PHYSICAL REVIEW E **84**, 031701 (2011)

Surface order at surfactant-laden interfaces between isotropic liquid crystals and liquid phases with different polarity

Xunda Feng[*] and Christian Bahr[†]

Max Planck Institute for Dynamics and Self-Organization, Am Faßberg 17, D-37077 Göttingen, Germany

(Received 20 April 2011; revised manuscript received 17 June 2011; published 1 September 2011)

We present an ellipsometry study of the interface between thermotropic liquid crystals and liquid phases consisting of various binary mixtures of water and glycerol. The liquid-crystal samples contain a small constant amount of a surfactant which induces a homeotropic anchoring at the interface. We determine the smectic or nematic order at the interface in the temperature range above the liquid-crystal–isotropic transition while the water to glycerol ratio is varied, corresponding to a systematic modification of the polarity of the liquid phase. The surface-induced order becomes less pronounced with increasing glycerol concentration in the liquid phase. The observed behavior is compared with previous studies in which the surfactant concentration in the liquid-crystal bulk phase was varied. The results indicate that in both cases the magnitude of the surfactant coverage at the interface is the key quantity which determines the liquid-crystal surface order at the interface.

DOI: 10.1103/PhysRevE.84.031701 PACS number(s): 61.30.Hn, 68.05.Cf, 82.70.Uv

I. INTRODUCTION

Heterogeneous systems consisting of a thermotropic liquid crystal (LC) and a second immiscible liquid have gained considerable interest in both fundamental and applied research. Investigated topics are, for example, novel colloidal interactions between isotropic droplets in a nematic matrix [1,2], pressure-induced layering transitions in smectic Langmuir films [3–5], electro-optic properties of nematic emulsions [6,7], defect structures in nematic droplets and shells [8–11], the anchoring behavior of LCs at surfactant-laden LC-water interfaces [12–15], or the assembly of biomolecules, polymers, and similar species at nematic LC-water interfaces [16–20].

A specific topic is the liquid-crystal order which appears at surfactant-laden interfaces with aqueous phases in the isotropic temperature range of the LC [21]. If the surfactant induces a homeotropic anchoring of the LC molecules, a thin nematic or smectic layer is present at the interface at temperatures several degrees above the bulk transition between the isotropic and the nematic or smectic phase. Usually, the thickness of this ordered layer grows as the temperature is decreased toward the bulk transition temperature. This pretransitional wetting behavior is well known for interfaces of LCs with air [22–27] or solid substrates inducing a homeotropic anchoring [28–33]. LC-aqueous interfaces provide the advantage that the surfactant coverage of the interface can easily be varied by changing the surfactant bulk concentration. The resulting well-defined control of the ordering surface field enabled the study of novel wetting behaviors [34], smectic layering transitions [35], and nematic prewetting transitions [36].

In the above-mentioned studies [21,34–36], we investigated the interface between LCs and either pure water or water doped with a small amount of surfactant (ionic surfactants were dissolved in the aqueous phase, nonionic surfactants in the LC bulk phase). In practice, liquid phases constituting emulsions are often multicomponent systems in which water is just one of several components. In the study of LCs, glycerol is frequently used as an immiscible liquid instead of water [37–39]. Thus, when studying LC-liquid interfaces, it is useful to extend these studies to different liquids in order to explore how the nature of the liquid phase influences the LC ordering behavior at the interface. In the present study, we prepare interfaces between LCs and various water-glycerol mixtures possessing different glycerol concentrations. Since the relative dielectric constant of glycerol ($\epsilon_r = 41$ at 20 °C) amounts to roughly one half of the value of water ($\epsilon_r = 80$ at 20 °C), the variation of the composition corresponds to a systematic variation of the polarity of the non-liquid-crystal fluid phase. For instance, in a 1:1 mixture (equal volumes) of water and glycerol, $\epsilon_r = 63.6$ at 20 °C [40]. By studying the smectic layering transitions and the nematic prewetting transitions of two LC compounds, we show that the polarity variation has a similar effect as a variation of the volume concentration of the surfactant (which is held constant in the present study). Our results indicate that in both cases (variation of polarity or surfactant concentration) the magnitude of the surfactant coverage of the interface is the essential quantity which determines the LC ordering behavior at the interface.

II. EXPERIMENT

The LC compounds under investigation are 9CB and 12CB, that is, two homologs of the 4-alkyl-4′-cyanobiphenyl series with alkyl chain lengths of 9 and 12 carbon atoms, respectively. The transition temperatures are smectic-*A* 48 °C nematic 50 °C isotropic for 9CB and smectic-*A* 59 °C isotropic for 12CB. The compounds were obtained from Synthon Chemicals and recrystallized from ethanol before use. The LC compounds were doped with a small amount of the surfactant 1-oleoylglycerol (monoolein) (Fluka, used as received); the mole fraction x_s of monoolein in the two samples used for the measurements was $x_s = 0.005$ (9CB sample) and $x_s = 0.016$ (12CB sample). The samples were prepared by mixing ≈300 mg of the LC with the corresponding amount of monoolein and stirring the mixture for about 30 min in the isotropic temperature range at ≈70 °C. The different aqueous phases were prepared by mixing Milli-Q water with various amounts of glycerol (Sigma-Aldrich, 99%).

---

[*] xunda.feng@ds.mpg.de

[†] christian.bahr@ds.mpg.de

The structure of the interface between the isotropic LC and the water-glycerol phase is studied by ellipsometry. The LC sample is placed into a Teflon tube (diameter 7 mm) which dips into a reservoir containing the water-glycerol phase. The thickness of the LC film amounts to several mm, so that the LC-air interface is well separated from the LC-liquid interface. Since the water-glycerol phase does not intrude between the organic LC and the Teflon surface, it is possible to tune the curvature of the LC-liquid interface by adjusting the immersion depth of the Teflon tube, and a plane interface, suitable for ellipsometric measurements, can be prepared. The LC-liquid 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. More details can be found in [34] and [36].

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-liquid 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. For the measurements of the temperature dependence, data are continuously collected while the temperature is changed at a slow constant rate (typically 20 mK/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 which differs in its optical properties from the two bulk media. In the first approximation, the magnitude of $\bar{\rho}$ can be considered as a linear measure of the thickness of a nematic or a smectic layer at the interface between the isotropic LC bulk phase and the water-glycerol phase.

The monoolein layer at the LC-aqueous interface induces a homeotropic anchoring of the LC bulk phase as is expected for surfactant molecules possessing the usual structure with a polar head and a nonpolar tail [12]. We should note that there are more complex behaviors in which the short-range surface interactions do not necessarily determine the anchoring of the bulk phase [41] or temperature-induced density changes in the surfactant layer lead to homeotropic-to-planar anchoring transitions [42]. However, in the present study, the anchoring of the bulk LC phase is homeotropic as is demonstrated by the decrease of θ_b by about 4° at the transition from the isotropic to the liquid crystalline phase (shown in, e.g., [36]). Also, the anchoring of the thin nematic or smectic layer that is present above the bulk transition is homeotropic since the measured ellipsometric quantities can be reproduced only by model systems containing a thin birefringent layer with its optical axis being oriented along the interface normal.

Each measurement of the temperature dependence of $\bar{\rho}$ for a given combination of LC sample and water-glycerol mixture was repeated at least once, usually yielding well reproducible results. For the exchange of the aqueous phase by a phase with a different glycerol content, we could use a simple procedure: When the measurements for a given water-glycerol phase were finished, we let the LC sample crystallize at room temperature, replaced the liquid phase by a new water-glycerol mixture, and heated again to the isotropic temperature range. Carrying out this procedure with liquid phases possessing the same glycerol content led to well-reproducible results. Furthermore, when for a given LC sample (which was in contact with a water-glycerol mixture for at least two runs, i.e., for 12 to 24 h) the water-glycerol mixture was replaced with pure water, we obtained again the results measured earlier for the interface with pure water. These findings indicate that the solubility of the monoolein surfactant in the water-glycerol mixtures can be neglected and that the monoolein concentration in the LC phase does not decrease during the course of a measurement. Another issue could be the possible diffusion of glycerol molecules into the isotropic LC phase. Such a diffusion occurs when the isotropic phase of a homologous LC, 5CB (4-pentyl-4′-cyanobiphenyl), is in contact with glycerol at temperatures far above the nematic-isotropic transition. This diffusion was used for the generation of glycerol droplets at the LC-air interface [38]: On cooling back to the nematic phase, glycerol separates from the LC phase, resulting in the desired droplet formation. However, in the present study of 9CB and 12CB, an indication for a diffusion of glycerol into the isotropic LC is not found: The diffusion would cause, during the course of a measurement, a shift of the refractive index of the isotropic LC phase which would show up in our ellipsometry data. Also, we do not observe the formation of glycerol droplets at the LC interface.

III. RESULTS AND DISCUSSION

The compound 12CB possesses a direct smectic-*A*–isotropic transition. An interface with air or a solid substrate which imposes a strong-enough homeotropic anchoring induces a thin smectic wetting film, consisting of a small number of molecular layers, in the isotropic temperature range [23,30]. The number of molecular smectic layers increases with decreasing temperature to a value between three and five (depending on the nature of the substrate) at the temperature of the transition to the smectic-*A* bulk phase. The same behavior is observed at interfaces with water in the presence of a suitable surfactant like monoolein [35]. Figure 1(a) shows the temperature dependence of the ellipticity coefficient $\bar{\rho}$ of the interface of our 12CB sample (doped with monoolein, mole fraction $x_s = 0.016$) to pure water. The stepwise increase of $\bar{\rho}$ with decreasing temperature indicates the subsequent formation of smectic layers at the interface. The first smectic layer forms 1.85 K above the bulk transition temperature T_b, the second and third layer form 0.7 K and 0.2 K above T_b, and just at T_b the data indicate the formation of a fourth smectic layer. Figures 1(b)–1(d) show data obtained for the same sample in contact with different water-glycerol mixtures. It is obvious that the temperature at which the first smectic layer forms decreases with increasing glycerol content. The first layering transition eventually merges with the second transtion: If the aqueous phase contains 60% glycerol or more, the formation of the first two layers proceeds in a single transition [cf. Fig. 1(d)].

Regarding the magnitude of the $\Delta\bar{\rho}$ steps corresponding to the formation of one molecular smectic layer, one observes an increase of $\Delta\bar{\rho}$ with increasing glycerol content. For a given smectic liquid-crystal–liquid system, the magnitude of $\Delta\bar{\rho}$ would be a linear measure of the thickness of one smectic layer.

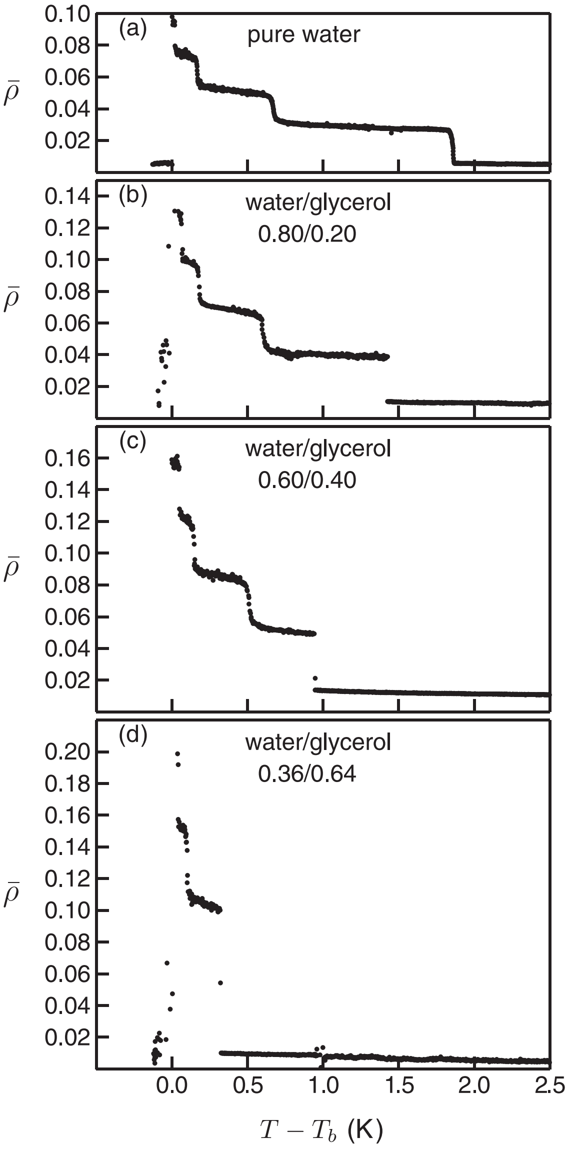

FIG. 1. Temperature dependence of the ellipticity coefficient $\bar{\rho}$ of the interface of 12CB (doped with monoolein, mole fraction $x_s = 0.016$) to aqueous phases with different glycerol content; the volume ratio between water and glycerol is indicated in each panel. T_b denotes the bulk smectic-A–isotropic transition temperature of the sample. The stepwise increase of $\bar{\rho}$ with decreasing temperature indicates the formation of molecular smectic layers.

However, in our experiment we vary the optical properties of the liquid phase: The increase of the $\Delta\bar{\rho}$ steps is just a result of the increase of the refractive index of the liquid phase with increasing glycerol content, it does not indicate an increase of the smectic layer spacing.

The behavior of the layering transitions of 12CB in response to a variation of the glycerol content of the water-glycerol phase is qualitatively very similar to the behavior which is observed when the monoolein content of the bulk 12CB phase is changed: An increase of the glycerol content in the aqueous phase has the same effect as a decrease of the monoolein concentration in LC volume phase [35]. In both cases, the influence on the layer transition temperatures is pronounced for the formation of the first smectic layer but very weak (or even not detectable) for the formation of the subsequent layers, demonstrating the short range of the ordering effect of the surfactant layer. However, the temperature of the formation of the first smectic layer can serve as a convenient measure of the magnitude of the ordering surface field. Before we discuss this behavior more quantitatively, we present the results obtained for the 9CB sample.

Whereas 12CB exhibits an isotropic to smectic-A phase transition, 9CB undergoes a phase transition from isotropic to nematic with decreasing temperature. Above the bulk transition temperature, a nematic wetting film is present at interfaces possessing homeotropic anchoring conditions and the thickness of the nematic wetting layer grows continuously as the transition to the bulk nematic phase is approached from above. This behavior is exemplified in Fig. 2(a), which shows the temperature dependence of $\bar{\rho}$ for the interface between our 9CB sample (doped with monoolein, mole fraction $x_s = 0.005$) and pure water. When we increase the glycerol content of the aqueous phase, the s-like feature of the $\bar{\rho}$ vs T curve [appearing at $T - T_b \approx 1.4$ K in Fig. 2(a)] shifts to lower temperatures and transforms into a discontinuity [cf. Figs. 2(b) and 2(c)]. The $\bar{\rho}$ discontinuity at $T - T_b = 0.6$ K in Fig. 2(c) is the signature of a prewetting transition at which the nematic wetting layer undergoes a discontinuous change of its thickness. The behavior of the 9CB sample, which we observe for a variation of the glycerol content of the aqueous phase, is very similar to the behavior observed in a previous study [36] in which the monoolein content in the bulk LC phase was varied. In the same way as described above for 12CB, an increase of the glycerol content has the same effect as a decrease of the monoolein concentration.

The data shown in Figs. 1 and 2 clearly demonstrate that a decrease of the water content in the water-glycerol phase has qualitatively the same effect as a decrease of the monoolein content in the LC volume phase. We can compare both effects quantitatively: Figure 3 (top) shows the shift of the temperature T_1, at which the first smectic layer is formed, as a function of the volume fraction of water, $x_{V,\text{water}} = V_{\text{water}}/(V_{\text{water}} + V_{\text{glycerol}})$, in the water-glycerol phase. The slope of the observed linear relation amounts to 2.05 K, that is, a decrease of $x_{V,\text{water}}$ by 10% from 1 to 0.9 would cause a decrease of T_1 by 0.205 K. Using the data presented in [35], we can estimate that the same shift of T_1 would be obtained if the mole fraction of monoolein, x_s, would be decreased from 0.016 to 0.013, corresponding to a decrease by 19%. For 9CB, in order to provide a quantitative measure of the influence of the glycerol content on the nematic surface order, we have applied the Landau model of Sheng [43] to our results. The Landau model assumes a linear coupling between the nematic order parameter and an effective surface field V. We determine the value of V by fitting calculated $\bar{\rho}(T)$ data to our measured $\bar{\rho}(T)$ curves. By this procedure, which is described in detail in [36], we obtain from each $\bar{\rho}$ vs T curve a value of V. The dependence of V on the volume fraction of water in the water-glycerol phase is shown in Fig. 3 (bottom). From the V vs $x_{V,\text{water}}$ data, we obtain a decrease of V by 1.29×10^{-4} J/m^2 for a decrease of $x_{V,\text{water}}$ from 1 to 0.9. The same effect would be obtained if we would decrease the monoolein mole fraction from 0.005 to 0.0042, corresponding to a decrease by 16%, as we can estimate on the basis of the data in Ref. [36]. In short, a 10% decrease of the water content

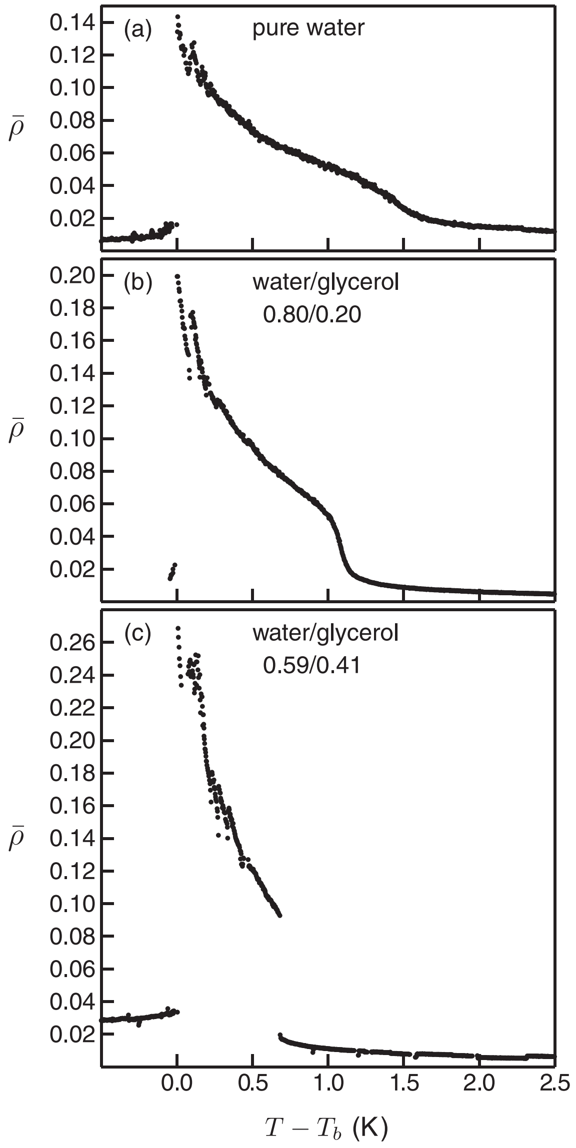

FIG. 2. Temperature dependence of the ellipticity coefficient $\bar{\rho}$ of the interface of 9CB (doped with monoolein, mole fraction $x_s = 0.005$) to aqueous phases with different glycerol content; the volume ratio between water and glycerol is indicated in each panel. T_b denotes the bulk nematic-isotropic transition temperature of the sample. With increasing glycerol content of the aqueous phase, a first-order prewetting transition emerges [discontinuity of $\bar{\rho}$ at $T - T_b = 0.6$ K in (c)].

corresponds to a decrease of the monoolein content in a range between 16% (9CB) and 19% (12CB).

The qualitative alikeness of the effects resulting from the variations of the surfactant concentration and the polarity of one of the volume phases as well as the quantitative similarity of the influence on two different surface phenomena (the smectic layering transitions and the nematic prewetting transition) could indicate that the experimental behavior results from a change of the coverage of the interface with the surfactant molecules. In principle, the observed behavior could also result from other reasons. For instance, glycerol could have a stronger planar anchoring strength than water and thus suppress the LC surface order (which requires a homeotropic anchoring). However, experimental studies of thin nematic films on glycerol and water indicate that the planar anchoring strengths of both liquids are similar [39]. Thus, it is not likely that different anchoring strengths of pure water and glycerol are the main reason for the experimental results. Another possible mechanism could be that the increase of the glycerol content enhances the solubility of monoolein in the aqueous phase, leading to a decrease of the monoolein concentration in the LC phase and finally to a smaller surfactant coverage of the interface. However, as described in Sec. II, there is no indication that the monoolein concentration in the LC decreases during the course of a measurement. As we discuss in detail below, we believe that the main reason for the experimental behavior is a decrease of the surfactant coverage of the interface that is caused by the decreased polarity of the aqueous phase due to its glycerol content.

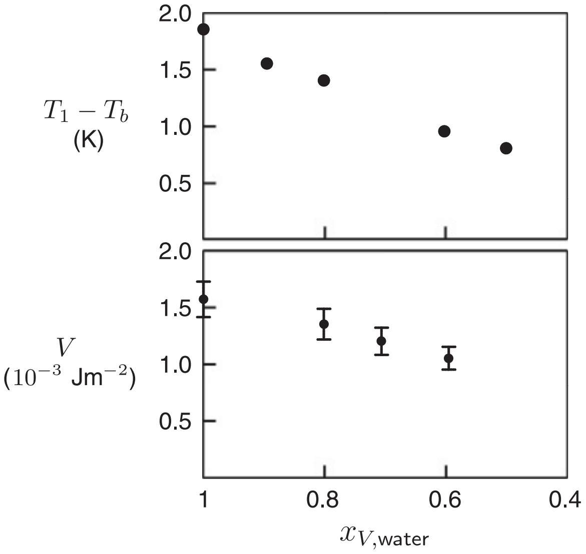

FIG. 3. (Top) Dependence of the temperature T_1, at which the first smectic layer is formed, on the volume fraction x_V of water in the water-glycerol phase. The uncertainty of T_1 is of the order of 0.05 K, corresponding approximately to the size of the symbols. (Bottom) Dependence of the surface field parameter V on the volume fraction x_V of water in the water-glycerol phase. The value of V is determined by a fitting procedure (see text), the quality of which was checked "by eye," resulting in an uncertainty of ≈10%, indicated by the error bars.

The adsorption of surfactant molecules at an interface and the resulting surfactant coverage of the interface depend on a number of factors such as the surfactant concentration in the bulk phase, the transport processes which carry the surfactant molecules to the interface, the interactions between the surfactant molecules, and the affinity of the surfactant to the interface which in turn depends on the structure of the surfactant molecules and the molecules constituting the bulk phases. Qualitatively, one observes in many cases the following behavior: When the concentration of the surfactant molecules in the bulk phase is increased from zero, the tension of the interface at which the surfactant accumulates first decreases and then stays approximately constant, indicating that the surfactant coverage of the interface has reached its maximum value. The surfactant concentration at which the interface tension changes its behavior is denoted as critical micelle concentration (CMC), since an increase of the surfactant concentration above this value results in the formation of surfactant micelles in the bulk phase. Several studies, mostly at liquid-air interfaces and employing binary mixtures as liquid bulk phases, have shown that the CMC of a given surfactant depends on the polarity of the liquid phase which is varied via the ratio of its two components; frequently used binary liquids are mixtures of water with ethylene glycol, glycerol, methanol or other alcohols, and other polar organic compounds [44–50]. In general, it was found that the CMC, and thus the concentration at which the interface coverage reaches its maximum, increases with decreasing polarity; that is, a decrease of the solvent polarity results in a decrease of the affinity of the surfactant to the interface and thus in a decrease of the coverage of the interface. Our experimental configuration is somewhat different since the surfactant is dissolved in the LC phase and not in the aqueous phase the polarity of which is varied. However, since the essential quantity which determines the affinity of a surfactant to an interface is the polarity difference between the two volume phases, it is reasonable to assume a similar variation of the surfactant affinity to the interface also in our case.

The equivalence of the variation of the polarity and of the surfactant concentration can also be seen in a more formal way. In theoretical models, the relation between the surfactant concentration in the bulk phase and the surfactant coverage of the interface is described by adsorption isotherms. A simple classical isotherm is the Langmuir isotherm [51]:

$$\Gamma = \frac{Kc}{1 + Kc}, \tag{1}$$

with Γ designating the dimensionless relative coverage (ranging from 0 to 1) and c the surfactant bulk concentration. The constant K describes the affinity of the surfactant to the interface; it can be considered as the ratio between the rates of surfactant adsorption and desorption. The Langmuir isotherm results if some idealized assumptions are made, especially interactions between the adsorbed surfactant molecules are not considered. An isotherm which takes into account possible interactions between the surfactant molecules is the Frumkin isotherm [52]:

$$Kc = \frac{\Gamma}{1 - \Gamma} \exp(-2\alpha\Gamma). \tag{2}$$

The parameter α describes, depending on its sign, attractive or repulsive interactions between the adsorbed surfactant molecules, for $\alpha = 0$ the Langmuir isotherm is obtained. Both isotherms yield $\Gamma = 0$ for $c = 0$ and $\Gamma \approx 1$ for large c. In our experiment, we consider the interface between two liquid bulk phases and vary the polarity of one of the bulk phases; that is, we vary the value of the affinity constant K of our interface. From Eqs. (1) and (2) it is obvious that for both isotherms a variation of K is completely equivalent to a variation of the surfactant bulk concentration c. The interfaces between a given liquid phase and isotropic 12CB or isotropic 9CB can be assumed to possess similar K values. Thus, when we compare the quantitative effects of a variation of K and of c, we can expect a similar behavior in both systems, as we have indeed observed experimentally.

IV. CONCLUSIONS

We have studied the LC surface order at the interface between isotropic liquid crystals (9CB and 12CB), containing a small constant amount of the surfactant monoolein, and various binary mixtures of water and glycerol. The variation of the water-to-glycerol ratio enabled a systematic control of the polarity of the aqueous phase which was in contact with the surfactant-doped isotropic LC phase. Using ellipsometry, we have determined the smectic layering transitions above the smectic-*A*–isotropic transition of 12CB and the prewetting behavior above the nematic–isotropic transition of 9CB. Previous studies [35,36] of these compounds at interfaces with pure water have shown that the temperatures of the smectic layering transitions and the nematic prewetting transition can be shifted by a variation of the monoolein concentration in the isotropic LC bulk phase. In the present study, we have shown that the same behavior can be observed when the polarity of the aqueous phase is varied while the surfactant concentration in the LC bulk phase is held constant. A comparison of the quantitative effects resulting from the variation of the polarity of the aqueous phase and from the variation of the surfactant concentration in the LC phase leads to the conclusion that in both cases the surfactant coverage of the interface is influenced in a similar way. This result is also expected when simple classical isotherms of surfactant adsorption are considered.

The results of the present study are of interest for future studies of surface order at isotropic LC-aqueous interfaces. In principle, it should not be an essential difference if a nonionic surfactant, dissolved in the LC phase, or a ionic surfactant, dissolved in the aqueous phase, is used, provided the surfactants induce a homeotropic anchoring of the LC at the interface. However, preliminary studies indicate that the behavior can be more complex: So far, we have the smectic layering transitions of 12CB observed only with a nonionic surfactant in the LC phase and not with a ionic surfactant in the aqueous phase; that is, the study of certain phenomena seems to rely on the configuration of a nonionic surfactant dissolved in the LC phase. Then, the possibility to vary the surfactant coverage at the interface without changing the surfactant bulk concentration in the LC phase is of interest in two respects. First, the experimental effort is considerably reduced since it is not necessary to prepare several LC-surfactant mixtures with different surfactant concentrations. Second, when quantitative results concerning surface phase transitions and critical phenomena are determined, it might be important that the bulk LC phase is not changed when the ordering surface field is varied. In a strict sense, the results of [35] and [36] are obtained for a number of slightly different LC bulk phases, containing different amounts of monoolein. This modification of the LC bulk phase could be avoided using the method described in the present study.

ACKNOWLEDGMENTS

Stimulating discussions with Stephan Herminghaus are gratefully acknowledged. Xunda Feng acknowledges financial support from the European Union (Marie Curie Initial Training Network “Hierarchical Assembly in Controllable Matrices,” HIERARCHY, Grant No. 215851).

[1] P. Poulin, H. Stark, T. C. Lubensky, and D. A. Weitz, Science **275**, 1770 (1997).
[2] V. G. Nazarenko, A. B. Nych, and B. I. Lev, Phys. Rev. Lett. **87**, 075504 (2001).
[3] B. Rapp and H. Gruler, Phys. Rev. A **42**, 2215 (1990).
[4] J. Xue, C. S. Jung, and M. W. Kim, Phys. Rev. Lett. **69**, 474 (1992).
[5] M. Ibn-Elhaj, H. Riegler, H. Möhwald, M. Schwendler, and C. A. Helm, Phys. Rev. E **56**, 1844 (1997).
[6] A. Fernandez-Nieves, D. R. Link, D. Rudhardt, and D. A. Weitz, Phys. Rev. Lett. **92**, 105503 (2004).
[7] F. P. Nicoletta, D. Cupelli, G. De Filpo, and G. Chidichimo, Appl. Phys. Lett. **84**, 4260 (2004).
[8] E. Tjipto, K. D. Cadwell, J. F. Quinn, A. P. R. Johnston, N. L. Abbott, and F. Caruso, Nano Lett. **6**, 2243 (2006).
[9] A. Fernandez-Nieves, D. R. Link, M. Marquez, and D. A. Weitz, Phys. Rev. Lett. **98**, 087801 (2007).
[10] A. Fernandez-Nieves, V. Vitelli, A. S. Utada, D. R. Link, M. Marquez, D. R. Nelson, and D. A. Weitz, Phys. Rev. Lett. **99**, 157801 (2007).
[11] T. Lopez-Leon and A. Fernandez-Nieves, Phys. Rev. E **79**, 021707 (2009).
[12] J. M. Brake, A. D. Mezera, and N. L. Abbott, Langmuir **19**, 6436 (2003).
[13] N. A. Lockwood, J. J. de Pablo, and N. L. Abbott, Langmuir **21**, 6805 (2005).
[14] M. I. Kinsinger, B. Sun, N. L. Abbott, and D. M. Lynn, Adv. Mater. **19**, 4208 (2007).
[15] A. D. Price and D. K. Schwartz, J. Am. Chem. Soc. **130**, 8188 (2008).
[16] J. M. Brake, M. K. Daschner, Y.-Y. Luk, and N. L. Abbott, Science **302**, 2094 (2003).
[17] J. M. Brake, M. K. Daschner, and N. L. Abbott, Langmuir **21**, 2218 (2005).
[18] A. D. Price and D. K. Schwartz, J. Phys. Chem. B **111**, 1007 (2007).
[19] N. A. Lockwood, J. K. Gupta, and N. L. Abbott, Surf. Sci. Rep. **63**, 255 (2008).
[20] M. I. Kinsinger, D. M. Lynn, and N. L. Abbott, Soft Matter **6**, 4095 (2010).
[21] Ch. Bahr, Phys. Rev. E **73**, 030702(R) (2006).
[22] D. Beaglehole, Mol. Cryst. Liq. Cryst. **89**, 319 (1982).
[23] B. M. Ocko, A. Braslau, P. S. Pershan, J. Als-Nielsen, and M. Deutsch, Phys. Rev. Lett. **57**, 94 (1986).
[24] S. Immerschitt, T. Koch, W. Stille, and G. Strobl, J. Chem. Phys. **96**, 6249 (1992).
[25] G. J. Kellogg, P. S. Pershan, E. H. Kawamoto, W. F. Foster, M. Deutsch, and B. M. Ocko, Phys. Rev. E **51**, 4709 (1995).
[26] P. de Schrijver, C. Glorieux, W. van Dael, and J. Thoen, Liq. Cryst. **23**, 709 (1997).
[27] R. Lucht, Ch. Bahr, and G. Heppke, Phys. Rev. E **62**, 2324 (2000).
[28] K. Miyano, Phys. Rev. Lett. **43**, 51 (1979).
[29] H. Hsiung, Th. Rasing, and Y. R. Shen, Phys. Rev. Lett. **57**, 3065 (1986).
[30] B. M. Ocko, Phys. Rev. Lett. **64**, 2160 (1990).
[31] G. P. Crawford, R. J. Ondris-Crawford, J. W. Doane, and S. Žumer, Phys. Rev. E **53**, 3647 (1996).
[32] B. Alkhairalla *et al.*, Europhys. Lett. **59**, 410 (2002).
[33] T. Jin, G. P. Crawford, R. J. Crawford, S. Zumer, and D. Finotello, Phys. Rev. Lett. **90**, 015504 (2003).
[34] E. Kadivar, Ch. Bahr, and H. Stark, Phys. Rev. E **75**, 061711 (2007).
[35] Ch. Bahr, Phys. Rev. Lett. **99**, 057801 (2007).
[36] Ch. Bahr, Europhys. Lett. **88**, 46001 (2009).
[37] D. R. Link, M. Nakata, Y. Takanishi, K. Ishikawa, and H. Takezoe, Phys. Rev. E **65**, 010701(R) (2001).
[38] A. B. Nych, U. M. Ognysta, V. M. Pergamenshchik, B. I. Lev, V. G. Nazarenko, I. Musevic, M. Skarabot, and O. D. Lavrentovich, Phys. Rev. Lett. **98**, 057801 (2007).
[39] U. Delabre, C. Richard, Y. Y. C. Sang, and A.-M. Cazabat, Langmuir **26**, 13368 (2010).
[40] G. Å. Kerlöf, J. Am. Chem. Soc. **54**, 4125 (1932).
[41] C. S. Mullin, P. Guyot-Sionnest, and Y. R. Shen, Phys. Rev. A **39**, 3745 (1989).
[42] K. Flatischler, L. Komitov, S. T. Lagerwall, and B. Stebler, Mol. Cryst. Liq. Cryst. **198**, 119 (1991).
[43] P. Sheng, Phys. Rev. A **26**, 1610 (1982).
[44] M. Sjoeberg, U. Henriksson, and T. Waernheim, Langmuir **6**, 1205 (1990).
[45] R. Palepu, H. Gharibi, D. M. Bloor, and E. Wyn-Jones, Langmuir **9**, 110 (1993).
[46] M. S. Bakshi, J. Chem. Soc., Faraday Trans. **89**, 4323 (1993).
[47] D. J. Lee and W. H. Huang, Colloid Polym. Sci. **274**, 160 (1996).
[48] C. C. Ruiz, J. A. Molina-Bolivar, J. Aguiar, G. MacIsaac, S. Moroze, and R. Palepu, Langmuir **17**, 6831 (2001).
[49] C. Seguin, J. Eastoe, S. Rogers, M. Hollamby, and R. M. Dalgliesh, Langmuir **22**, 11187 (2006).
[50] M. L. Moya, A. Rodriguez, M. M. Graciani, and G. Fernandez, J. Colloid Interface Sci. **316**, 787 (2007).
[51] I. Langmuir, J. Am. Chem. Soc. **39**, 1848 (1917).
[52] A. N. Frumkin, Z. Phys. Chem. **116**, 466 (1925).