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2009 EPL 88 46001

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# Experimental study of prewetting transitions by systematic variation of the surface field at nematic liquid crystal/water interfaces

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received 7 October 2009; accepted in final form 6 November 2009

published online 2 December 2009

PACS 61.30.-v – Liquid crystals

PACS 61.30.Hn – Surface phenomena: alignment, anchoring, anchoring transitions, surface-induced layering, surface-induced ordering, wetting, prewetting transitions, and wetting transitions

PACS 68.05.Cf – Liquid-liquid interface structure: measurements and simulations

**Abstract** – An ellipsometric study of the interface between a nematic liquid crystal and water in the presence of a nonionic surfactant is presented. The surfactant induces a nematic wetting layer at temperatures above the bulk nematic-isotropic transition and the surfactant concentration serves as a handle to tune the strength of the ordering surface field. At low surfactant concentrations, a discontinuous jump in the thickness of the nematic wetting layer is observed at a temperature a few tenths of one centigrade above the bulk nematic-isotropic transition. With increasing surfactant concentration, this prewetting transition is driven towards a critical point.

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**Introduction.** – Wetting phenomena play important roles in fundamental and applied research [1]. If two coexisting fluid phases  $\alpha$  and  $\beta$  (*e.g.*, liquid and vapor phase of a substance) are in contact to a third phase  $\gamma$  (*e.g.*, a solid substrate), fundamental arguments predict that the interface to  $\gamma$  is inevitably wetted completely by one of the two phases (say:  $\alpha$ ) if the critical point is approached at which  $\alpha$  and  $\beta$  become indistinguishable [2]. The onset of complete wetting is expected at a wetting transition at a temperature  $T_w$  well below the critical point temperature  $T_c$ . Below  $T_w$ , droplets of  $\alpha$  on  $\gamma$  possess a finite contact angle which becomes zero for  $T \geq T_w$ . If  $T_w$  is not too close to  $T_c$ , the wetting transition is expected to be a first-order transition, accompanied by the discontinuous formation of a macroscopically (in principle infinitely) thick film of  $\alpha$  on  $\gamma$ . The first-order wetting transition at coexistence should give rise to a line of first-order surface transitions, terminating at a critical point, in the off-coexistence region. At these prewetting transitions, a discontinuous but finite jump of the thickness of the  $\alpha$  phase is expected [2–4].

Two field variables are important for the experimental study of these phenomena: the bulk field  $h$  coupled

to the order parameter of the transition (*e.g.*, the pressure in the case of a liquid/gas transition) and the surface field  $h_1$  which describes the interactions between  $\alpha$  and  $\gamma$ . Global phase diagrams of surface transitions in the space of temperature and  $h$  and  $h_1$  have been studied by Landau theory [5]. Experimentally, many systems of liquid adsorbates on solid substrates show complete wetting in the whole temperature range between  $T_c$  and the triple point temperature  $T_p$  of the adsorbate. In these cases (triple point wetting),  $h_1$  is too large to allow for an experimental observation of the prewetting line. The first experimental studies of prewetting transitions could be conducted for noble gases [6] and hydrogen [7] on alkali metal surfaces where the fluid-substrate interactions are comparable or weaker than the intermolecular interactions within the fluid [8]. Other examples are methanol/cyclohexane mixtures at their vapor interface [9], as well as mercury [10] and potassium/potassium chloride mixtures [11] on sapphire. In these studies, the prewetting transitions are investigated by varying either the vapor pressure of the fluid or the composition of the binary mixtures, *i.e.*, the bulk field  $h$  is varied while the surface field  $h_1$  is held constant. In the present letter, we report the experimental observation of prewetting transitions for a nematic liquid crystal (LC) in contact with

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a surfactant-laden interface to an aqueous phase. The surfactant amount serves as a handle to tune the magnitude of the surface field  $h_1$ . It is shown that with increasing magnitude of  $h_1$  the first-order prewetting transition is driven towards a critical point. The signature of the prewetting transition is still discernable in the supercritical region at higher values of  $h_1$ . To the best of our knowledge, this is the first experimental study in which the prewetting line has been realized by a systematic variation of the surface field.

Nematic LCs are orientationally ordered liquids consisting of rodlike molecules which tend to align along a common direction described by a unit vector  $\mathbf{n}$ . The order parameter  $S = \langle 3 \cos^2 \theta_i - 1 \rangle / 2$  ( $\theta_i$  being the angles of the individual molecules with  $\mathbf{n}$ ) decreases with increasing temperature and drops to zero at a first-order transition at which the LC compound forms an ordinary isotropic liquid phase. The nematic and isotropic phases correspond here to the phases  $\alpha$  and  $\beta$ : when the nematic-isotropic transition is approached from the isotropic side, a nematic wetting layer can form at an interface while the bulk is still in the isotropic phase. When the bulk transition temperature  $T_{NI}$ , *i.e.*, the nematic/isotropic coexistence, is approached, the thickness of the nematic layer usually diverges (corresponding to complete wetting), in some cases it stays finite at  $T_{NI}$  (corresponding to partial wetting). This behaviour has been studied for many LC compounds at various kinds of interfaces [12–20]. Despite the extensive experimental work, and long-standing theoretical predictions [21–23], prewetting transitions are usually not found. There are only two LC systems in which a distinct surface transition near a nematic-isotropic bulk transition has been observed. The first comprises compounds of the  $\bar{n}.O.\bar{m}$ . series<sup>1</sup> for which ellipsometry [24] and calorimetric [25] studies revealed a possible prewetting transition for some compounds. The feature is most prominent in I2.O.6. [26], but this compound shows a smectic-A–isotropic bulk transition and the nature of the surface phase is not clear. The second system is a commercial multicomponent LC mixture for which a surface transition well separated from a nematic-isotropic bulk transition was reported [27]. However, in that case the surface transition is broadened over a temperature interval of 1.6 °C or more, and it might be difficult to prove the first-order nature of the surface transition.

First-order prewetting transitions are expected for low surface fields, *i.e.*, under conditions where the interactions between the substrate  $\gamma$  and the wetting phase  $\alpha$  are just sufficient to induce complete wetting for  $\alpha/\beta$  coexistence. For nematic LCs, the relevant surface interactions are those which promote the orientation of the molecules along a certain direction. In practice, the orientation of LCs can be controlled by coating solid substrates

with suitable organic chain molecules. If these molecules are bound at one end to the substrate, so that their alkyl chains extend away from the interface, the LC molecules are aligned perpendicular to the interface (homeotropic anchoring) [16,19,28]. Surfactant molecules which possess the common polar head/nonpolar tail structure and accumulate at LC/water interfaces can also be used for this purpose: whereas on a bare water surface LC molecules align parallel to the surface, the presence of suitable surfactant molecules results in a perpendicular alignment [29,30]. Moreover, the variation of the concentration of the surfactant can be used to tune the strength of the alignment, *i.e.*, the strength of the effective surface field controlling the nematic or smectic wetting behaviour at LC/water interfaces [20,31,32]. In the present work, we show that careful control of the surfactant concentration at LC/water interfaces enables the experimental realization of nematic prewetting transitions and the study of their surface field dependence.

**Experiment.** – The compound under investigation, 4-nonyl-4'-cyanobiphenyl (9CB), was bought from Synthron Chemicals, Germany, and recrystallized from ethanol and hexane; its nematic-isotropic transition is at  $T_{NI} = 49.5$  °C. The surfactant, monoolein (1-oleoylglycerol), was bought from Fluka and used as received. For each measurement, about 300 mg 9CB were mixed with the appropriate amount of monoolein by stirring the mixture 30 min at 70 °C; we studied samples with the value of the surfactant mol fraction in the bulk LC phase,  $x_s$ , ranging from 0 to 0.007.

The presence and thickness of the nematic wetting layer is determined by ellipsometry. The experimental configuration is shown in fig. 1. The LC sample is placed into a teflon tube (diameter 7 mm) which dips into a water reservoir. The thickness of the LC sample amounts to several mm, so that the LC/air interface is well separated from the LC/water interface. Since the aqueous phase does not intrude between the organic liquid crystal and the teflon surface, it is possible to tune the curvature of the LC/water interface by adjusting the immersion depth of the teflon tube and a plane interface, suitable for ellipsometric measurements, can be prepared. 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.

A phase-modulated ellipsometer is used to determine the magnitude  $\tan \Psi$  and the argument  $\Delta$  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, typically several hours, before a measurement run is started. The equilibration period is monitored by measuring  $\tan \Psi$  and  $\Delta$  as a function of time at

<sup>1</sup> $\bar{n}.O.\bar{m}$ . designates alkyloxyphenylesters (chain length  $m$ ) of alkyloxybenzoic acids (chain length  $n$ ).

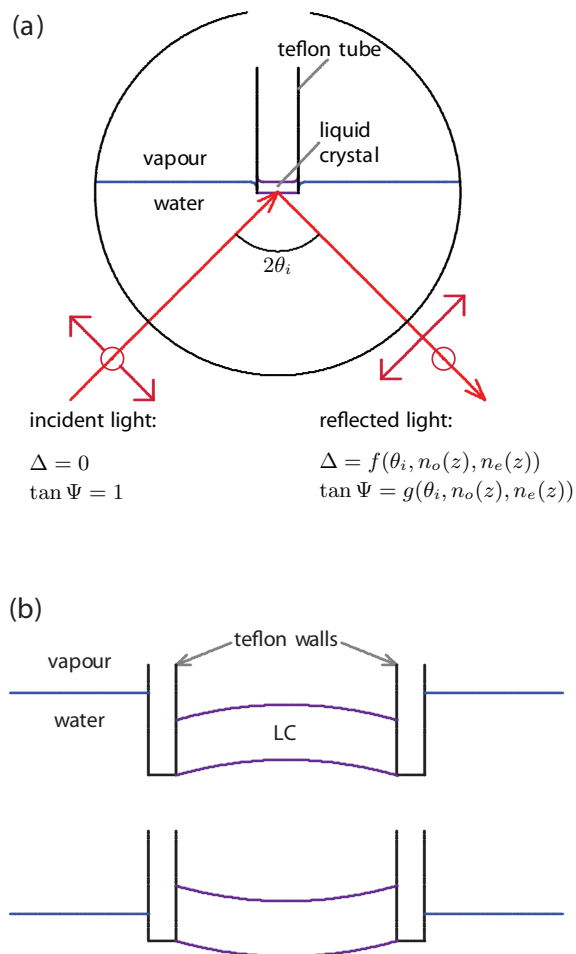


Fig. 1: (Colour on-line) a) Schematic drawing of the experimental geometry. The LC/water interface is localized in the center of a spherical glass container. The ellipsometric parameters  $\Delta$  and  $\Psi$  of the reflected light depend on the angle of incidence  $\theta_i$  and the refractive index profile of the interface. b) Control of the curvature of the LC/water interface. The LC sample is prepared as a mm thick film at the bottom of a teflon tube which dips into the water phase. For small changes of the immersion depth of the tube, the LC film behaves as if it was pinned to the opening of the teflon tube and a plane LC/water interface can be realized by adjusting the immersion depth. If the immersion depth is too large (top), the hydrostatic pressure bends the LC film upwards. If the immersion depth is too small (bottom), the opposite bend results.

constant temperature just above  $T_{NI}$ . It is assumed that the adsorption equilibrium is established when the ellipsometric parameters remain constant.

For the measurements of the temperature dependence, data are continuously collected while the temperature is changed at a slow constant rate. Unless stated otherwise, the data presented here are obtained from cooling runs with a rate of  $0.01^\circ\text{C}/\text{min}$ . The angle of incidence  $\theta_i$  is permanently adjusted so that the value of  $\Delta$  is between  $85^\circ$  and  $95^\circ$ . Under this condition,  $\theta_i$  is a good approximation of the Brewster angle  $\theta_B$  and the value of  $\tan \Psi$ , then

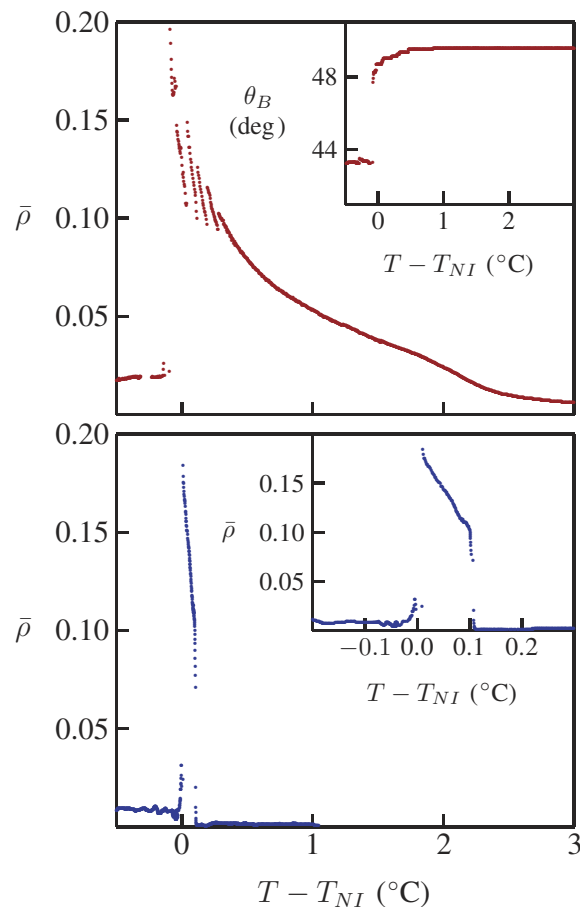


Fig. 2: (Colour on-line) Temperature dependence of the ellipticity coefficient  $\bar{\rho}$  at 9CB/water interfaces near the nematic-isotropic transition. 9CB is doped with a small amount of the surfactant monoolein. Top: sample with  $x_s = 6.63 \times 10^{-3}$  ( $x_s$  designates the surfactant mol fraction in the LC bulk phase), the inset shows the temperature dependence of the Brewster angle  $\theta_B$ . Bottom: sample with  $x_s = 1.44 \times 10^{-3}$ , the inset shows the same data with a higher temperature resolution.

designated as ellipticity coefficient  $\bar{\rho}$ , is most sensitive to the presence of an interface layer which differs in its optical properties from the two bulk media. In first approximation, the magnitude of  $\bar{\rho}$  can be considered as a linear measure of the thickness of a nematic layer at the interface between the isotropic LC bulk phase and the water phase.

**Results.** – Figure 2 demonstrates the striking influence of the concentration of the surfactant monoolein on the wetting behaviour. For a surfactant mol fraction in the bulk LC phase  $x_s = 6.63 \times 10^{-3}$ , the ellipticity coefficient  $\bar{\rho}$  increases continuously with decreasing temperature. The strong increase of  $\bar{\rho}$  near the bulk transition temperature  $T_{NI}$ , together with a simultaneous decrease of the Brewster angle  $\theta_B$ , indicates complete wetting of the isotropic LC/water interface by a nematic phase with  $\mathbf{n}$  being perpendicularly oriented to the interface. In a

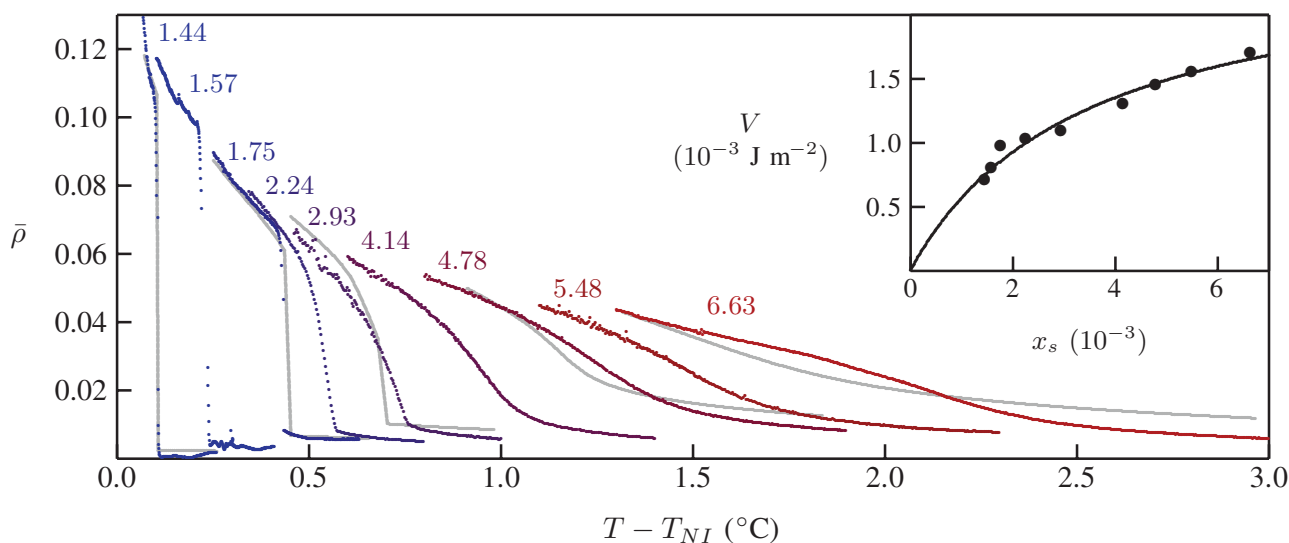


Fig. 3: (Colour on-line) Temperature dependence of the ellipticity coefficient  $\bar{\rho}$  at 9CB/water interfaces near the nematic-isotropic transition. The data sets are obtained for different values of the monoolein mol fraction  $x_s$  in the LC bulk phase (given for each set in units of  $10^{-3}$ ). The grey solid lines (for clarity shown only for every second data set) represent calculated  $\bar{\rho}$  values based on the Landau model of eq. (1), the parameter values are  $a = 1.4 \times 10^5 \text{ J m}^{-3} \text{ K}^{-1}$ ,  $B = 5.7 \times 10^6 \text{ J m}^{-3}$ ,  $C = 7.0 \times 10^6 \text{ J m}^{-3}$ , and  $L = 5.5 \times 10^{-11} \text{ J m}^{-1}$ . The value of the surface potential  $V$  was varied between  $0.71 \times 10^{-3} \text{ J m}^{-2}$  (sample with  $x_s = 1.44 \times 10^{-3}$ ) and  $1.7 \times 10^{-3} \text{ J m}^{-2}$  (sample with  $x_s = 6.63 \times 10^{-3}$ ). The inset shows the relation between  $V$  and  $x_s$ , the solid line is calculated assuming that  $V$  is proportional to the surfactant coverage  $\Gamma$  of the interface and that the relation between  $\Gamma$  and  $x_s$  is described by a Langmuir adsorption isotherm, *i.e.*,  $V = \kappa\Gamma = \kappa K x_s / (1 + K x_s)$  with  $\kappa$  and  $K$  being constants.

temperature interval of  $\approx 0.3^\circ\text{C}$  around  $T_{NI}$ ,  $\bar{\rho}$  shows a kind of fluctuation behaviour for which we do not have an explanation so far. This behaviour, which is not observed in samples with lower surfactant content, is currently studied in detail and might be connected to the broader (a few tenth of one centigrade) nematic/isotropic coexistence range at the bulk first-order transition in samples with larger surfactant concentrations. However, the continuous complete wetting of a homeotropic anchoring interface by a nematic surface phase as  $T \rightarrow T_{NI}^+$  is similar to the behaviour observed already in numerous other LC systems [12–20].

For considerably smaller surfactant mol fraction  $x_s = 1.44 \times 10^{-3}$ , a different behaviour is observed:  $\bar{\rho}$  is almost zero for all temperatures above  $T_{NI} + 0.1^\circ\text{C}$ . At this temperature,  $\bar{\rho}$  jumps to  $\approx 0.1$ , followed by a slower increase up to  $\bar{\rho} \approx 0.19$  at  $T_{NI}$ . This behaviour is expected for complete wetting accompanied by a prewetting transition. The discontinuity  $\Delta\bar{\rho} \approx 0.1$  at the prewetting transition corresponds to a thickness change of  $\approx 25 \text{ nm}$ , *i.e.*, below the prewetting transition a nematic film with a thickness corresponding to about 10 lengths of the 9CB molecule is present. Above the prewetting transition of this sample, the ellipsometric data do not allow to distinguish between either a nematic film with sub-monolayer thickness or the complete absence of nematic order.

Figure 3 shows how the prewetting transition develops with increasing surfactant mol fraction  $x_s$ . For values of  $x_s$  up to  $1.75 \times 10^{-3}$ , a clear discontinuity in  $\bar{\rho}$  is

observed indicating the presence of a first-order prewetting transition. With increasing values of  $x_s$ , the magnitude of the first-order discontinuity decreases and its temperature is shifted to higher values. The value of  $\bar{\rho}$  just above the prewetting transitions also increases with increasing  $x_s$ : in the sample with  $x_s = 1.75 \times 10^{-3}$ , the ellipsometric data indicate the presence of a nematic film with a thickness of about one monolayer just above the prewetting transition.

The three samples with the lowest surfactant concentration, which show a clear discontinuity of  $\bar{\rho}(T)$ , also exhibit thermal hysteresis at the prewetting transition. Figure 4 shows for the  $x_s = 1.75 \times 10^{-3}$  sample heating and cooling runs obtained at a slow rate of  $0.002^\circ\text{C}/\text{min}$ , demonstrating a hysteresis of  $\approx 0.04^\circ\text{C}$ . Both the hysteresis and the discontinuity in  $\bar{\rho}(T)$  emphasize that we observe here a classical example of a first-order prewetting transition characterized by a discontinuous thickness change of the wetting layer.

The data obtained for the  $x_s = 2.24 \times 10^{-3}$  and  $2.93 \times 10^{-3}$  samples show a rapid change of  $\bar{\rho}$  in a narrow temperature interval, but it is difficult to decide if a first-order transition is still present. Samples with  $x_s \geq 4.14 \times 10^{-3}$  clearly show a continuous temperature dependence of  $\bar{\rho}$ . However, the signature of the prewetting transition is still discernible for the  $x_s = 6.63 \times 10^{-3}$  sample by the inflection point in the  $\bar{\rho}(T)$  curve. For all samples studied, we observe that a change of the surfactant mol fraction in the volume LC phase,  $x_s$ , has a significant effect on the  $\bar{\rho}$  vs.  $T$  curve, *i.e.*, the change of  $x_s$  alters the surfactant

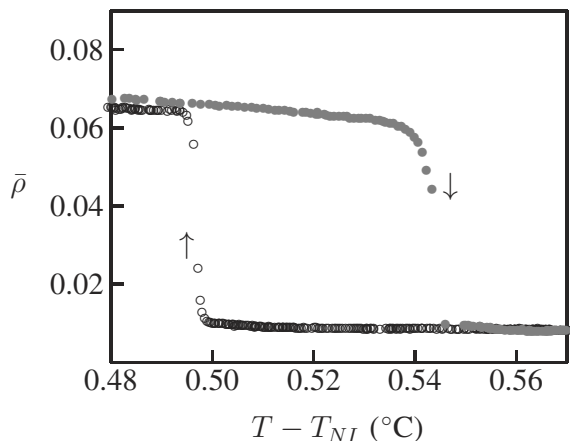


Fig. 4: Temperature dependence of the ellipticity coefficient  $\bar{\rho}$  near the prewetting transition of the  $x_s = 1.75 \times 10^{-3}$  sample, demonstrating the thermal hysteresis (open circles: cooling run, filled circles: heating run, temperature rate  $0.002^\circ\text{C}$ ).

coverage at the LC/water interface. Thus, we can conclude that the surfactant monolayer at the interface is always in a nonsaturated state and that a value of  $x_s = 6.63 \times 10^{-3}$  in the volume phase is not large enough to produce a dense saturated monolayer at the interface.

Since the value of  $x_s$  in our system controls the strength of the surface field  $h_1$ , our experimental data demonstrate the presence of a first-order prewetting line in the  $T/h_1$  plane which ends at a critical point located approximately  $0.8\text{--}0.9^\circ\text{C}$  above  $T_{NI}$ . The first theoretical prediction of this behaviour, based on Landau theory, was made by Sheng [21] (independently of the work of Cahn [2] and Ebner and Saam [3]). In the following, we apply Sheng's model to our results. The Landau free energy density is given by:

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

The first three terms are the usual Landau expansion in powers of the order parameter  $S$  with  $T^*$  being the stability limit of the isotropic phase, the last term describes the coupling to the interface potential  $V$  (corresponding to  $h_1$ ), 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. Minimization of eq. (1) yields order parameter profiles  $S(z, T)$  which are transformed (as described in [15]) to refractive index profiles  $n_o(z, T)$ ,  $n_e(z, T)$  from which values of  $\bar{\rho}(T)$  are calculated and compared with the experimentally measured  $\bar{\rho}(T)$  values. We should note that the refractive index profiles calculated as described above do not contain a contribution from the surfactant layer adsorbed at the interface. The presence of an ordered dense monolayer consisting of mainly aliphatic moieties at an alkane/water interface changes the value of  $\bar{\rho}(T)$  by  $0.004$  [33]. The effect

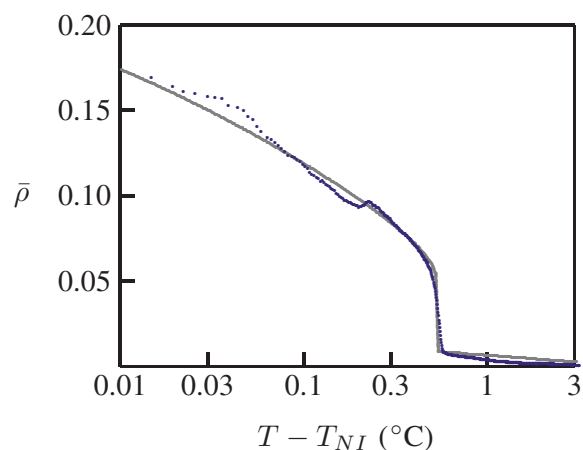


Fig. 5: (Colour on-line) Temperature dependence of the ellipticity coefficient  $\bar{\rho}$  of the  $x_s = 2.24 \times 10^{-3}$  sample on a logarithmic temperature scale (small dots: experimental data, solid line: calculated values resulting from the Landau model). The nearly linear increase of  $\bar{\rho}$  below the prewetting transition indicates the logarithmic divergence expected for the complete wetting case (the small bend discernible in the calculated  $\bar{\rho}$  curve results from the fact that the linear relation between  $\bar{\rho}$  and the thickness of the wetting film is not strictly valid for larger film thicknesses).

of a dilute surfactant monolayer can be estimated to be much smaller, corresponding to a small offset of our  $\bar{\rho}(T)$  curves, and is thus neglected here in the model refractive index profiles.

We tried to reproduce our experimental results with a single set of parameters  $a$ ,  $B$ ,  $C$ , and  $L$ , with values similar to those known for other  $n\text{CB}$  compounds [34]; only the value of  $V$  is varied in order to describe the influence of the surfactant concentration  $x_s$ . When the bulk transition temperature  $T_{NI}$  is approached, the Landau model predicts in the complete wetting case a logarithmic divergence of the thickness of the nematic wetting film. The logarithmic divergence is also indicated experimentally when plotting the measured  $\bar{\rho}$  values on a logarithmic temperature scale. An example is shown in fig. 5.

The modelling of the prewetting transitions based on eq. (1) is shown in fig. 3. A fair description of the experimental behaviour at the first-order prewetting transitions can be achieved. The temperature of the prewetting critical point (obtained numerically by calculating various  $\bar{\rho}(T)$  curves with  $V$  ranging from  $1.0$  to  $1.5 \times 10^{-3} \text{ J m}^{-2}$ ) is at  $T_{c,pre} - T_{NI} \approx 0.9^\circ\text{C}$ , the corresponding value of the interface potential is  $V_{c,pre} \approx 1.3 \times 10^{-3} \text{ J m}^{-2}$ . In the supercritical range, however, the Landau model predicts a faster flattening of the  $\bar{\rho}(T)$  curves with increasing  $V$  than observed experimentally. The values of  $V$  as a function of  $x_s$  are shown in the inset of fig. 3. The slightly nonlinear relation can be explained with an adsorption behaviour of the surfactant according to a Langmuir isotherm (see the caption of fig. 3).

**Conclusion.** – The results of the present study show that careful control of the surfactant amount at LC/water interfaces enables the experimental realization of otherwise rarely observed prewetting transitions near nematic-isotropic phase transitions. Increasing the surfactant concentration, corresponding to an increase of the surface field  $h_1$ , drives the first-order prewetting transition towards a critical point. Although the technique described here might enable the implementation of many LC systems showing prewetting transitions, we should note that there are probably also many LCs in which prewetting transitions remain unobservable: in the homologous compound 8CB a distinct prewetting transition could not be observed when studied by the same method [20,31]. Obviously, in 8CB the temperature difference between the nematic-isotropic bulk transition and the prewetting critical point is smaller than  $0.1^\circ\text{C}$  so that a prewetting transition cannot be found by studies with usual experimental resolution. Nevertheless, the study of a larger number of LC compounds by this method might lead to a LC system in which the prewetting behaviour is pronounced enough to allow for the determination of critical exponents related to the prewetting critical point.

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Stimulating discussions with S. HERMINGHAUS as well as financial support by the Deutsche Forschungsgemeinschaft (Grant Ba 1048/7) are gratefully acknowledged.

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