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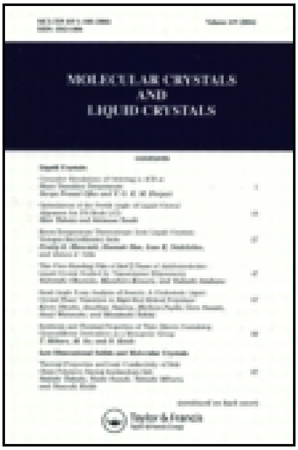

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The Interface between the Lamellar and the Sponge Phases

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The Interface between the Lamellar and the Sponge Phases

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We have studied the interface between the sponge phase and the lamellar phase in different lyotropic systems. Bilayers of the lamellar phase are either tilted, or tangential to the interface. According to a current model, the situation depends on the values of the elastic constants. We have investigated the cyclohexane/ SDS/ water/ pentanol system in which the elastic constants can be changed by tuning the concentration ϕ of magnetic particles in cyclohexane and we have observed a transition between the two types of interface. Finally the magnetic properties have been used to estimate the very low interface tension.

Keywords: lamellar phase; sponge phase; interface; ferrosmectics

The L_α lamellar phase is a stack of parallel layers of surfactants and cosurfactants in solvent with an interlamellar distance d_α. The L_3 sponge phase is made of an infinite and multi-connected membrane which divides the solvent into two equivalent subvolumes. L_3 phase is a disordered and isotropic medium but it exhibits a characteristic length d_3[1]. The L_α and L_3 phases have the same local structure (a membrane) but different characteristic lengths and their interface is characterized by a large anisotropy of the interface tension as a function of the direction of the L_α layers at the interface. An epitaxy phenomenon is reported in the Cetylpyridinium chloride(CPCl)/brine/hexanol

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system[2, 3]: the tilt angle of the L_α layers at the interface is close to the angle $\theta_0=\arcsin(d_\alpha/d_3)$ and corresponds to a geometric matching of the characteristic lengths d_α and d_3 (Fig. 1). An other geometry is reported in reference[4]: the droplets of a L_α phase embedded in L_3 phase are spherical, the layers forming a stack of concentric spheres. This organization is interpreted as the consequence of a tangential anchoring of the L_α phase at the interface compatible with the continuity of the layers at the interface (Fig 1). We denote this parallel geometry PG and the tilt-angle interface TG.

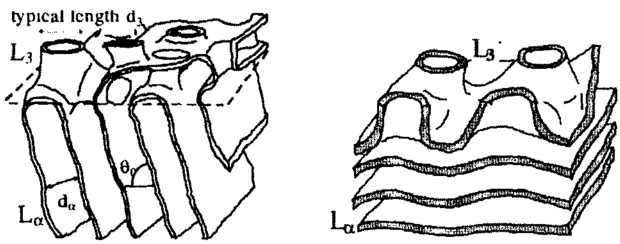

FIGURE 1 Tilt angle matching TG and parallel anchoring PG[4].

The aim of this paper is to present an experimental optical study of the interface between the L_α phase and the sponge phase in the pentanol/ SDS/ cyclohexane/ water system. In this system, a transition between the two geometries occurs, when this system is doped with magnetic nanoparticles.

DIFFERENT TYPES OF INTERFACES

Studied system

The undoped lyotropic system is the quaternary mixture water/ cyclohexane/ sodium dodecylsulfate (SDS)/ pentanol. The doped system consists in the same quaternary mixture but the cyclohexane has been replaced by a suspension of magnetic iron oxyde particles (diameter≈7nm) in cyclohexane usually called

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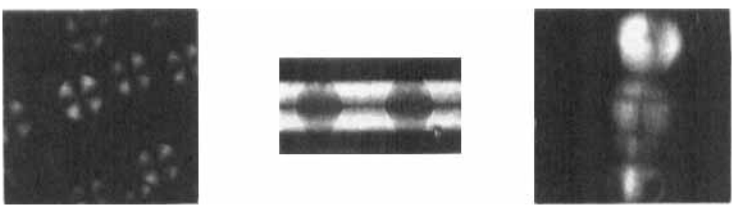
ferrofluid. Such systems have been thoroughly studied[5-9], especially the lamellar phase which forms a ferrosmectic system when it is doped.

The common (L_α-L_3) membrane consists of water between two monolayers of surfactants and cosurfactants (thickness ≈5nm for a wt ratio water/ SDS=2.5). The solvent («oil») is either pure cyclohexane or ferrofluid. The swelling $G=\phi_{oil}/\phi_{water+SDS}$ (volumic fraction) varies between 4 and 8 and the volume fraction of particles in oil ϕ between 0% and 3%.

Observations under microscope

Samples, prepared in the L_α phase or in the L_α-L_3 domain, are observed in sealed rectangular capillaries (thickness: 100, 200 or 300 μm) in an oven (±0.1°C) under polarizing microscope. The L_α phase changes into L_3 phase at different temperatures according to the composition of the system and droplets of L_α phase nucleate by cooling down a sample in L_3 phase. The optical absorption of the particles shows that their concentration is nearly the same in the two phases and thus is given by the total concentration (except for $G > 7$ where the L_α phase contains more particles than the L_3 phase: see below).



a) b) c)

FIGURE 2 a) Tangential anchoring ($\phi_p \approx 0.5 < \phi_c$ G=6)

b) c) Tilt angle matching ($\phi_p \approx 1.5 > \phi_c$ G=6)

Below a critical concentration ϕ_c of particles, the L_α droplets are spherical (see Fig. 2) and the layers are parallel to the interface. Above ϕ_c, the shapes of the L_α droplets are similar to the droplets studied in the CPCl system. A quantitative measurement of the tilt-angle θ_0 can be achieved using a cylindrical capillary[3], in which the lamellar phase is oriented in a leek-like way by the glass capillary (Fig. 2). The observed angle is close to $\theta=\arcsin(d_\alpha/d_3)\approx 45°$, with $d_\alpha/d_3\approx 1.4$[10] (see Fig. 3). Note that the transition is not brutal in the vicinity of ϕ_c where a large range of orientations are observable.

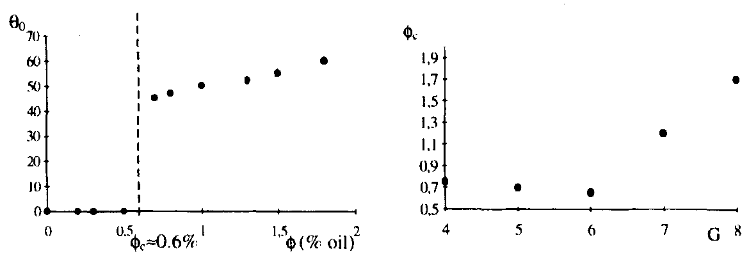


FIGURE 3 (left) Variation of the contact angle with ϕ (swelling G=6) (right) Variation of ϕ_c with the swelling G.

INTERFACE ENERGY

Discussion

Far from ϕ_c, the anisotropy of surface tension is certainly large and a single contact angle is observed. The model in reference[4] proposes that only the PG geometry and the TG geometry disturb the least the bulk near the interface: the L_3 phase is connected to the L_α phase by bridges and passages (Fig. 1). The interface energy is estimated assuming the elastic curvature of the membrane in the vicinity of the interface is the leading part. The model yields $\sigma_t\approx\kappa/d^2$ in both cases with an additional cost for the PG interface $\sigma_p\approx\kappa/\lambda d$ where λ is the smectic penetration length, κ the elastic curvature modulus of a layer and $d\approx d_3$. This cost is due to the deformation of the L_α phase in the vicinity of the

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interface (Fig. 1). It has been shown[6] that λ decreases with ϕ_p, which has been employed to explain the existence of the different interfaces[4] (a small value of λ gives a large σ_p). However, a strong decrease of λ in the bulk L_α phase is observed only above $\phi\approx 1.5\%$ for comparable swellings. In order to test this model, we have measured the penetration length of the L_α phase at the boundary of the L_3-L_α domain, in the vicinity of ϕ_c, using the Cano wedges method. The method employed here is described in references[6, 11]. The experiments confirm that the penetration length is nearly constant in the vicinity of ϕ_c (λ=34 nm±5% at G=6, ϕ_p=0.5,0.7 and 1.5%). Thus the decrease of λ is not the main cause of the transition.

Let us reconsider the parallel anchoring (Fig. 1). If we suppose, as in reference [4], that σ_p is due to the undulations of the L_α phase near the interface of type $u\approx d\cos(\pi x/d)$ with $d\approx d_3\approx d_\alpha$, it follows that $\sigma_t\approx K/\lambda$ (classic calculation of a perturbed smectic phase[12]). Now, it has been shown that K is different from κ/d_α and strongly increases with ϕ[13] in the considered range of concentration ($K\approx 4.10^{-13}$N at ϕ=0% and $K\approx 9.10^{-13}$N at $\phi\approx 1\%$ for a comparable swelling). Since σ_p increases with ϕ, the TG interface is favoured for large values of ϕ. The qualitative explanation of the transition is thus still valid if the modification of the elastic constant K with the concentration in particles is taken into account.

EFFECTS OF MAGNETIC FIELDS

The main features of the ferrosmectic phase are related to its high magnetic susceptibility and anisotropy [9]. When a magnetic field is applied to a sample of L_α droplets embedded in L_3 sponge phase, two distinct effects are observed: the field orients the layers parallel to its direction and elongates the droplets in

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its direction. The first effect can be observed at low field (between 10^2–10^3 $A.m^{-1}$), in the absence of a strong elongation of the droplet (Fig. 4). This effect is due to the susceptibility anisotropy χ_a, defined as $\chi_a=\chi_\perp-\chi_{//}$ where $\chi_{//}$ is the susceptibility parallel to the lamellae and $\chi_\perp$, the perpendicular one. The relative value $\chi_a/\chi_{//}\approx-0.13$[9] and thus the orientation parallel to the field is favoured. Here, contrary to the pure L_α phase, in which focal conic domains nucleate[8], the lamellae freely rotate and the orientation is nearly perfect in the small droplets (typical size $\approx$10-20μm)(Fig. 4).

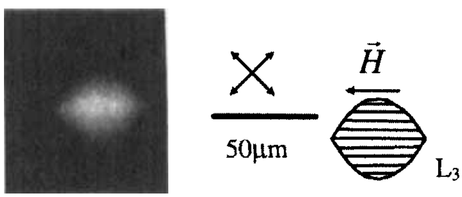

FIGURE 4 The layers are oriented in the direction of the field and the tilt angle gives facets. ($\phi\approx1\%$, G=6)($H\approx600 A.m^{-1}$).

The elongation of L_α droplets is not due to specific properties of the L_α phase, but rather to the difference of magnetic susceptibility in the two phases. It has been shown[9] that the average susceptibility of the L_α phase is given by the low field limit of the Langevin paramagnetism calculation. Thus the ferrofluid we have used (similar to the ferrofluid used in reference[9]) gives a magnetic susceptibility proportional to the volume fraction φ of the particles in the phase (L_3 or L_α phase) $\chi=\alpha_0\varphi$ with $\alpha_0=13.4$[9]. Since the concentrations of particles are slightly different in the two phases of the domain of coexistence, the magnetic susceptibilities are also different. Thus the elongation of the droplets is the same phenomenon than the elongation of a magnetic fluid drop in an other magnetic fluid. Following the classic study of the deformation of magnetic ferrofluid drops under magnetic field[14], we have estimated the L_3-

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L_α interface tension as follows. Sealed rectangular capillaries are filled with a L_α-L_3 mixture (about 50% of L_α phase). The best experimental conditions are obtained for $G \approx 7$ and $\phi \approx \phi_c \approx 1.2\%$ (the total volume fraction is $\varphi \approx 1\%$): the difference of concentration ϕ between the phases is large and the anisotropy of interface tension is low (the large droplets are nearly spherical). The concentrations of particles in the two phases, obtained by optical comparison with samples of known concentration are $\varphi_\alpha = 1.2 \pm 0.05$ % for the L_α phase and $\varphi_3 = 0.8 \pm 0.05$ % for the L_3 phase. An uniform magnetic field is then applied and we follow the deformation of initially nearly spherical L_α droplets (Fig. 5 left).

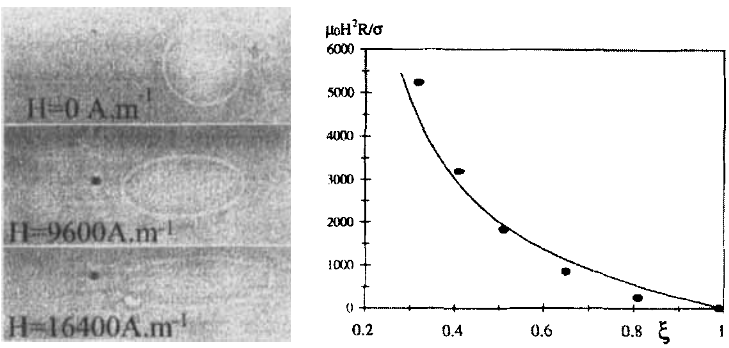

FIGURE 5 (left) Elongation of a L_α droplet in a magnetic field ($R_0 \approx 30\mu m$); (right) Plot of $\mu_0 H^2 R_0/\sigma$ as a function of ξ: experiment and fit according to [14]. For this drop, we have obtained $\sigma \approx 1.9.10^{-6}$ J.m^{-2}.

Assuming that the shape of the elongated droplet is an ellipsoid of semi-major axis a and semi minor axis b, its aspect ratio $\xi = b/a$ is given by[14]:

$$\frac{\mu_0 H^2 R_0}{\sigma} = \frac{2(n+\alpha)^2 \varepsilon^2 \xi^{-4/3}\left(1+2\xi^2+\left(1-4\xi^2\right)\varepsilon^{-1}\xi^{-1}\arcsin\varepsilon\right)}{\mu_a\left(-6+\varepsilon^{-1}\left(2+\xi^2\right)\ln\left((1+\varepsilon)/(1-\varepsilon)\right)\right)}$$

where $\mu_3=1+\chi_3\approx 1.107$ is the permeability of the L_3 phase, $\varepsilon=(1-\xi^2)^{1/2}$, $n=\xi^2\varepsilon^{-3}(\mathrm{arcth}(\varepsilon)-\varepsilon)$, $\alpha=\mu_3/(\mu_\alpha-\mu_3)$, $\mu_\alpha=1+\chi_\alpha\approx 1.16$ is the permeability of the L_α phase and R_0 the radius of the droplet in zero field. The interface tension σ is thus obtained from this relation (see Fig.5). The measurements are not very precise but give values of σ contained between 10^{-6}J.m^{-2} and 3.10^{-6}J.m^{-2}. These values agree with the estimation[4] $\sigma\approx\kappa/d_3^2\approx 4.10^{-6}$J.m^{-2} with $\kappa\approx 3k_BT$[9] and $d_3=1.4d_\alpha\approx 56$nm.

CONCLUSION

We have confirmed the existence of a transition between two types of L_α-L_3 interface in the SDS/pentanol/cyclohexane/water system when it is doped with ferrofluid. This transition can be explained by a change in the elastic constants due to the presence of the particles. Lastly we have estimated the low interface tension by studying the deformation of droplets under magnetic field.

References

[1] G. Porte *et al., J. Phys. France,* **49,** 511 (1988).
[2] C. Quilliet *et al., C.R. Acad. Sci. Paris, t. 319, Série II,* 1469 (1994).
[3] C. Quilliet, C. Blanc, and M. Kleman, *Phys. Rev. Lett.,* **77,** 522 (1996).
[4] O. Lavrentovitch, C. Quilliet and M. Kleman, *Phys. chem. B,* **101,** 420 (1997).
[5] P. Fabre *et al., Phys. Rev. Lett.,* **64,** 539 (1990).
[6] C. Quilliet, P. Fabre, and M. Veyssié, *J. Phys. II France,* **3,** 1371 (1993).
[7] V. Ponsinet and P. Fabre, *J. Phys. Chem.,* **100,** 5035 (1996).
[8] V. Ponsinet, P. Fabre, and M. Veyssié, *Europhys. Lett.,* **30,** 277 (1995).
[9] V. Ponsinet *et al., J. Phys. II France,* **4,** 1785 (1994).
[10] V. Ponsinet, these Université Paris VI, Paris, (1994).
[11] F. Nallet and J. Prost, *Europhys. Lett.,* **4,** 307 (1987).
[12] P.G. De Gennes and J. Prost, *The Physics of Liquid Crystals.* (Clarendon Press, Oxford, 1993).
[13] V. Ponsinet and P. Fabre, *J. Phys. II france,* **6,** 955 (1996).
[14] J.C. Bacri and D. Salin, *J. Phys. (Paris),* **43,** L-649 (1982).

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