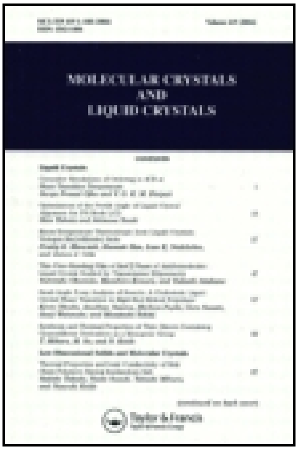

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Nonionic $C_{12}E_5$ Aqueous Lamellar Phases: a Light Scattering Study And a Temptative Scenario of the Transition to the Isotropic Phase

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Nonionic $C_{12}E_5$ Aqueous Lamellar Phases: a Light Scattering Study And a Temptative Scenario of the Transition to the Isotropic Phase

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We present a light scattering study of the nonionic lamellar system C_{12} $(EO)_5$-water. These experiments confirm that the interfacial film undergoes a transition from an undulated to a flat state within the existence domain of the lamellar phase. This change could be associated to a strong increase of the rigidity constant but also may be attributed to a nonzero spontaneous radius of curvature at low T due to the hydration of the hydrophilic part of the surfactant.

INTRODUCTION

Ethoxylated alcohols nonionic surfactants ($C_{12}Ei$) exhibit fascinating phases diagrams when mixed with water. Particularly, the phase diagram of $C_{12}E_5$ established by Mitchell *et al.*[1] is represented on Figure 1. Two striking features should be pointed out in the water rich region:

i) the system has a lower consolute point (it separates when heating up), associated with nonuniversal critical coefficents,[2]

ii) moreover, when temperature is further increased, the system enters the lamellar domain which is "reentrant" above the isotropic

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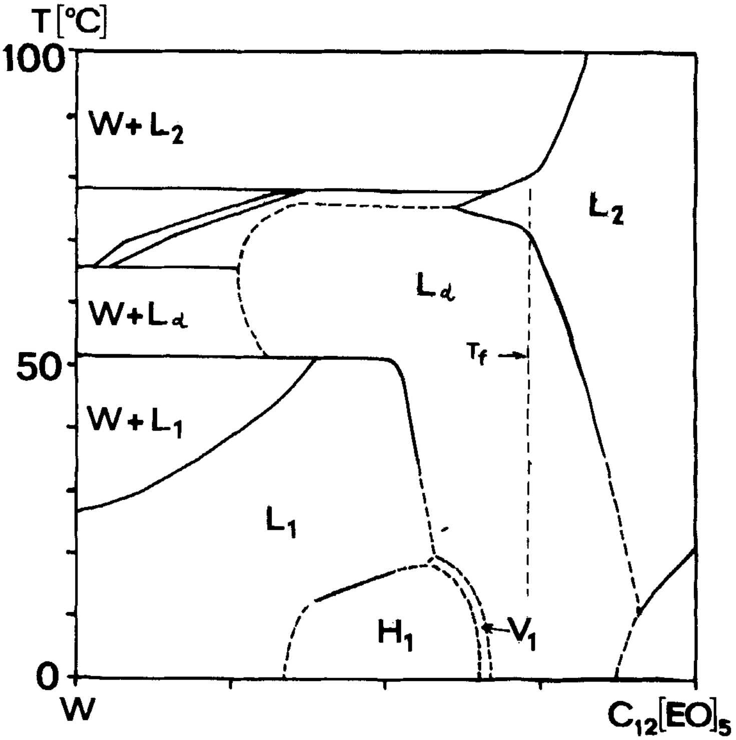

FIGURE 1 Phase diagram of $C_{12}EO_5$ in water after Reference 17. L_1 stands for direct micelles, L_2 for inverse micelles, L_α for lamellae, H_1 for hexagonal phases, V_1 for cubic and W for water. T_f is the flexibility transition temperature (see text).

phase. These nonionic systems also have the capability of forming isotropic microemulsions without the help of cosurfactant and this might indicates that their rigidity constant is pretty low (of order kT).[3]

In a previous work,[4,5] we have studied the lamellar phase of a 73% w/w lamellar phase of $C_{12}EO_5$ in water. The structural properties (reticular distance and surface area per polar head) have been determined by small angle X-ray scattering. A spin labelling study of the interfacial film system has shown a very striking phenomenon; the lamellae are undulated at low temperature and become flat above a certain threshold T_f defining a flexibility transition (Figure 2). This transition should correspond to a local modification of the interfacial film (as a decrease in the hydration rate of the POE chain)[6] and exactly corresponds to the transition micellar → lamellar in the water-rich domain. This phenomenon was also observed for $C_{12}E_6$ except

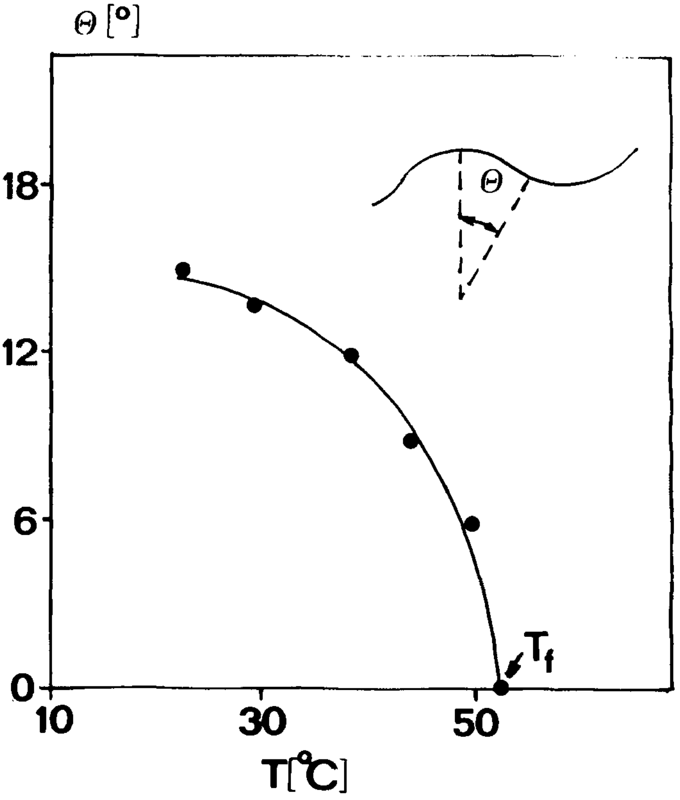

FIGURE 2 Angular disorientation of the lamellae versus temperature (after Reference 5).

that there is no transition from the isotropic state to the lamellar state in this case. Up to now, no theory addresses the relationship between detailed molecular interactions and macroscopic rigidity apart from a formal model of spring lattices[7] and a numerical procedure.[8] We present here a study by quasielastic light scattering of the orientation fluctuations of the lamellae to check if this flexibility transition affects the hydrodynamical modes.

RIGIDITY AND UNDULATIONS OF LAMELLAR PHASES: THEORETICALS

We consider a saturated ($\gamma = 0$) single film; the curvature energy per unit area reads as[3]:

$$E = \frac{1}{2} K \left[\frac{1}{R} - \frac{1}{R_0} \right]^2 \qquad (1)$$

where K is the rigidity constant (in energy units), R the radius of curvature:

$$R^{-1} = \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}$$

(u is the z-component out of the xy reference plane) and R_0 is the spontaneous radius of curvature, i.e., the natural radius that the film would adopt in absence of any interaction[5] because of packing constraints of the surfactant molecules. Equation (1) allows to compute $\langle\theta^2\rangle$, the average of the quadratic angular spread of the interfacial film[3]:

$$\langle\theta^2\rangle = \frac{kT}{\pi K} \log \frac{r}{a} \qquad (2)$$

where r is taken along the film and a is a microscopic cutoff equal to the minimum radius of curvature which is in a first approximation the length of the surfactant. Equation (2) defines ξ_K, the persistence length of the film[3]:

$$\xi_K = a \exp \left[\frac{2\pi K}{kT} \right]$$

for $r < \xi_K$, the interface is flat while for $r > \xi_K$, the interface is undulated.

For multilayers systems, one should take into account the interlayer interactions. Four types of interaction could be distinguished (d is the distance between lamellae and e is the thickness of one lamella):

—electrostatic interactions due to the repulsion of charged species (unrelevant for nonionic systems):

$$F_e \propto \exp(-\kappa d)$$

with κ^{-1} the Debye screening length

—hydration forces due to the presence of water in the hydrophilic part of the surfactant molecule:

$$F_h = H \exp(-d/\Lambda)$$

H and Λ are two constants which are well known for phospholipidic systems ($H = 245$ ergs/cm^2 and $\Lambda = 2.45$ Å).[10]

—van der Waals forces

$$F_v = -\frac{A}{12\pi}\left[\frac{1}{d^2} + \frac{1}{(d + 2e)^2} - \frac{2}{(d + e)^2}\right]$$

A is the Hamaker constant (of order 10^{-13} ergs).

—steric repulsion[11]

$$F_s = 0.42\ (kT)^2/Kd^2$$

the relevance of this interaction is now widely recognized in the stability of swollen lamellar phases.[12]

The lamellar phase under study has a reticular distance of 43 Å which can be divided into 30 Å for the surfactant bilayer and 10 Å for the interlayer water. This nonionic system can form microemulsions without cosurfactant so we assume that $K \simeq kT$; we will also assume in the following that the bilayer has a constant thickness and that only the water thickness is fluctuating. We will at least assume that $R_0^{-1} = 0$. The only left term is F_h and the curvature energy (1) ($F_h >> F_s$). According to de Gennes and Taupin:

$$E = \frac{1}{2}\frac{K}{R^2} + \frac{1}{2}U''u^2$$

U'' is the curvature of the interaction potential and u is the deviation of the lamella from the mean reference plane:

$$U'' = \left[\frac{\partial^2 F_h}{\partial z^2}\right]_{z=0} = \frac{2\,H}{\Lambda^2}\exp(-d/\Lambda)$$

The interaction can be related to B, the compressibility coefficient:

$$B = (d + e)^2 \frac{\partial^2}{\partial d^2}\left[\frac{F_h}{d + e}\right]$$

$$= \frac{2\,H}{\Lambda^2}(d + e)\exp(-d/\Lambda)$$

The undulation amplitude is now given by[3]:

$$\langle \theta^2 \rangle = \frac{kT}{\pi K} \log \left[\frac{\xi u}{a} \right] \qquad \text{with } \xi u = \left[\frac{K}{U''} \right]^{1/4}$$

DYNAMICS OF THE FLUCTUATIONS IN MULTILAYER SYSTEMS

In this section we describe the different hydrodynamic modes of multilayer systems and estimate for each of them their frequency in order to determine the possibility of observation by QELS. The following values have been taken for computation: $d = 10$ Å, $e = 30$ Å, $\rho_w = \rho_s = 1$ g · cm^{-3}, $\eta_w = 0.01$ poise, $c = 10^{21}$ molecules · cm^{-3}, $A_0 = 40$ Å^2, $K = 10^{-14}$ ergs and a mean q of 60,000 cm^{-1} ($\theta_{\text{scat}} = 30°$).

Modes with *q*-vector in the lamellae plane:

(Those modes were originally derived for swollen lecithins)[13]

—slipping mode:

This mode is associated with the coupling of one elastic medium (the surfactant bilayer) with the viscous interlayer solvent (water). The optical index modulation is due to the surfactant density fluctuations inside the interfacial film. The dispersion relationship is:

$$-i\omega = \mu\, D_{33} q^2 \qquad \text{with } \mu = \frac{1}{12} \frac{\rho_w d}{\rho_w d + \rho_s e} \frac{d(d + e)}{\eta_w}$$

μ is the slipping coefficient relating drag and velocity ρ's are the volumic masses and

$$D_{33} = \chi\, c\, A_0^2$$

where χ is a compressibility coefficient associated with the deviation from the equilibrium surface A_0 [the energy per polar head is $\frac{1}{2}\chi\,(A - A_0)^2$]. χ could be determined from the elasticity E of the film measured on a film balance, one get: $\chi = E/A_0$ with $E = -d\gamma/d(\text{Log}\, A)$. c is the molecular concentration of surfactant. With $E = 70$ dyn · cm^{-1},[14] this gives a frequency of order 10^5 s^{-1} which is rather too large for observation.

—undulation mode:

This collective mode is characterized by a constant distance between layers. The dispersion equation reads as:

$$-i\omega = \frac{K}{\mu(d + e)} q^2$$

which yields $\omega = 10^4 \text{ s}^{-1}$ which is still observable. Note that, in this mode, the light modulation is due to the fluctuation of the birefringence.

Modes with q-vector out of the lamellae (oblique modes)[15]:

The relevant damped mode is the slipping mode. The dispersion relation is:

$$-i\omega = \mu\ B\ q^2$$

where B is the compressibility of the layers and q the projection of the q-vector in the lamellae-plane. B has been measured [16] by studying the mechanical response of a sample. This gives $\omega = 10^4 \text{ s}^{-1}$ which also is in the range of observation.

One should thus take care to have the q-vector inside the layers if we want to observe the undulation mode.

EXPERIMENTAL PART

Sample preparation:

Lamellar samples were prepared from pure $C_{12}EO_5$ (Nikko Chemicals Co., Tokyo, Japan) and tridistilled water (73% w/w in surfactant). They were homogenized by heating in the isotropic state (T > 70°C). All our experiments were performed in parallel glass-wall containers with a path length of 200 μm (Vitro Dynamics, Rockaway NJ, USA). The samples were oriented according to the following process:

—pipetting through the containers induces a partial orientation. Containers were then sealed at both ends by an epoxide glue or by soldering.

—samples were then heated in a Mettler FP 52 furnace while observed through crossed polarizers under microscope. The temperature was raised above the lamellar–isotropic transition and then decreased very slowly (0.2°C/mn) down to room temperature.

This process was the best we found to avoid getting too many defects such as focal conics or oily streaks. Each sample orientation was checked before the light scattering experiment.

Light scattering set-up:

Our experimental set-up consists of an ion laser (λ = 530g nm, Spectra Physics) with a homemade goniometer and a photomultiplier tube set at about 1 meter of the sample. Pulses coming from the photomultiplier were then standardized in a discriminator amplifier and sent to a numerical correlator (ATNE) which computes in real time the autocorrelation function and sends it to a laboratory computer (HP 9825) for processing. The sample is set so that the **q** scattering vector is parallel to the lamellar planes. The incident beam was polarized along the **q** vector. No analyzer was used.

RESULTS AND DISCUSSION

Room temperature:

Figure 3 shows results for a scattering angle up to 38° ($q = 4\pi/\lambda \sin \theta/2$). The static part of the signal (probably due to defects of orientation or intrinsic defects) is very important and is larger than the dynamic part; this static signal acts as an local oscillator and thus ensures an heterodyne detection but it practically limits experiments to scattering angles below 45°. The results reveal a very striking feature which was not present in a similar experiment on birefringent microemulsions[17]: the correlation time does not decrease to zero for $q = 0$ but increases on the contrary. This phenomenon was already observed in thermotropic liquid crystals[18] and is caused by wall quenching of the undulations for $q^2 < q_c^2$ with q_c defined as follow:

$$q_c^2 = \frac{\pi}{\lambda D}$$

λ is the penetration length of de Gennes:

$$\lambda = \sqrt{\frac{K}{B(d + e)}}$$

and D is the path length of the container. This peculiar feature eliminates the slipping mode.

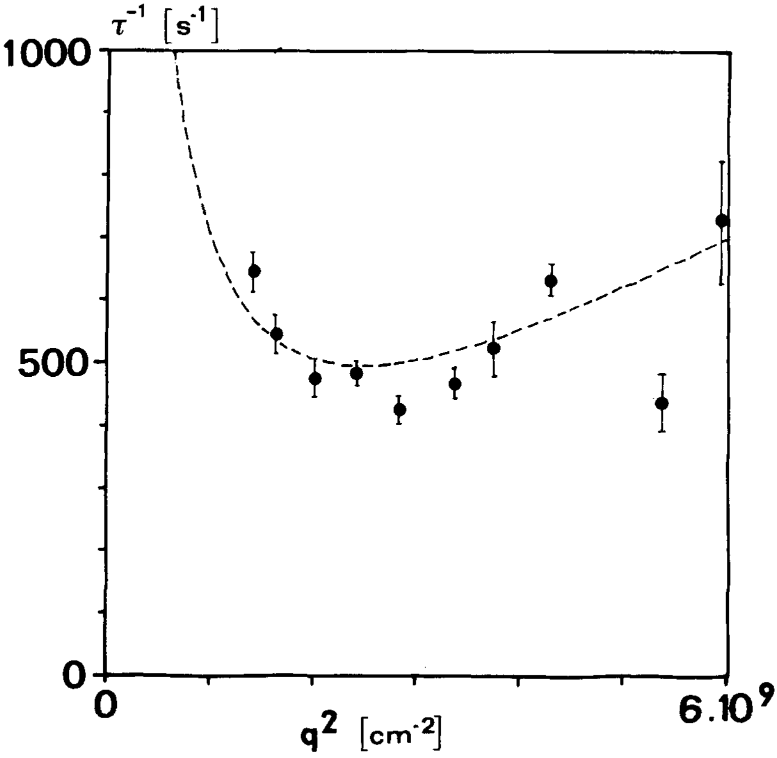

FIGURE 3 Inverse of the correlation time versus the square of the scattering vector. The dashed line is the fit according to Reference 18.

The reticular distance (43 Å) is much smaller than for swollen lamellar phases such as birefringent microemulsions and so the system should have a larger compressibility coefficient: that is why the wall quenching effect is observable while it was not for birefringent microemulsions. The presence of this phenomenon also ensures us to observe the undulation mode. The dispersion equation is in this case[18]:

$$-i\omega = \frac{1}{\tau} = \frac{K}{\eta(d+e)}\left[q^2 + \frac{q_c^4}{q^2}\right]$$

The best fit of the form $\alpha(q^2 + \beta/q^2)$ is also shown on Figure 3 ($\alpha = 10^{-7}$ and $\sqrt{\beta} = 2.48\ 10^9$). We got $\lambda = 6.3$ Å from β. This value is in close agreement with the one found by Ostwald and

Allain.[16] Two quantities can be obtained from the plot:

$$\frac{K}{B} = 1.72\ 10^{-21}\ \mathrm{cgs}$$

$$\frac{K}{\eta} = 4.3\ 10^{-14}\ \mathrm{cgs}$$

The problem now is that the relationship between K and B is unknown (in swollen lamellar phases, B is entirely determined by Helfrich repulsive interaction and thus determined by K and $d + e$). Anyway B was measured for $C_{12}E_5$ [16] by measuring the mechanical response and found equal to 2.5 10^7 ergs/cm^3. This gives a K value of $\simeq 1$ kT. We should take care of the length scale of the experiment to compare this value to other systems. For swollen ionic lamellar phases K was of the order of 0.1 kT (also measured by QELS).[17] So this nonionic system seems to be more rigid (but nevertheless less rigid than lecithin system by a factor of 10).

The viscosity of the interlayer water is found equal to 1 Poise, same value as the macroscopic viscosity of the sample. This value seems reasonable if we consider that we may enter a regime where the viscosity of water is higher than the bulk water viscosity (0.01 Poise). This is still questionable, but the thickness of the water layer is about 10 Å, and at this scale, water behaves like a structured liquid; furthermore part of the water enters the hydrophilic part of the surfactant.[6] This may explain this high viscosity.

Temperature effects

We have performed two kinds of experiment at a scattering angle of 30°.

—Static scattering:

Figure 4 represents $I(T)$, the scattered intensity versus temperature. Y-units are arbitrary, no rescaling with respect to a known reference has been made. The theoretical expression of the intensity is:

$$I\ \alpha\ \langle\delta\theta\rangle^2 = q^2\langle u^2\rangle = \frac{kT}{K}\frac{1}{(q^2 + q_c^4/q^2)}$$

As the scattering intensity decreases with temperature (Figure 4) and B is only decreasing from 2.5 10^7 to 2 10^7 ergs/cm^3 between 25 and 50°C,[16] the experimental results would suggest that K is strongly increasing with temperature.

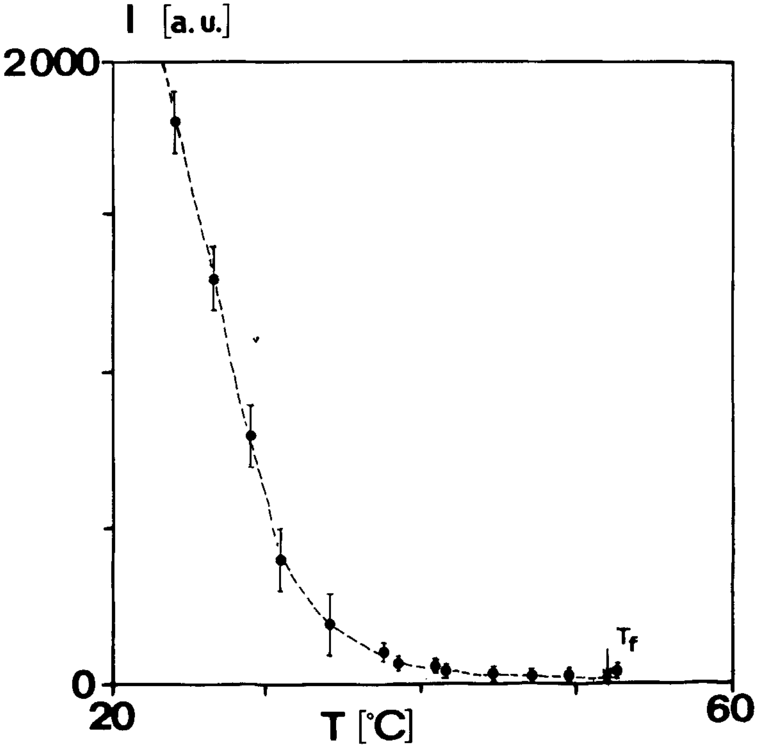

FIGURE 4 Intensity of the scattered light versus temperature ($\theta = 30°$). The dashed line is a guide for the eye.

—dynamic scattering:

Figure 5 shows the inverse of the correlation time for $\theta = 30°$ with respect to temperature. The theoretical expression for τ^{-1} is:

$$\tau^{-1} = \frac{K}{\eta(d + e)} [q^2 + q_c^4/q^2]$$

X-ray scattering experiments[5] have shown that the reticular distance $d + e$ does not change with temperature. Assuming that the viscosity has the same behavior with respect to temperature, the behavior of the mode frequency would also suggest that K is increasing, but only by about a factor of 2.

The point is now to compare our three sets of experiments, i.e.: spin labelling, dynamic light scattering and static light scattering. If

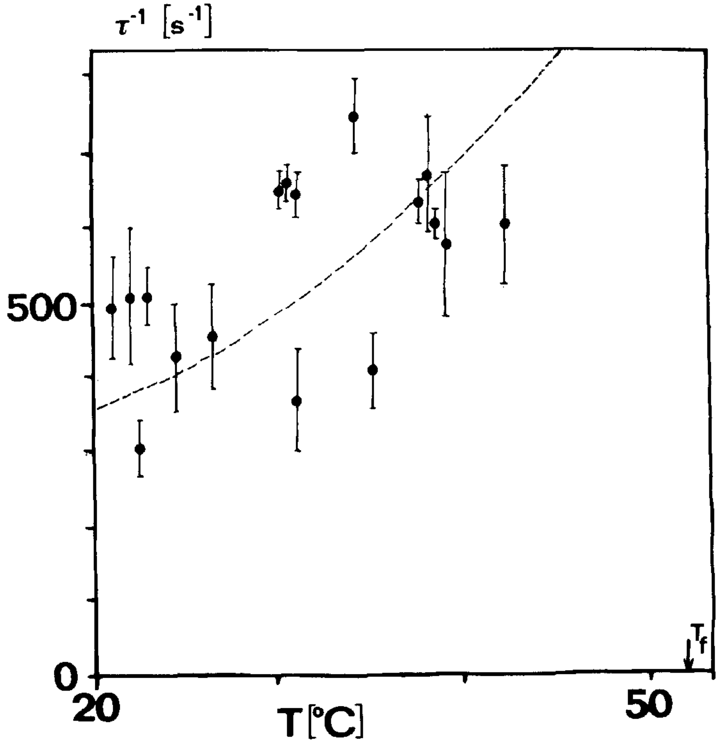

FIGURE 5 Inverse of the correlation time versus temperature ($\theta = 30°$). The dashed line is a guide for the eye.

we neglect the variation of B with T, we can say by a crude way that:

—for ESR: $\theta^2 \alpha kT/K$
—for dynamic scattering $\tau^{-1} \alpha K/\eta$
—for static scattering $I \alpha kT/K$

It is obvious that the three obtained temperature behaviors will not match: for instance, one would get from ESR and static scattering a drastic increase for K (occurring for different temperatures) which is not observed by dynamic scattering.

An attractive idea[19] for the description of this nonionic lamellar system has been given by Manuel Allain and could remove this apparent discrepancy: at low temperature, more water enters the hydrophilic part of the interfacial film than at high temperature, so at low temperature, the interfacial film is bent towards the oily part because of this "frustration."[20] The spontaneous radius of curvature is not equal to zero at low T and this leads to static distortions (of characteristic size 0.4 μm) of the lamellae that have been recently observed by electron microscopy.[19] ESR and static light scattering would probe these undulations and dynamic light scattering the rigidity changes.

This experiment and previous work done on this system suggests a very special scenario for the transition from lamellae to the isotropic state:

—at low T, the lamellae are undulated. These undulations are mostly static and their size compares with light wavelength. They might be correlated to the vicinity of curved phases (the involved curvatures are nevertheless different) but could also reveal a lack of orientation.

—at high T ($T > T_f$), the lamellae are flat. The phase is a patch of lamellae domains separated by screw dislocations walls and disoriented with respect to each other. The rigidity constant of the film has increased by a factor of 2.

—then the system enters the isotropic domain.

It would be interesting to repeat these light scattering experiments in a thicker cell to exclude any surface effect on the occurrence of the defects, but the homeotropic orientation would be hard to obtain and we cannot use any field-induced orientation with this type of surfactant.

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