Modification of Elastic Constants by Charge Addition to a Nonionic Lamellar Phase

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Modification of Elastic Constants by Charge Addition to a Nonionic Lamellar Phase

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We have investigated a lamellar phase (L_α) composed of a nonionic surfactant tetraethylene glycol monododecyl ether ($C_{12}E_4$), water, and decane, where a fraction of the nonionic surfactant has been replaced by an anionic one: sodium dodecyl sulfate (SDS). Changes induced by the addition of SDS have been determined by small-angle X-ray scattering (SAXS) and observations between crossed polarizers. Investigations have been carried out in both the water-rich and the oil-rich parts of the phase diagram. Changes in the Bragg distance, the Landau-Peierls order parameter η and the elastic constants κ and $\bar{B}$ have been particularly examined. In the decane-swollen L_α phase, SAXS spectra did not present any changes. The Bragg distance d_B, as well as η, remained constant as the nonionic surfactant was replaced by the anionic one. On the other hand, the water-swollen L_α phase was stiffened and η was decreasing dramatically with charge addition. For the same membrane volume fraction, d_B decreased slightly as SDS concentration increased. The dependence of the membrane rigidity $\kappa = K d_B$ and the smectic compressibility modulus $\bar{B}$ with the SDS concentration have been determined and compared with recent theoretical predictions. It was found that κ increased with SDS concentration whereas $\bar{B}$ presents a maximum when the Gouy–Chapman length is equal to the half of the water thickness.

Introduction

In the last 20 years, aqueous solutions of surfactants have been widely studied.[1,2] Mixed with one or two solvents, they display a rich variety of phases such as the micellar, lamellar and spongelike phases. The present work deals with the lamellar phase (L_α). In a ternary system, a L_α phase consists of two monolayers of surfactant, enclosing a solvent, periodically separated by another solvent. As one changes the surfactant concentration, the periodicity can be continuously varied. In the water-rich part of the diagram, membranes are composed of surfactant and oil, swollen by water. This situation corresponds to a direct lamellar phase. In the oil-rich part of the diagram, membranes are composed of surfactant and water, swollen by oil corresponding to the so-called reverse lamellar phase. In both cases, the lamellar phase can be considered as periodic stacks of water and oil, separated by monolayers of surfactant. By changing the oil-to-water ratio, one can move continuously from the direct lamellar phase to the reverse one. Two main forces stabilize the expanded lamellar structure. Nonionic systems are stabilized by steric interactions, which originate in the loss of entropy caused by confining a membrane between its neighbors,[3] whereas ionic systems are governed by electrostatic interactions.[4]

In the present work, the problem was to determine the interplay between steric and electrostatic interactions, as the membranes were progressively weakly charged. In the studied ternary lamellar phase composed of water, oil (decane), and a nonionic surfactant ($C_{12}E_4$), small amounts of $C_{12}E_4$ were progressively replaced by an anionic surfactant: sodium dodecyl sulfate (SDS), to move from a steric interaction driven regime toward an electrostatic driven regime. In recent papers, Fukuda et al.[5] and Rajagopalan et al.,[6] in an analogous system, investigated the effect of such an addition on the phase diagram at fixed oil-to-water ratio and in the water-rich corner, as temperature was increased. The present ternary system has been studied at a constant temperature in the water-rich part and in the oil-rich part of the phase diagram. After presenting the results, the discussion will deal with the variations of the Bragg distance d_B, the Landau-Peierls order parameter η, and the elastic constants κ and $\bar{B}$ as a function of the molar ratio χ of ionic to total surfactant. These results will be compared with recent theoretical predictions.[7,8]

Materials and Methods

Decane was purchased from Sigma (purity > 99%). The surfactant NIKKOL BS-4LY tetraethylene glycol monododecyl ether (denoted $C_{12}E_4$) was obtained from Nikko Chemicals Co. Ltd. and sodium dodecyl sulfate (SDS) from Sigma, both at a purity ≥99%; they were used without further purification. SDS was selected because its tail has the same length as $C_{12}E_4$ and both surfactants yield almost the same area per polar head[9,10]

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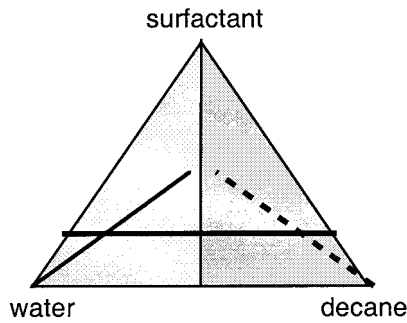(10) Sottman, T.; Strey, R.; Chen, S.-H *J. Chem. Phys.* **1997**, *106*, 6483.

Figure 1. Phase diagram scheme: the left continuous line represents the dilution of the direct L_α phase ($V_s/(V_s + V_{decane})$) = 0.55), the dotted line the dilution of the reverse L_α phase ($V_s/(V_s + V_{water})$) = 0.62), the horizontal line represents the variation of α at constant $\phi_s = 0.2$. In this diagram, in contrast to the usual conventions, we consider volume ratios.

in lamellae, around 54 Å². Water was purified by a Milli-Q system from Millipore.

The molar ratio of ionic to total surfactant is denoted $\chi \equiv$ SDS/(SDS + C$_{12}$E$_4$). Mixtures of SDS and C$_{12}$E$_4$ at molar ratios between 0.1% and 4% were prepared by weighing the components and mixing them. Mixtures were then put in an ultrasonic bath for about 1 h to solubilize SDS in C$_{12}$E$_4$. Here, 0.1% of SDS corresponds to a mean value of one charge per 54 000 Å², whereas 4% corresponds to a mean value of one charge per 1350 Å². The surfactant mixture densities were measured with a pycnometer and found to be 0.942 g/mL for pure C$_{12}$E$_4$, 0.9435 g/mL for χ = 0.6%, 0.945 g/mL for χ = 1% and 0.949 g/mL for χ = 4%. Samples were then prepared by weighing the surfactant mixture, water, and decane in correct amounts, directly in screw-cap tubes. Ingredients were mixed and then centrifuged at 5000 rpm during 10 min. The process was a slightly different for dilution lines. Mother solutions of surfactant and decane or water at the desired concentrations were prepared and solvent (water or decane) was then added. This process allows one to minimize concentration errors along the dilution lines.

The reverse lamellar phase has been studied along a dilution line in the decane-rich part of the phase diagram (Figure 1): the membrane thickness is kept constant (e.g., volume ratio $V_s/(V_s + V_{water})$ = 0.62) while the periodicity increases with decane dilution. The direct lamellar phase has been studied also along a dilution line in the water-rich part of the phase diagram (Figure 1): the membrane thickness is kept constant (e.g., $V_s/(V_s + V_{decane})$ = 0.55) while the periodicity is increasing with water dilution. For some samples, the volume fraction of surfactant $\phi_s \equiv V_s/(V_s + V_{water} + V_{oil})$ was kept constant equal to 0.2, whereas the ratio $\alpha \equiv V_{oil}/(V_{oil} + V_{water})$ was varied from 0.2 to 0.8 by 0.2 steps (Figure 1).

Small-angle X-ray scattering experiments were performed with a rotating anode (Rigaku) with a copper target and an effective source size of 0.1 × 0.1 mm². Samples were sealed in 1 mm diameter and 10 μm thick glass capillaries (Mark-Röhrchen), and placed in a sample holder whose temperature was regulated with an accuracy of ±0.1 °C. All spectra were performed at room temperature (20 °C). The scattered intensity was corrected from the absorption of the sample. The background scattering of pure solvent and glass was measured and subtracted from the sample signal.

Theoretical Background

It has been shown[4,11,12] that the following free energy density could model a system of stacked membranes

$$f = \frac{\bar{B}}{2}\left(\frac{\partial u}{\partial z}\right)^2 + \frac{K}{2}\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right)^2 \tag{1}$$

where $u(r)$ is the layer displacement in the z-direction normal to the layers. Two main elastic constants appear in this expression: K, the smectic mean rigidity, which is related to the membrane bending rigidity κ, and to the smectic periodicity d_B ($K = \kappa/d_B$), and $\bar{B}$, the smectic compressibility modulus, which characterizes interactions between membranes. The elastic constants K and $\bar{B}$ are related to Landau-Peierls order parameter η by[13]

$$\eta = q_0{}^2 \frac{k_B T}{8\pi\sqrt{K\bar{B}}} \tag{2}$$

where $q_0 = 2\pi/d_B$ is the position of the first-order quasi-Bragg singularity. To obtain η, related the width of the quasi-Bragg singularity, the whole X-ray spectrum has been fitted (except for very low q) using Nallet et al.'s[14] analytical approach based on Caillé's model.[13]

The rigidity of a membrane is obtained using the correction to the "classical" dilution law. From geometrical considerations for stiff non undulating membranes, the membrane thickness $d_{membrane}$ is related to the Bragg distance d_B and the membrane volume fraction $\phi_{membrane}$ by[15]

$$\phi_{membrane} = \frac{d_{membrane}}{d_B} \tag{3}$$

called the classical dilution law. When the lamellar phase is stabilized by Helfrich interactions, membranes are fluctuating, so the projected area of a membrane is smaller than the real area: thus the classical dilution law is not valid anymore. The corrected dilution law becomes then[16-18]

$$d_B\phi_{membrane} = V - W\ln(\phi_{membrane}) \tag{4}$$

with

$$W = d_{membrane}\frac{k_B T}{4\pi\kappa} \tag{5}$$

and

$$V = d_{membrane}\left(1 + \frac{k_B T}{4\pi\kappa}\ln\left(\sqrt{\frac{32\kappa}{3\pi k_B T}}\frac{d_{membrane}}{a}\right)\right) \tag{6}$$

where a is a molecular dimension. In a first approximation, $d_{membrane}$ has been deduced from the classical dilution law and then combined with the W value obtained from the fit to eq 4 in order to estimate κ.

In the case of lamellae stabilized only by steric interactions, according to Helfrich,[3] variation of η with d_B also allows one to accede to the membrane thickness $d_{membrane}$:

$$\eta^{0.5} = \sqrt{\frac{4}{3}}\left(1 - \frac{d_{membrane}}{d_B}\right) \tag{7}$$

When electrostatic interactions are dominant, the above relation is no longer valid and η scales as a function of d_B, the charge surface density σ, and d_{water}, as proposed by Roux and Safinya.[4]

The interplay between steric and electrostatic interactions in lamellar phases has been examined both theoretically[7,8,19-25] and

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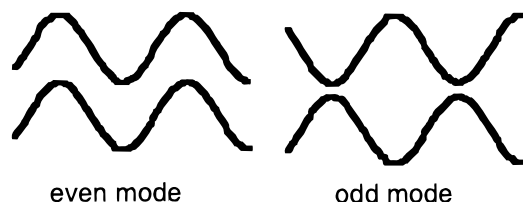
Figure 2. Odd (left) and even (right) modes of fluctuations according to Fogden et al.[8]

experimentally[5,6,26–30] in the past decade. Two models attracted our attention in particular. The first one has been proposed by Harden et al.[7] in 1992. It introduces electrostatic corrections to steric interactions and calculates a renormalized bending constant of a bilayer of surfactant $\kappa = \kappa_0 + \Delta k_{el}$. Different regimes are considered such as the Gouy–Chapman regime and the ideal gas regime. A more recent model has been proposed by Fogden et al.[8] in 1996, to calculate the electrostatic contribution to the rigidity of charged membranes in systems without salt, for all ranges of surface charge density and surfactant concentrations. The pertinent parameter of the model is Λ, defined as follows: $\Lambda = d/2L_{GC}$, where d is the distance between two charged surfaces (in our case $d = d_{solvent} = d_B - d_{membrane}$), and the Gouy–Chapman length is

$$L_{GC} = \frac{e}{2\pi l_B \sigma} \qquad (8)$$

where e is the electronic unit charge and σ the charge surface density. The Gouy–Chapman length corresponds to the layer thickness of the counterions confined near the charged surface. The Bjerrum length is defined by

$$l_B = \frac{e^2}{4\pi\epsilon_0\epsilon_w k_B T} \qquad (9)$$

with ϵ_w the dielectric constant of the aqueous solvent (for water, $\epsilon_w \approx 80$, implying $l_B \approx 7.1$ Å at 293 K) and ϵ_0 the vacuum permittivity. When $\Lambda \approx 1$, the two counterion layers of two neighboring membranes are in contact. Two modes of fluctuations are considered, an odd and an even (Figure 2), each one leading to a different expression of the electrostatic contribution $\Delta\kappa_{el}$ to the rigidity $\kappa = \kappa_0 + \Delta\kappa_{el}$. Writing $D \tan D = \Lambda$, one gets

$$\frac{\Delta\kappa_{even}}{k_B T} = 2\frac{d}{l_B}\left[\frac{\Lambda(2\Lambda + 1 - D^2)}{\Lambda^2 + D^2} - \left(1 + \frac{D^2}{3}\right)\right] \qquad (10)$$

and

$$\frac{\Delta\kappa_{odd}}{k_B T} = \frac{2}{3}\frac{d}{l_B}\frac{(\Lambda^2 + D^2)^2}{(\Lambda^2 + \Lambda + D^2)^3}\left[\left(1 - \frac{D^2}{15}\right)\Lambda^2 + 2\Lambda\left(2 - \frac{D^2}{5}\right) + \left(3 - D^{-2}\frac{D^4}{15}\right)\right] \qquad (11)$$

A factor of 2 appears in these expressions since we consider bilayers and Fogden et al.[2] monolayers. The even mode corre-

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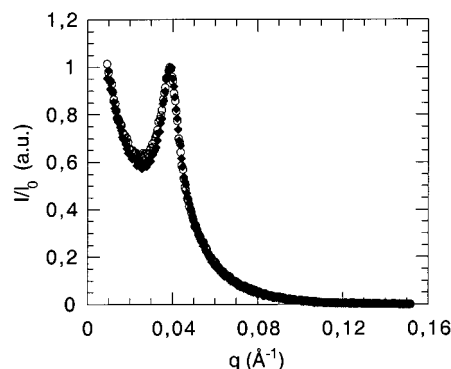

Figure 3. Normalized SAXS spectra of sample at $\phi_s = 0.2$ and $\alpha = 0.8$ for $\chi = 0$ (○) and $\chi = 4\%$ (◆).

sponds to in phase undulations of lamellae, whereas the odd mode corresponds to in opposition of phase undulations (or peristaltic mode).[31] Within specific limits for Λ, expressions 10 and 11 are consistent with scaling forms given by Pincus et al.,[21] Higgs and Joanny,[22] and Harden et al.[7] In absence of added salt in water, and because of the limits of existence of the lamellar phase, the $C_{12}E_4$–SDS–decane–water system is between two regimes defined by Harden et al.,[7] and their model cannot be applied. Values of κ determined experimentally will be compared with Fogden's model[8] in the discussion.

Results and Discussion

Optical Observations. Observations between crossed polarizers indicated that all studied samples were in the L_α phase region at room temperature (20 °C), as proved by their birefringence and the characteristic focal conic defects present under polarized microscope. We have observed an unexpected viscosity variation upon dilution by water of the direct lamellar phase. Qualitatively, for SDS concentrations larger than 2%, the viscosity increases to a maximum and then decreases upon dilution. These changes will be studied in more detail in a forthcoming paper.

Oil-Rich (or Reverse) Lamellar Phase ($\alpha = 0.6$ and 0.8). The reverse lamellar phase is made of stacks of membranes, composed of two monolayers of surfactant enclosing water, separated by decane. In this oil-rich part of the phase diagram, the shape of X-ray spectra does not seem to be influenced by SDS addition as shown on Figure 3. The Bragg distance d_B as well as η is independent of SDS concentration in the range 0–4%. The oil-swollen L_α phase has been studied along dilution lines for different values of χ: the L_α phase has been progressively swollen with decane, whereas the volume ratio $V_s/(V_s + V_{water})$ has been kept constant and equal to 0.62 (Figure 1). In the limits of existence of the L_α phase, the Bragg distance varies from 80 to 180 Å.

η values have been extracted from Nallet's fit[14] of the SAXS spectra for the different Bragg distances. In Figure 4, $\eta^{0.5}$ has been plotted vs d_B^{-1}, for $\chi = 0$, 1 and 4%. In all cases the variation is linear indicating that even for $\chi = 4\%$ the L_α phase is stabilized by steric interactions. The fit to eq 7 leads to $d_{membrane} = 51 \pm 3$ Å for SDS-free as well as SDS-containing samples.

The membrane thickness $d_{membrane}$ was obtained from the classical dilution law (eq 3) and then the membrane rigidity κ was deduced from the correction to the dilution law. In Figures 5 and 6, variations of d_B vs $1/\phi_{membrane}$ and $d_B\phi_{membrane}$ vs $\ln(\phi_{membrane})$ for $\chi = 0$, 1, and 4% are presented. All the points gather on the same straight line regardless of χ. The classical dilution law gives $d_{membrane}$

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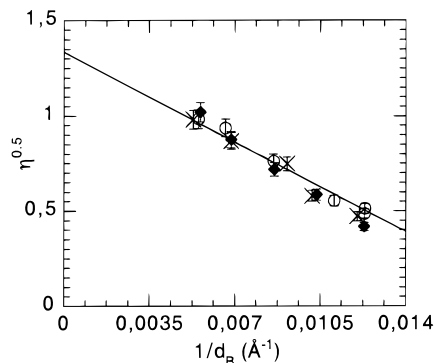
Figure 4. Plot of $\eta^{0.5}$ vs d_B^{-1} for $\chi = 0$ (○), $\chi = 1\%$ (×), and $\chi = 4\%$ (◆) at constant membrane thickness ($V_s/(V_s + V_{water}) = 0.62$). The continuous line is the fit to eq 7.
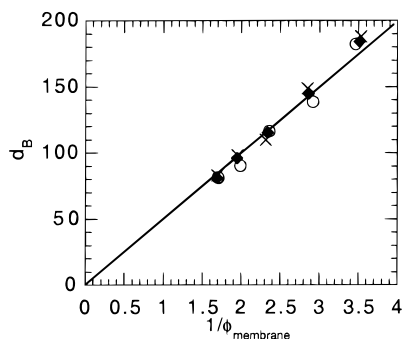

Figure 5. Classical dilution law of the reverse L_α phase for $\chi = 0$ (○), $\chi = 1\%$ (×), and $\chi = 4\%$ (◆), under the same conditions as Figure 4. The continuous line is the fit to eq 3.
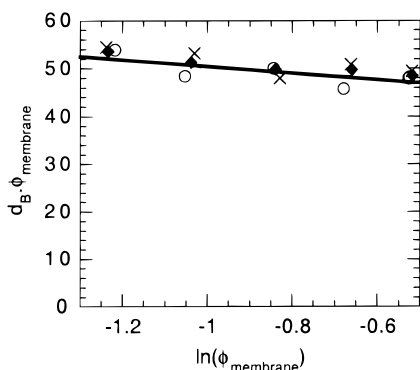

Figure 6. Correction to the classical dilution law of the reverse L_α phase for $\chi = 0$ (○), $\chi = 1\%$ (×), and $\chi = 4\%$ (◆), under the same conditions as Figure 4. The continuous line is the fit to eq 4.

$= 51 \pm 2$ Å and the fit to eq 4, $\kappa = 0.7 k_B T \pm 0.2$, in excellent agreement with the above determination. The $C_{12}E_4$ monomer concentration in decane (11 g/L) has been taken into account in calculations of the membrane volume fraction. The agreement with eq 7 confirms that no change occurs when the reverse lamellar phase is charged. Porcar et al.[28,29] who added small amounts of cetylpyridinium chloride (CpCl) in the oil-rich TritonX100−water−decane L_α phase, noticed a change neither in the Bragg distance nor in the rigidity. We have checked that the even electrostatic contribution to rigidity, calculated according to Fogden's model, gives values which can be neglected when compared to κ_0. On the other hand, the odd contribution gives infinite values that can be considered as unrealistic.

In the decane-swollen lamellar phase, the presence of charged membranes does not induce changes. No increase
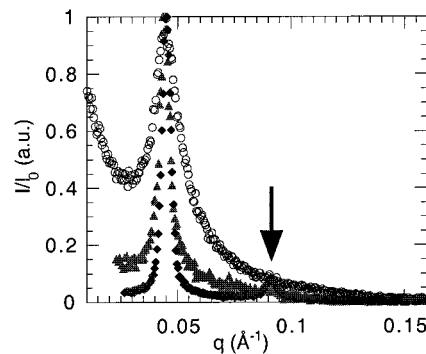

Figure 7. Normalized SAXS spectra of sample with $\phi_s = 0.2$ and $\alpha = 0.2$ for $\chi = 0$ (○), $\chi = 0.4\%$ (▲), and $\chi = 3.5\%$ (◆).
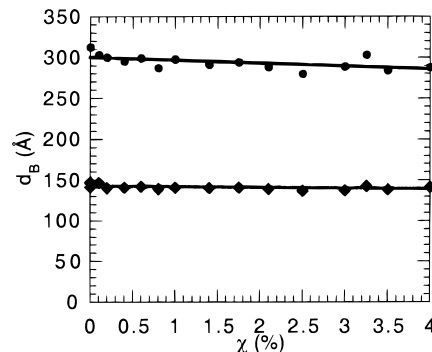

Figure 8. Variation of the Bragg distance d_B vs χ for $\phi_{membrane} = 0.2$ (●) and $\phi_{membrane} = 0.4$ (◆) for $V_s/(V_s + V_{water}) = 0.55$.

of the bending rigidity is observed. The small amount of water (thickness of water 20 Å) is so dense in counterions that they screen each other, and electrostatic interactions are still concealed by steric interactions.

Water-Rich (or Direct) Lamellar Phase ($\alpha = 0.2$ and 0.4). The direct lamellar phase is made of stacks of membranes composed of two monolayers of surfactant enclosing decane, separated by water. A rapid inspection of Figure 7 shows that SAXS spectra are influenced by SDS concentration. SDS-containing samples exhibit spectra with sharper peaks than SDS-free samples of the same membrane volume fraction. When the SDS to surfactant molar ratio χ increases, the small angle signal quickly decreases and a second-order peak appears (see arrow in Figure 7). As for the reverse L_α phase, the direct L_α phase has been studied along a dilution line, for χ ranging from 0 to 4% and for $V_s/(V_s + V_{decane})$ kept constant equal to 0.55 (Figure 1). The presence of SDS expands the limits of existence of the L_α phase: for $\chi = 0\%$, the largest d_B obtained without demixtion was 160 Å, whereas Bragg distances as large as 350 Å could be observed as soon as SDS was added in very small concentrations ($\chi = 0.1\%$). For the same membrane volume fraction, one can notice that the quasi-Bragg peak is shifted to higher q values when SDS concentration increases. This shift is more important for "high" dilutions ($\phi_{membrane} = 0.2$) than for "low" dilutions ($\phi_{membrane} = 0.45$). The corresponding decrease of d_B with charge addition can be explained by a reduction of membrane fluctuations which leads to lower d_B values (Figure 8). This result is in agreement with results obtained by Jonströmer, Schomäcker, and Strey[26,27] in the binary system $C_{12}E_5$−water where SDS has been added.

To verify that the modifications reported above are not due to sterical constraints induced by SDS addition, we have screened electrostatics by replacing water by brine (0.1 M NaCl). The X-ray spectrum obtained for the charged
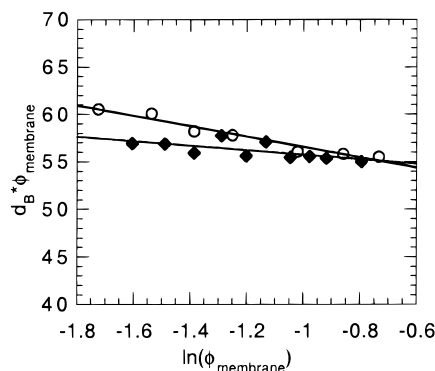
Figure 9. Correction to the classical dilution law of the direct L_α phase for $\chi = 0.2\%$ ($\bigcirc$) and $\chi = 3.5\%$ ($\blacklozenge$) at constant membrane thickness ($V_s/(V_s + V_{water}) = 0.55$). The continuous line is the fit to eq 4.
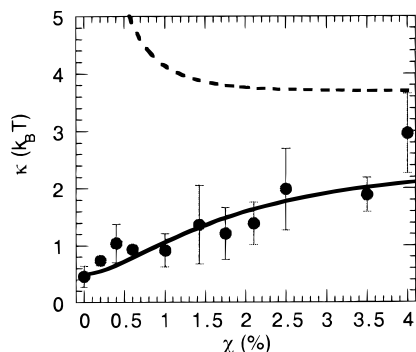

Figure 10. Variation of the membrane rigidity κ of the direct L_α phase vs χ for a membrane volume fraction of 0.2 and $V_s/(V_s + V_{water}) = 0.55$. The continuous line represents Fogden's calculations for the even mode of fluctuation, the discontinuous one the odd mode. Points represent experimental values.

Figure 11. Variation of the membrane rigidity κ of the direct L_α phase vs χ for a membrane volume fraction of 0.45 and $V_s/(V_s + V_{water}) = 0.55$. The continuous line represents Fogden's calculations for the even mode of fluctuations, the discontinuous one the odd mode. Points represent experimental values.

Figure 12. Typical variation of the Landau-Peierls parameter η vs χ ($\phi_{membrane} = 0.4$, $V_s/(V_s + V_{water}) = 0.55$).

lamellar phase in brine exactly overlays on the spectrum of nonionic one, at the same membrane volume fraction (not shown here). This indicates the electrostatic origin of changes.

As soon as χ is larger than 0.1%, the Helfrich's formula for $\eta^{0.5}$ vs $1/d_B$ is not valid anymore. η does not follows the law determined by Roux and Safinya[4] for a charged lamellar phase because the surface charge density is too weak. So the membrane thickness has been determined from the dilution law and the membrane rigidity from the correction to the dilution law, for different values of χ. The fit of eq 3 leads to a membrane thickness $d_{membrane} = 57 \pm 2$ Å, independent of SDS concentration. Membrane rigidity is estimated from the fit to eq 4 with a much larger error (around 15%) since the very low slope of $d_B\phi_{membrane}$ vs $\ln(\phi_{membrane})$ is poorly fitted. In Figure 9, two of these fits are presented: the correction is obvious for small χ, whereas the slope is very low for high χ. The membrane bending rigidity dependence with χ is plotted in Figures 10 and 11: the rigidity is increasing with SDS concentration. The continuous/dotted lines are the fits to Fogden's expression for the even/odd mode respectively. In both cases, the dotted lines are very far from the experimental data. As already pointed out by Harden et al.,[7] the peristaltic mode involves not only the bending of the membrane but also the compression of the ionic solution between membranes. This compression costs a lot of energy, leading thus to very high values of the corrected bending constant. This mode of fluctuations is then energetically less favorable than the usual undulation mode. For those reasons, the peristaltic mode of fluctuations can be considered as irrelevant in our system. On
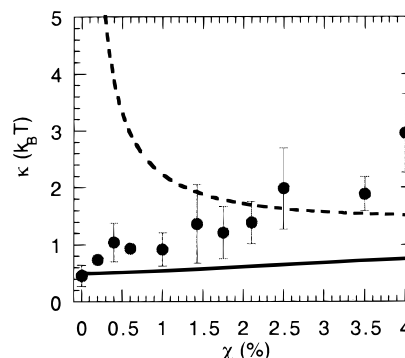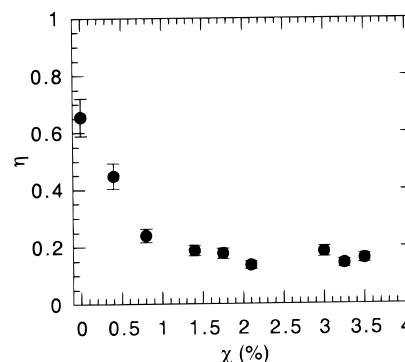
the other hand, values of the even mode calculated for "high" dilutions ($\phi_{membrane} = 0.2$) fit experimental data quite well (Figure 10). This is not the case for "low" dilutions ($\phi_{membrane} = 0.45$) (Figure 11). This discrepancy may arise from an assumption of the model: Fogden at al.[8] neglect all electrostatic coupling between the opposite sides of the membranes and between second neighbors membranes. In the case of concentrated lamellar phases, coupling between membranes should be taken into account. Then a straightforward comparison between Fogden's model and our experimental data might not be valid.

The smectic compressibility modulus $\bar{B}$ variation with χ is easily deduced using the expression (eq 2) for the Landau−Peierls order parameter η.[13] For a given membrane volume fraction and at different χ, SAXS spectra have been fitted giving η values which have been used to estimate $\bar{B}$. In Figure 12, the dependence of η with χ is presented: η decreases when χ increases from 0 to 2%, and then seems to stabilize around 0.15 for upper values of χ. As expected, the smectic order is observed to be increasing as lamellae are charged and stiffened. The observed variation is well fitted by an exponential: $\eta = a + b \exp(-c\chi)$, but no model of such a behavior can be proposed at this stage. A typical variation of $\bar{B}$ vs χ is reported in Figure 13. The error in experimental values is estimated around 25%, due to the experimental error in determining κ and η (Figures 10−12). The behavior of $\bar{B}$ is the same for all studied membrane volume fractions: as χ increases, $\bar{B}$ first increases sharply until a maximum value $\bar{B}_{max}$, and then decreases slightly. To understand this behavior, the Gouy−Chapman length corresponding to the value of χ for which $\bar{B} = \bar{B}_{max}$ has been plotted vs the water thickness d_{water} in Figure 14. Obviously $\bar{B}$ is a
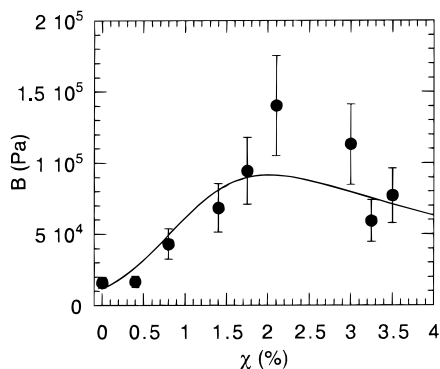
Figure 13. Variation of the smectic compressibility modulus $\bar{B}$ of the direct L_α phase vs χ ($\phi_{membrane} = 0.4$ and $V_s/(V_s + V_{water}) = 0.55$). The continuous line has been obtained by the following phenomenological approach: $\kappa(\chi)$ has been fitted by a second-order polynom, η by a decreasing exponential as stated above, and $q_0(\chi)$ has been deduced from the fit of $d_B(\chi)$ (Figure 9) for the different membrane volume fractions. $\bar{B}$ has been then obtained from these equations and the expression of the Landau−Peierls order parameter (eq 2). Points represent experimental values.
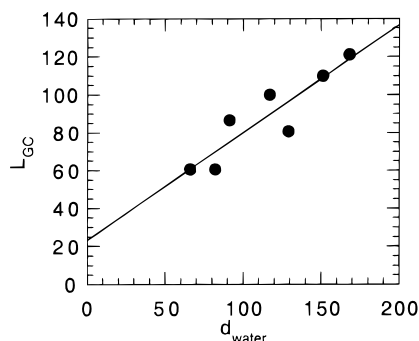

Figure 14. Variation of the Gouy−Chapman length L_{GC} vs the water thickness d_{water}. Straight line represents the best fit.

maximum when $L_{GC} \approx d_{water}/2$, e.g., when the counterions layers of two neighboring membranes are in contact. The increase of $\bar{B}$ for small χ can be explained by an electrostatic effect: it is much more difficult to compress charged surfaces than undulating membranes repelled only by steric forces. As χ further increases, L_{GC} decreases and thus the "effective" distance between membranes ($d' = d_{water} - 2L_{GC}$) increases and $\bar{B}$ decreases. Since the small angle signal has been shown to be reversely proportional to $\bar{B}$, the increase of $\bar{B}$ with χ explains the decrease of the small angle signal with SDS concentration. Adding SDS in the system introduces long-range electrostatic interactions inside and between the bilayers: these interactions make position fluctuations decrease. As the small angle signal represent position fluctuations[32,33] it decreases as well.

In Figure 15, a typical plot of $\bar{B}$ vs d_{water} at a given SDS concentration is shown: $\bar{B}$ scales as $(d_{water})^{-n}$. The dependence of the exponent n with χ is given on Figure 16: for $\chi = 0$, n is equal to 4.1 ± 0.2 in good agreement with the theoretical predictions of Helfrich,[3] and then the exponent decreases and fluctuates around 3, the value theoretically predicted[4,34] for infinitely dilute lamellae stabilized by electrostatic interactions.
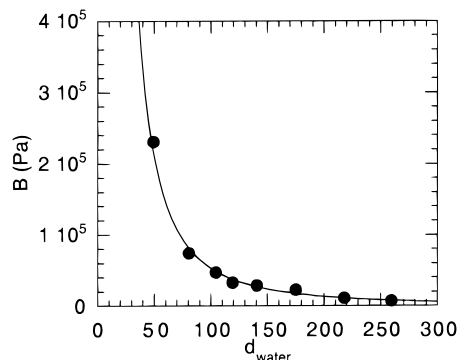
(32) Porte, G.; Marignan, J.; Bassereau, P.; May, R. *J. Phys. Fr.* **1988**, *49*, 511.
(33) Porte, G.; Marignan, J.; Bassereau, P.; May, R. *Europhys. Lett.* **1988**, *7*, 713.
(34) Bouglet, G.; Ligoure, C. *Eur. Phys. J. B* **1999**, *9*, 137.

Figure 15. Typical variation of $\bar{B}$ vs d_{water} fitted by a power law ($\chi = 1\%$, $V_s/(V_s + V_{water}) = 0.55$ and $n = 2$).
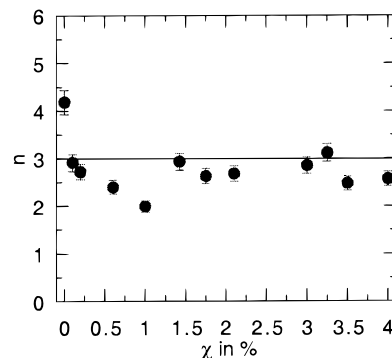

Figure 16. Dependence of the exponent n with χ. The straight line ($n = 3$) is only an eye guide.
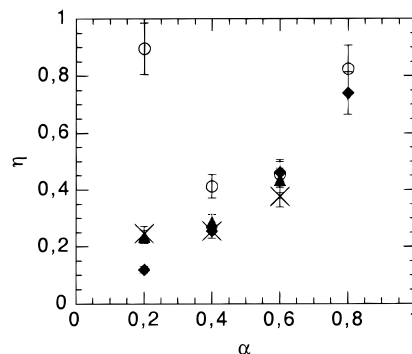

Figure 17. Dependence of η vs α for a fixed surfactant volume fraction $\phi_s = 0.2$. for $\chi = 0$ (○), $\chi = 0.6\%$ (▲), $\chi = 1\%$ (×), and $\chi = 4\%$ (◆).

To compare our results to those of Oda and Litster,[35] the variation of η with $\alpha \equiv V_{oil}/(V_{oil} + V_{water})$ has also been investigated at constant surfactant volume fraction $\phi_s = 0.2$ (horizontal line on Figure 1). When α increases, one moves continuously from a water-swollen to a decane-swollen lamellar phase. For SDS-free samples, η exhibits a minimum around $\alpha = 0.5$ (Figure 17). The smaller η, the better the ordering of the lamellar phase. For the uncharged phase, monolayers of surfactant separated by equal amounts of water and oil are better ordered than membranes with excess water or oil, as previously shown by Oda and Litster[35] for the $C_{12}E_5$−water−octane system. For $\chi \neq 0$, in contrast to the nonionic system, the minimum of η is found for small α values. In the oil-swollen L_α phase ($\alpha > 0.5$), η remains almost constant with SDS addition, whereas in the water-swollen L_α phase ($\alpha < 0.5$), for a given α value, η decreases with the amount of in-plane charges (see also Figure 12). In the case of charged

(35) Oda, R.; Litster, J. D. *J. Phys. II Fr.* **1997**, *7*, 815.

membranes, because of electrostatic interactions, membranes of surfactant and oil separated by water exhibit a better quasi-long-range order than in the symmetrical situation.

Conclusion

The interplay between steric and electrostatic interactions has been investigated experimentally in the $C_{12}E_4$–SDS–water–decane system, both in the water-swollen and decane-swollen lamellar phases. We have performed systematic determination of the Landau–Peierls order parameter η, the membrane bending rigidity κ, and the smectic compressibility modulus $\bar{B}$ upon increasing concentration of the charged surfactant SDS in the nonionic system. Our lamellar phases SAXS spectra are very well fitted by the analytical model proposed by Nallet et al.[14] Results obtained were more accurate as lamellae are charged and stiffen. We are therfore confident of our elastic constants.

Charging membranes leads to a totally different behavior in the direct and reverse lamellar phases. In the oil-swollen lamellar phase, in agreement with theoretical predictions of Fogden et al.,[8] steric interactions still dominate over electrostatic ones as SDS concentration increases up to 4%. For a given membrane volume fraction, the Landau–Peierls order parameter η, the smectic compressibility modulus $\bar{B}$, the Bragg distance d_B, and the membrane rigidity κ are independent of the SDS to total surfactant molar ratio χ. The small volume fraction of water could explain this phenomenon: water (thickness of water 20 Å) is so dense in counterions that they screen each other.

On the other hand, replacing $C_{12}E_4$ by SDS induces a significative variation of these constants in the direct lamellar phase. When χ increases from 0 to 4%:

- The Landau-Peierls order parameter η decreases, indicating that the smectic order is getting better.
- The smectic compresibility modulus $\bar{B}$ scales as $(d_{water})^{-n}$ where d_{water} is the intermembrane distance and n depends on the SDS concentration in the membrane.

- For a given membrane volume fraction, $\bar{B}$ is increasing sharply with SDS concentration for low surface charge densities and then presents a bump and a slow decrease. The behavior of $\bar{B}$ can be understood qualitatively: the increase originates from electrostatic interactions and the position of the maximum corresponds to the molar ratio of ionic to total surfactant, where the two layers of counterions of facing membranes are in contact. However a complete analytical model is lacking to interpret our experimental data.

- The Bragg distance d_B decreases slightly when SDS is added to the membrane. Membrane undulations seem to be frozen by charges, which leads to a decrease of the Bragg distance d_B. The latter interpretation is confirmed by the increase of the membrane rigidity κ: fluctuating membranes tend to stiffen. Fogden's model fits perfectly the experimental increase of κ for high dilutions while it fails obviously for low dilutions. This fact may arise from the assumption of no electrostatic coupling between opposite sides of a membrane and between second neighbor membranes. For this reason, a comparison between the model and our results might not be valid for low dilutions.

The next logical step would be to extend the study in order to explore the lamellar behavior in other regimes as defined by Harden et al.[7] Together with Fogden's model[8] it would lead to a better comprehension of lamellar constants behavior for all ranges of surface charge and salinity.