Prewetting Critical Point in a Binary Liquid-Crystal System

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We study the wetting behavior at the free surface of the isotropic phase of various mixtures of two thermotropic liquid crystal compounds. Both pure compounds show complete wetting of the isotropic liquid-vapor interface by an interposing anisotropic phase when the transition to the bulk liquid-crystal phase is approached, but only one of the compounds shows in addition a discontinuous prewetting transition. The prewetting discontinuity is found to vanish at a critical point in the temperature-composition plane. [S0031-9007(98)05951-1]

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When a critical point, at which the difference between two fluid phases α and β vanishes, is approached along the α/β coexistence curve, a first-order wetting transition at the interface to a third (inert) phase γ is expected at a temperature T_w which is well below the critical temperature T_c [1–3]. Above T_w, the interface to the γ phase is covered by a macroscopically, in principle infinitely thick film of, e.g., the α phase excluding direct contact of the β phase with the γ phase (complete wetting). Below T_w, the interface to the γ phase is covered with an only microscopically thin film (partial wetting). The first-order wetting transition at coexistence, where the film thickness jumps to infinity, implies the existence of a line of first-order prewetting transitions off coexistence, characterized by a finite (thin to thick) film thickness jump. The prewetting line is expected to terminate at a prewetting critical point (PCP) where the film thickness discontinuity vanishes. Although wetting transitions can be studied in a number of systems [3], experimental observations of corresponding prewetting transitions are much less frequent [4]. Recently, we have observed a prewetting transition at the free surface of the isotropic phase of a smectic liquid-crystal compound [5]. Here, we report on our study of a two-compound liquid-crystal system which enables the realization of the prewetting line in the temperature-composition plane. This is the first observation of a PCP in thermotropic liquid crystals.

Liquid crystals provide examples of orientational wetting [6]: Above an isotropic—nematic transition an interface layer exhibiting the nematic parallel ordering of the rodlike molecules is formed while the bulk is isotropic. This behavior is observed at free surfaces [7–9] and at interfaces to a solid wall [10–13]. The nematic wetting at free surfaces is usually complete, whereas at wall interfaces both partial and complete wetting occurs. In the case of complete wetting a logarithmic divergence of the absorption parameter $\Gamma = \int [S(z) - S_b]\,dz$ is found [6] (z being the distance from the interface and S the nematic orientational order parameter, the bulk value S_b equals zero in the isotropic phase). A prewetting transition has not been observed in these studies, although a partial to complete wetting transition at coexistence was obtained by modifying the wall surface [13].

In the smectic-*A* (Sm-*A*) phase a positional order exists in addition to the nematic parallel orientational order: The molecules are arranged in layers with a thickness of approximately one molecular length. If an isotropic–Sm-*A* transition is approached from above, the successive formation of smectic layers at interfaces is observed [14–17]; the number of smectic layers seems to remain finite at the bulk transition temperature (partial wetting).

Theoretical models exist of both nematic [6,18,19] and smectic wetting [20] of the isotropic liquid/vapor or liquid/wall interface. The theories predict the experimentally observed behaviors (e.g., the logarithmic divergence of Γ or the appearance of a finite number of smectic layers), and in addition several behaviors which have not been observed experimentally so far (e.g., complete wetting via an infinite number of smectic layering transitions or prewetting transitions above isotropic-nematic transitions).

The first example of a prewetting transition in liquid crystals was observed recently by us at the free surface of the smectic compound "$\overline{12}$.O.$\overline{6}$" (4-hexyloxyphenylester of 4-dodecloxybenzoic acid): At a temperature 1 K above the bulk isotropic–Sm-*A* transition a discontinuous jump of Γ occurs which corresponds to an approximate thickness change of the wetting layer from submonolayer size to about two molecular lengths; with decreasing temperature the data indicate a logarithmic divergence of Γ [5]. We report here on our measurements of several binary mixtures of $\overline{12}$.O.$\overline{6}$ and a second compound, "9O.4" (4-nonyloxybenzylidene–4′-butylaniline) which shows at the free surface complete wetting at its isotropic–Sm-*A* transition without an accompanying prewetting transition. Our aim is to study the approach of the prewetting transition of $\overline{12}$.O.$\overline{6}$ to a PCP which can be expected to occur at a certain composition in this binary system.

Binary mixtures are prepared by weighing corresponding amounts of $\overline{12}$.O.$\overline{6}$ and 9O.4 in a small glass tube (the total amount of each mixture was about 250 mg), then heating the mixture into its isotropic liquid phase with thoroughly stirring for several minutes. Phase structures

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and transition temperatures of each mixture were determined using a polarizing microscope equipped with a microscope hot stage.

For the study of the free surface an approximately 1 mm thick film (area $\approx 2\ \mathrm{cm}^2$) of each mixture is prepared on a rough glass substrate and placed into a temperature-controlled oven possessing a temperature stability of the order of 0.02 K. A phase-modulated ellipsometer is used to study the change of polarization of a laser beam ($\lambda = 633$ nm) upon reflection by the free surface of the sample film; reflection from the second (liquid crystal-glass) interface is suppressed by the substrate roughness. As usual in ellipsometry, 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 reflected light is measured.

The value of r_p/r_s is most sensitive to the surface structure when the angle of incidence θ_i equals the Brewster angle $\theta_B$where $\Delta = 90°$; the corresponding value of $\tan\Psi$ is commonly designated as elipticity coefficient $\overline{\rho}$. The temperature dependence of $\overline{\rho}$ is determined by continuously collecting values of $\tan\Psi$ and Δ and adjusting θ_i so that $85° < \Delta < 95°$ while the temperature is changed at a slow rate (between 0.005 and 0.02 K/min).

For an idealized steplike interface one expects $\overline{\rho} = 0$, whereas for a fluid interface one finds always a value of $\overline{\rho} > 0$. The deviation of $\overline{\rho}$ from zero has two origins: the finite width or roughness of the interface and the presence of a layer interposing the interface between the two bulk media [21]. The measured value of $\overline{\rho}$ is the sum of these two contributions, i.e., $\overline{\rho} = \overline{\rho}_0$ (surface roughness contribution) + $\overline{\rho}_\Gamma$ (surface layer contribution) provided that the relevant lengths are considerably smaller than the wavelength of light used for the measurements [7]. Further, under this condition the value of $\overline{\rho}_\Gamma$ is proportional to $\int[n_e^2(z) - n_o^2(z)]\,dz$ where n_o and n_e are the ordinary and extraordinary refractive indices of an uniaxial (optical axis along surface normal) surface layer on an isotropic bulk liquid. Since the difference $[n_e^2(z) - n_o^2(z)]$ is proportional to the orientational order parameter S, the measured $\overline{\rho}$ vs T curves can be seen as curves of the adsorption parameter Γ vs T with an offset corresponding to $\overline{\rho}_0$. We should note two drawbacks: First, we can measure only the orientational order; in the case of smectic wetting we cannot prove the presence of smectic layers. Second, the linear relation between $\overline{\rho}$ and Γ is restricted, for typical refractive index values of liquid-crystal materials, to surface layer thicknesses below 50–70 nm; it is thus difficult to prove a divergence of Γ.

Figure 1 shows the temperature dependence of $\overline{\rho}$ for both pure compounds near their Sm-A–isotropic bulk transition temperature T_{AI}. The prewetting transition of $\overline{12}.\mathrm{O}.\overline{6}$, on which we report in detail in [5], is seen 1 K above T_{AI} where $\overline{\rho}$ shows a steplike discontinuity. In contrast, the $\overline{\rho}$ values of 9O.4 increase continuously when T_{AI} is approached. Although the bulk phase below the isotropic phase is Sm-A, there is no indication of a smectic layering as observed in other compounds [14–17]. In the region where a linear relation between $\overline{\rho}$ and Γ exists, the increase of $\overline{\rho}$ is in both compounds of the present study consistent with a logarithmic divergence of Γ at T_{AI} as demonstrated in the insets of Fig. 1 where $\overline{\rho}$ is plotted on a logarithmic temperature scale. We can also reproduce the measured $\overline{\rho}$ values close to T_{AI} by adjusting the parameters of a phenomenological model [19] predicting a logarithmic divergence of Γ. The logarithmic divergence, with the restrictions mentioned above, is exhibited also by all mixtures of the present system.

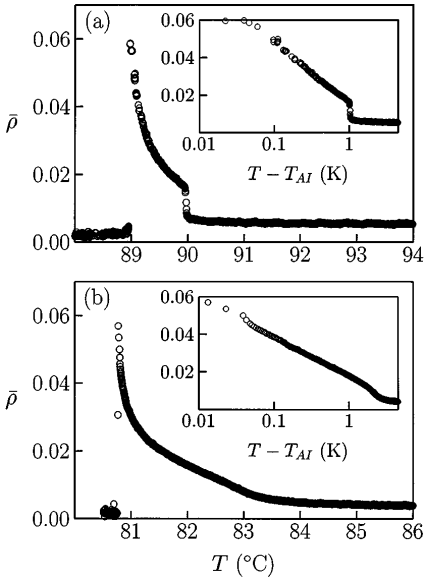

FIG. 1. Temperature dependence of the ellipticity coefficient $\overline{\rho}$ of the free surface near the bulk Sm-A–isotropic transition of the compounds $\overline{12}.\mathrm{O}.\overline{6}$ (a) ($T_{\mathrm{AI}} = 89.05$ °C) and 9O.4 (b) ($T_{\mathrm{AI}} = 80.76$ °C). The prewetting jump of $\overline{12}.\mathrm{O}.\overline{6}$ is seen at 90 °C. The insets show the same $\overline{\rho}$ data as a function of $\log(T - T_{\mathrm{AI}})$.

It is evident that pure 9O.4 does not show a discontinuous prewetting transition; nevertheless, there is obviously a change of the slope of the $\overline{\rho}$ vs T curve $\approx$2.2 K above T_{AI} indicating the onset of the surface layer growth. On the logarithmic temperature scale [inset of Fig. 1(b)] a weakly pronounced S-like shape of the curve is discernible; we thus interpret this feature as a trace of the nearby PCP. Indeed, as will be described below, all mixtures of the present system which are on the "supercritical" side of the PCP exhibit this feature, and it becomes more pronounced on approaching the PCP.

Because both compounds, $\overline{12}.\mathrm{O}.\overline{6}$ and 9O.4, show direct isotropic to Sm-A transitions, we expected the same behavior for each binary mixture. However, for all mixtures the phase sequence isotropic–nematic–Sm-A is observed; already a mixture possessing a mole fraction $x_{9\mathrm{O}.4}$ of only 0.026 shows a 0.2 K broad nematic phase between its isotropic and Sm-A phase. Remarkably, the wetting behavior seems to be completely unaffected by this change of the bulk phase structure: Apart from a small shift of the temperature scale and the indication of the narrow nematic phase, the $\overline{\rho}$ data of the $x_{9\text{O}.4} = 0.026$ mixture coincide with those of the pure $\overline{12}.\text{O}.\overline{6}$ compound, showing a prewetting jump 1 K above the bulk coexistence temperature.

As is demonstrated in Fig. 2, the prewetting discontinuity is with increasing $x_{9\text{O}.4}$ clearly observed up to $x_{9\text{O}.4} = 0.121$. A $x_{9\text{O}.4} = 0.148$ mixture shows still a steep increase of $\overline{\rho}$ in a narrow T interval but it is difficult to decide whether there is a discontinuity or not. The discontinuity has definitely vanished in a $x_{9\text{O}.4} = 0.173$ mixture, where it is replaced by a continuous variation of $\overline{\rho}$ with T exhibiting an infection point. A similar behavior is found when the thermal hysteresis is regarded. As described in [5], the prewetting transition of pure $\overline{12}.\text{O}.\overline{6}$ shows a weakly pronounced thermal hysteresis. Already in the $x_{9\text{O}.4} = 0.121$ mixture, where the $\overline{\rho}$ vs T curve shows still a discontinuous appearance, the hysteresis cannot be detected with the present experimental resolution. Together, these observations clearly indicate that a line of prewetting discontinuities exists in the T-x plane which terminates at a critical point. As estimated from the appearance of the $\overline{\rho}$ vs T curves the coordinates of the PCP are approximately $x_{9\text{O}.4} = 0.15$ and $T = 86.9\,^\circ\text{C}$. In the "supercritical" region, the inflection point exhibited by the $x_{9\text{O}.4} = 0.173$ curve becomes more and more smeared out with further increasing $x_{9\text{O}.4}$; it is, however, in a very weakly pronounced shape discernible even in pure 9O.4.

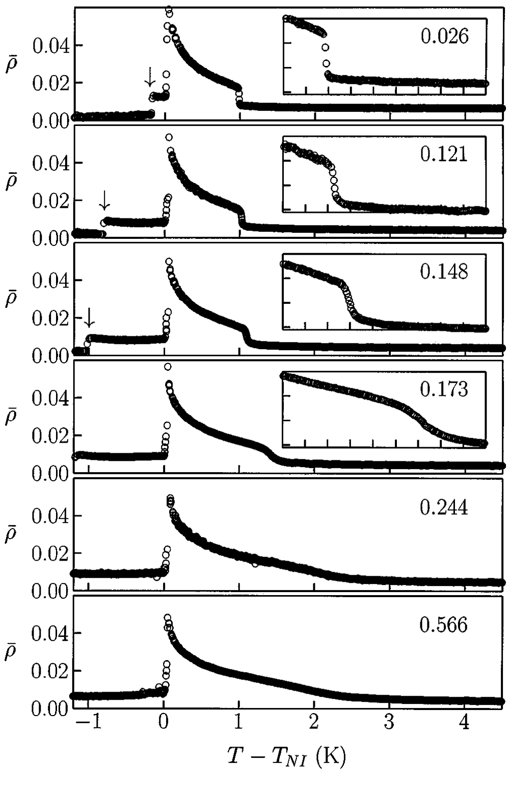

FIG. 2. Temperature dependence of the ellipticity coefficient $\overline{\rho}$ for several binary mixtures of $\overline{12}.\text{O}.\overline{6}$ and 9O.4 (the numbers in the upper right corners give the mole fraction $x_{9\text{O}.4}$). T_{NI} corresponds to the bulk nematic–isotropic transition temperature. For the $x_{9\text{O}.4} = 0.026$, 0.121, and 0.148 mixtures the bulk nematic to Sm-A transition can be seen (indicated by the arrows) as a steplike decrease of $\overline{\rho}$ indicating that the free surface of the Sm-A phase is sharper than that of the nematic phase. The insets show the prewetting transitions (or inflection point) on an enlarged scale, one division of the x axis (T) corresponds to 0.1 K, one division of the y axis ($\overline{\rho}$) to 0.005.

Figure 3 shows in the T vs $x_{9\text{O}.4}$ plane the bulk phase diagram together with the detected prewetting transitions of all samples studied. The PCP is expected to belong to the two-dimensional Ising universality class [22], its order parameter being in our case the magnitude of the adsorption parameter discontinuity $\Delta\Gamma$ which should vanish at the prewetting critical point according to $\Delta\Gamma \propto t^{\beta}$, with $t = |T - T_{\text{pc}}|/T_{\text{pc}}$ (T_{pc}: prewetting critical temperature) and $\beta = 1/8$. To our knowledge, there exists only one attempt to determine the value of β experimentally [4b]. In the present study, the magnitude of the measured $\Delta\overline{\rho}$ values is well within the range of the linear relation between $\overline{\rho}$ and Γ, thus $\Delta\overline{\rho}$ is a direct measure of $\Delta\Gamma$. The inset of Fig. 3 shows a double logarithmic plot of $\Delta\overline{\rho}$ vs t. Our data are not contradictory to the theoretically expected value $\beta = 1/8$, but there is some uncertainty because of the small number of data points [23]: Linear least mean square fits lead to $\beta = 0.11 \pm 0.04$ if we localize T_{pc} near the inflection point of the $\overline{\rho}$ vs T curve of the $x_{9\text{O}.4} = 0.173$ mixture, and to $\beta = 0.09 \pm 0.03$ if we assume that T_{pc} is close to the discontinuity (or inflection point) of $x_{9\text{O}.4} = 0.148$ mixture. The average of these two limiting values results in $\beta = 0.10 \pm 0.04$.

Further points which need to be addressed are the structures of the thin and thick films above a below the

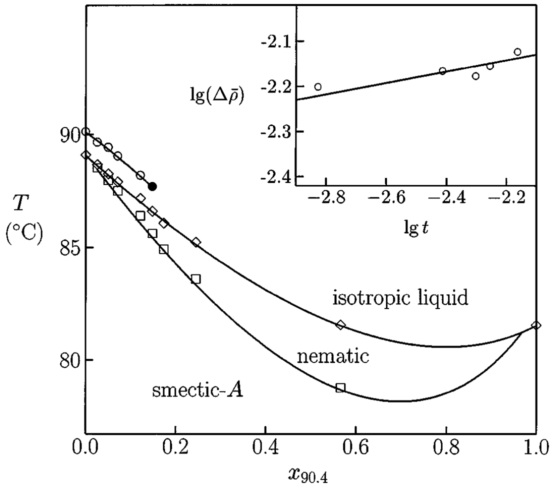

FIG. 3. Binary bulk phase diagram of the compounds $\overline{12}.\text{O}.\overline{6}$ and 9O.4. Both pure compounds show direct Sm-A–isotropic transitions, whereas all mixtures show an intermediate nematic phase. The solid lines are meant as guides to the eye; we have no data points in the region $0.566 < x_{9\text{O}.4} < 1$. The ∘ symbols designate the prewetting transitions and the • symbol the approximate location of the PCP. Inset: Double logarithmic plot of the $\overline{\rho}$ jump at the prewetting transition as a function of reduced temperature t for $T_{\text{pc}} = 86.9\,^\circ\text{C}$ (inflection point of the $\overline{\rho}$ vs T curve of the $x_{9\text{O}.4} = 0.148$ mixture). The slope of the solid line corresponds to the theoretical expectation of $\beta = 1/8$.

prewetting transition and the nature of the surface phase in relation to the bulk phase. The difference between the surface films above and below a prewetting transition is the magnitude of Γ. In our case, the magnitude of $\overline{\rho}$ above the prewetting transition corresponds approximately to the value expected for the free surface, without any surface layer, of an isotropic liquid consisting of molecules of a dimension of $\approx 3 \times 0.5 \times 0.5\ \mathrm{nm}^3$. Thus, if there is already some excess surface order above the prewetting transition, it is restricted to submonolayer dimension.

Below the prewetting transition there is an optically uniaxial surface layer with its optical axis parallel to the surface normal. The layer thickness amounts to several nm just below the prewetting transition and to at least 70 nm close to the bulk transition; possibly there is complete wetting at coexistence. Besides the optical uniaxiality, the ellipsometric data do not reveal structural details, i.e., we cannot decide whether the surface phase is nematic or smectic. Since all samples, with the exception of the two pure compounds, are nematic below their isotropic phase, we expect the surface phase also to be nematic. Concerning the two pure compounds, which are Sm-*A* below their isotropic phase but do not show smectic layering transitions at the surface, x-ray reflectivity studies would be necessary to clarify the structure of the surface phase.

In conclusion, we have studied binary mixtures of liquid-crystal compounds which show different wetting behaviors at the free surface of the isotropic phase. In particular, we have shown that in several mixtures, which all possess an isotropic-nematic bulk transition, a discontinuous prewetting transition exists which vanishes at a PCP when the mole fraction of one component exceeds a certain value. The decrease of the magnitude of the prewetting jump of Γ on approaching the critical point can be described by a power law with a critical exponent $\beta = 0.10 \pm 0.04$. Despite this relatively large uncertainty, we would like to emphasize that liquid crystals are well suited for ellipsometric studies of prewetting effects since the changes in $\overline{\rho}$ are, because of the birefrigence of the liquid-crystal surface layer, about 1 order of magnitude larger than in ellipsometric studies of binary mixtures of simple fluids [4b].

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