exist. In smectic compounds with shorter alkyl chains, the smectic surface layers are less well-defined and the interface to the isotropic interior may be additionally roughened by a thin nematic-like region between surface and bulk phases. This may be an explanation for the observed alkyl chain dependence since sharp interfaces favor layering transitions whereas rough interfaces do not.⁶

Conclusion

We have reported an ellipsometric study of the free surface above the Sm-A–isotropic phase transition of a nonpolar liquid crystal compound possessing a long alkyl chain. A series of at least eight layering steps, corresponding to the formation of single smectic layers, is observed on approaching the transition to the Sm-A phase. The first smectic layer at the surface is formed continuously within a temperature interval of several K. At least the first of the following steps is a first-order transition (confirmed by the observation of thermal hysteresis), where the wetting layer thickness jumps discontinuously by the thickness of a single smectic layer. It is thus clear that the occurrence of surface layering is not restricted to polar compounds of the nCB or $nOCB$ type and that the tendency to show sharper layering transitions with increasing alkyl chain length is probably a general feature of thermotropic smectic liquid crystals. Our data do not yield an indication for partial wetting, contrary to the behavior observed in nCB and $nOCB$ compounds.^{9,10} Our study may thus represent the first example

of complete wetting of a liquid/vapor interface by a Sm-A phase via a series of discrete layering transitions; a definite proof of complete wetting, however, could be obtained only with a better temperature resolution.

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