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## Flexibility of molecular films as determined by deuterium solid state NMR

F. Auguste, P. Barois, L. Fredon (\*), B. Clin (\*\*), E. J. Dufourc and A. M. Bellocq

Centre de Recherche Paul Pascal, CNRS, Av. Albert Schweitzer, 33600 Pessac, France

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**Abstract.** — A new technique is proposed for the measurement of the bilayer bending modulus  $\kappa$ , in the lamellar phase  $L_\alpha$  of lyotropic systems. It resides in the measurement of quadrupolar splittings by deuterium solid state NMR. By separating the different motional contributions accounting for the reorientation of the C-D bond with respect to the magnetic field, we have calculated within a simple Gaussian theory the effect of thermal fluctuations of the film upon the recorded quadrupolar splitting. This has been applied to the study of the effects of membrane composition on the mean bending modulus  $\kappa$  in ternary and pseudo ternary systems of water-(salt)-sodium dodecyl sulfate-alcohol. It is found that  $\kappa$  is sensitive both to the amount of alcohol in the membrane and to the alcohol chain length, with typical values increasing between  $1.3 k_B T$  and  $13.0 k_B T$  from hexanol to decanol systems. Our results allow to attribute the reduction in  $\kappa$  obtained by replacing surfactant by alcohol to the thinning of the membrane and to the increase of the area occupied by the surfactant at the interface.

### 1. Introduction.

An interesting variety of structures and behaviors are encountered in the study of surfactant/solvent systems also known as lyotropic phases [1, 2]. In many cases, amphiphilic molecules build bilayers which can self-organize on a large scale either with long range order (liquid crystalline and crystalline phases) or only short range correlations (liquid isotropic phases). Examples of such structures are for instance lamellar  $L_\alpha$  phases or cubic phases [1, 2] and sponge or vesicle phases [3-5]. Theoretical studies have shown that the ultimate structure depends strongly on two important intrinsic parameters of the bilayer: the mean bending modulus  $\kappa$  and the Gaussian bending modulus  $\bar{\kappa}$  [6, 7]. Among the various observed structures, the lamellar phase has received considerable experimental [8-11] and theoretical [12-14] attention. This phase consists of a regular stack of parallel bilayers of amphiphilic molecules separated by a solvent, usually water. It has the symmetry of a smectic A phase, it is

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(\*) *Present address* : ROC, 48 rue de Seine, 92703 Colombes Cedex, France.

(\*\*) *Present address* : DRIRE, rue de la Liberté, 33000 Bordeaux, France.

optically birefringent and uniaxial. In favourable cases, the  $L_\alpha$  phase is stable for a large range of water content so that the repeat distance,  $d$ , can be varied continuously upon addition of solvent from molecular sizes ( $d \approx 20 \text{ \AA}$ ) to extremely large values (100-1000  $\text{\AA}$ ). Mixtures of water, ionic surfactant and alcohol are examples of such systems. Their ability to swell the smectic structure with water is associated with strong electrostatic repulsions. If the dilution is made with brine instead of water, the  $L_\alpha$  phase is stable at even lower surfactant concentration. The larger swelling exhibited by such systems is due to a non electrostatic long range repulsive interaction between bilayers. This interaction, known as the undulation interaction, originates in the high flexibility of the surfactant bilayers through a mechanism of entropy reduction proposed by Helfrich [12]. The amplitude of this undulation interaction which is dominant once the electrostatic ones are screened out, is proportional to the inverse of the bending constant,  $\kappa$ . It has been early recognized that the main effect of alcohol in surfactant-alcohol mixtures is to produce flexible, thermally fluctuating bilayers. Up to now, the bending modulus of films of surfactant in lamellar phases has been measured by dynamic light scattering [11, 15], high resolution X-ray scattering by analysis of the line shapes (Landau-Peierls effect) [10] or of the peak position [16, 17], small angle X-ray scattering [18, 19] and electron spin resonance [8]. We show in the present paper that the bending modulus of the layers can be measured by  $^2\text{H-NMR}$  spectroscopy in the same systems. The values of  $\kappa$  are in good agreement with earlier reported values [20] and we propose this method as a routine technique for measuring the bending modulus of the amphiphilic bilayers in lyotropic lamellar phases. Using this technique, we have investigated the effect of membrane composition on film elasticity. The amount of alcohol, taken as the cosurfactant was first varied in the lamellar phase of water/sodium dodecyl sulfate (SDS)/octanol system and subsequently, we varied the alcohol chain length from C6 to C10 in the water/SDS/alcohol system and brine (20 g/l NaCl)/SDS/alcohol system.

Outline of the paper is as follows : the systems under study are presented in the next section. The theoretical background of the  $^2\text{H-NMR}$  experiments is then explicated in section 3. The effect of thermal fluctuations of the films upon the recorded quadrupolar splitting is calculated within a simple mean field model. Section 4 is experimental : NMR results are given for a series of ternary systems with different alcohols and different membrane compositions (i.e. various alcohol/surfactant ratios). Section 5 is devoted to discussion.

## 2. Experimental systems.

We have investigated the lamellar phase of ternary systems composed of water, sodium dodecyl sulfate (SDS) and alcohol. Five different alcohols have been used : hexanol, heptanol, octanol, nonanol and decanol. For NMR experiments, we have used either  $\alpha$ -deuterated surfactant or  $\alpha$ -deuterated alcohol, synthesized according to standard methods [21], or perdeuterated surfactant, purchased from Commissariat à l'Energie Atomique (France). Alcohols were purchased from Aldrich (France); water was purified *via* an ion exchange purification train (Milli-Q system, Millipore); protonated SDS was obtained from Touzard et Matignon (France). Samples were prepared with 50 mg of perdeuterated SDS, or 200 mg of  $\alpha$ -deuterated SDS, mixed with the appropriate quantity of protonated SDS, in order to give a total weight of about 1 g to 2 g of lamellar phase. Alcohol and water are first added to realize « stock solutions », composed of 40-45 % water. After a sufficient delay (one week to reach the equilibrium), these solutions are diluted in order to realize samples on dilution lines. The samples are sealed in order to prevent solvent evaporation and centrifugated. Experiments were carried out on a Bruker MSL 200 spectrometer, operating at 30.7 MHz for deuterium. The temperature was regulated to  $298 \pm 1 \text{ K}$ . NMR signals were recorded either with a quadrupole echo technique ( $\pi/2$  pulse width of 6-8  $\mu\text{s}$ , pulse spacing of 25-30  $\mu\text{s}$ ) or a

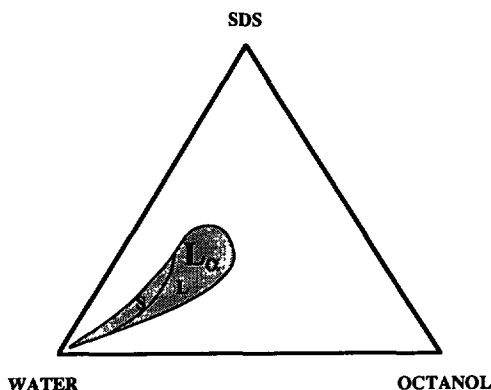


Fig. 1. — Location of the lamellar  $L_\alpha$  phase in the water/SDS/octanol system. The lamellar phase can be separated in two domains, corresponding to : L, lamellar structure and S, structural defects of the lamellar phase, referred to spherulites.

composite quadrupole echo pulse sequence [22]. Data treatment was accomplished on a VAX/VMS 8600 computer (DEC, USA).

PHASE DIAGRAMS. — The lamellar phase was located in all studied systems by polarizing microscopy and, when necessary, by deuterium-NMR and small angle X-ray diffraction. In all the systems, the extension of the lamellar phase is very large, both in membrane composition and in dilution, which enables to carry out experiments on dilution lines with samples containing from 40 to 90 % water (wt%) and to change membrane composition from 1 to 3 alcohol molecules per surfactant. As an example, we report in figure 1 the location of the  $L_\alpha$  phase in the water/SDS/octanol system.

### 3. Theoretical background.

3.1 DEUTERIUM NMR. — The observed quadrupolar splitting,  $\Delta\nu_Q$ , of deuterated SDS embedded in a lamellar liquid crystalline  $L_\alpha$  phase can be expressed as [23-26] :

$$\Delta\nu_Q = \frac{3}{2} A_Q \left( \frac{3 \cos^2 \theta_L - 1}{2} \right) S_{C-D} . \quad (3.1)$$

The angle  $\theta_L$  represents the orientation of the normal to the membrane with respect to the magnetic field direction  $B_0$ ,  $A_Q = 170$  kHz is the quadrupolar coupling constant for a methylenic C-D bond [27] and  $S_{C-D}$  is the orientational order parameter accounting for the fast (in NMR time scale) contributions of anisotropic motional averages in the bilayer. Figure 2 shows a typical spectrum of the  $\alpha$ -labelled surfactant in a non oriented sample in the lamellar phase. The frequency separation between the two most intense peaks of the Pake doublet gives the quadrupolar splitting for  $\theta_L = 90^\circ$ .

The  $S_{C-D}$  order parameter can be decomposed into three contributions originating from different axially symmetric motions (Fig. 3) : i) intramolecular motions, i.e. isomerisations of  $-CH_2-$  groups around the molecular axis (angle  $\theta_1$ ), ii) molecular motions, that is, anisotropic reorientation of the molecule with respect to the normal to the local surface,  $\mathbf{n}$ . (angle

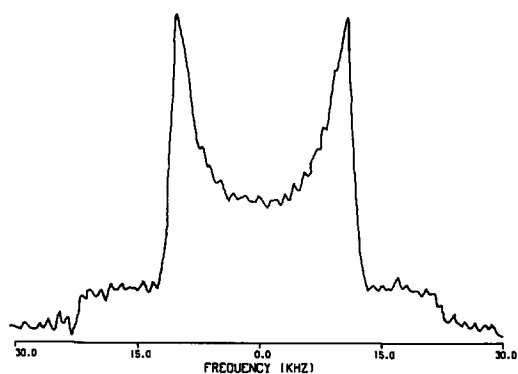


Fig. 2. — Typical spectrum of the  $\alpha$ -labelled surfactant in a non oriented sample in the lamellar  $L_\alpha$  phase of the water/SDS/octanol system. The composition of the sample is 60 % water, 22 % octanol and 18 % SDS (wt%). The experiment has been carried out at 298 K, on a Bruker MSL 200 spectrometer.

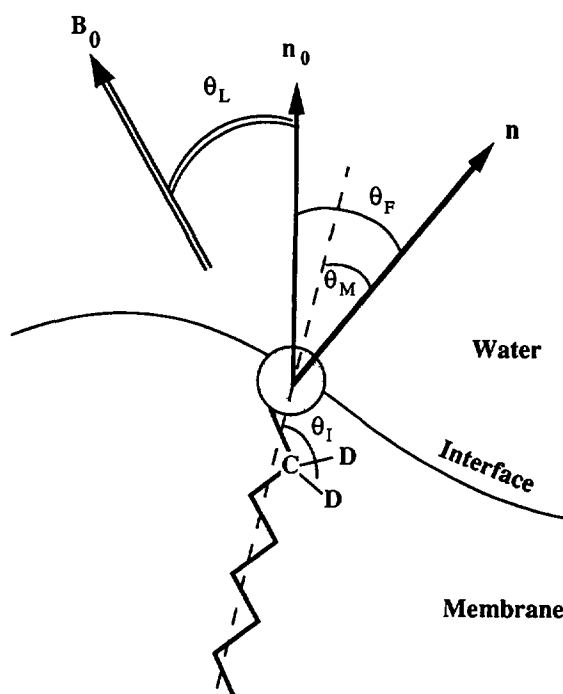


Fig. 3. — Schematic representation of the various axially symmetric motions of an amphiphilic molecule in a lamellar phase.  $\theta_I$  is the angle between the C-D bond and the molecular axis and accounts for the isomerisations of the C-D<sub>2</sub> groups ;  $\theta_M$  is the angle between the molecular axis and the normal to the local surface,  $\mathbf{n}$ , and accounts for the anisotropic reorientation of the molecule ;  $\theta_F$  is the angle between  $\mathbf{n}$  and the axis of the smectic liquid-crystal,  $\mathbf{n}_0$ , and accounts for the fluctuations of the bilayer.

$\theta_M$ ), and iii) fluctuations of bilayer domains, i.e. fluctuation of  $\mathbf{n}$  with respect to the optical axis of the smectic liquid-crystal  $\mathbf{n}_0$  (angle  $\theta_F$ ) :

$$S_{C-D} = S_I S_M S_F = \left\langle \frac{3 \cos^2 \theta_1 - 1}{2} \right\rangle \left\langle \frac{3 \cos^2 \theta_M - 1}{2} \right\rangle \left\langle \frac{3 \cos^2 \theta_F - 1}{2} \right\rangle. \quad (3.2)$$

The angular brackets denote a time and space average. To derive equation (3.2), it is assumed that motions operate at very different time scales [28] and are fast enough to average the residual quadrupolar interaction. In fact, we do not need to assume that  $\theta_1$  and  $\theta_M$  are uncorrelated, we shall only assume for the time being that the product  $S_I S_M$  remains constant once the composition of the membrane is fixed. This assumption will be discussed later.

The term  $S_F$  in equation (3.2) accounts for the fluctuations of bilayers of surfactant in the lamellar structure and is controlled by the statistical mechanics of the membranes.

**3.2 THERMAL UNDULATIONS OF THE BILAYERS IN A LAMELLAR PHASE.** — The fluctuations of membranes in a lyotropic lamellar phase of period  $d$  can be described by the local displacement  $U_i(\mathbf{r})$  of the  $i$ -th membrane at position  $\mathbf{R} = (\mathbf{r}, id)$  with respect to the ideal undistorted network of planes.  $\mathbf{R}$  denotes a 3-d vector and  $\mathbf{r}$  its projection on the  $(x, y)$  plane of the layers.  $z$  is then the optical axis. The description of the fluctuations that we shall develop here is very similar to the approach of Golubovic and Lubensky [14].

Like in any smectic phase, the energy of the fluctuations can be expanded at lowest order in terms of compression and bending. Instead of  $U_i(\mathbf{r})$ , a continuous hydrodynamic variable  $\tilde{u}(\mathbf{R})$  is generally used [29]. The continuous description implies that  $\tilde{u}(\mathbf{R})$  is a coarse-grained variable fluctuating at wavelengths longer than some cutoff length  $L_1$  of order  $d$ . Note that the cutoff length  $L_1$  satisfies  $a < L_1 \ll L$  in which  $a$  is a molecular size parallel to the film and  $L$  the size of the sample. The Landau free energy of these fluctuations reads :

$$\Delta F [\tilde{u}] = \int_{\pi/L}^{\pi/L_1} \frac{d^3 q}{(2\pi)^3} \left( \frac{\bar{B}}{2} q_z^2 + \frac{K}{2} q_\perp^4 \right) |\tilde{u}(q)|^2 \quad (3.3)$$

in which  $\bar{B}$  denotes the layer compression at constant chemical potential [13] and  $K$  the bending modulus.

The disorientation  $\tilde{\theta}_F(\mathbf{R})$  arising from  $\tilde{u}(\mathbf{R})$  can be easily calculated :

$$\cos^2 \tilde{\theta}_F(\mathbf{R}) = \frac{1}{1 + (\nabla_\perp \tilde{u})^2} \quad (3.4)$$

and

$$\begin{aligned} \langle (\nabla_\perp \tilde{u})^2 \rangle &= \int \frac{d^3 q}{(2\pi)^3} q_\perp^2 \frac{k_B T}{\bar{B} q_z^2 + K q_\perp^4} \\ &\approx \frac{\pi}{16} \frac{k_B T}{L_1^2 \sqrt{K \bar{B}}}. \end{aligned} \quad (3.5)$$

The fluctuations of wavelength shorter than  $L_1$  (crumpling) are not included in (3.5) although they contribute significantly to the disorientation of the films. They can be taken into account by considering the statistics of a single membrane embedded in the lamellar phase.

Let  $u_i(\mathbf{r})$  be the deviation of the film from the smooth sheet at position  $\tilde{u}(\mathbf{r}, z = id)$  :  $u_i(\mathbf{r}) = U_i(\mathbf{r}) - \tilde{u}(\mathbf{R})$ . Note that  $u_i(\mathbf{r})$  and  $\tilde{u}(\mathbf{R})$  describe the same undulations but with

different wavelengths. It follows that (i) the Fourier contribution of  $u_i$  and  $\tilde{u}$  cannot be redundant and (ii) the two variables are decoupled to Gaussian order. The free energy of this particular film can be written as :

$$\Delta F [u_i] = \int_s d^2r \left[ \frac{\kappa}{2} (\Delta u_i)^2 + V_{\text{eff}}(u_i) \right]. \quad (3.6)$$

The first term in the integral (3.6) is the bending energy of the membrane of projected area  $S$  whereas the effective potential  $V_{\text{eff}}$  arises from the interaction with the neighbouring membranes. It is assumed in (3.6) that the curvature is small, that the spontaneous curvature is zero and that there is no change of topology.  $V_{\text{eff}}(u)$  is by symmetry an even function and can be expanded as a series of even powers of  $u_i(\mathbf{r})$ . Since the present model is essentially a mean field approach, we shall restrict our attention to a Gaussian truncation of this series :

$$\Delta F [u_i] = \int_s d^2r \frac{1}{2} (\kappa (\Delta u_i)^2 + r_0 u_i^2) \quad (3.7)$$

which yields :

$$\langle (\nabla_{\perp} u_i)^2 \rangle = \frac{1}{8} \frac{k_B T}{\pi \kappa} \text{Ln} \left( \frac{r_0 + \kappa (\pi/a)^4}{r_0} \right). \quad (3.8)$$

The microscopic cutoff  $a$  is a molecular size parallel to the film (a few angstroms).

The interactions one can think of are :

- i) the van der Waals attraction which falls off as  $d^{-2}$  for short separations  $d$  between the films and as  $d^{-4}$  for  $d > 200 \text{ \AA}$  [30] ;
- ii) hydration forces arising from the short range ordering of the solvent [31]. They fall off exponentially with separation and are negligible beyond  $10 \text{ \AA}$  ;
- iii) electrostatic repulsion of charged sheets. Two cases need to be distinguished : unscreened interactions (dilution with pure water) which decay as  $1/d$  [30] whereas screened interactions (dilution with brine) fall off exponentially [30] ;
- iv) steric interaction. These repulsive forces of pure entropic origin were first discussed by Helfrich [12]. He proposed the following form of the free energy per unit area of infinitely thin membrane at a distance  $d$  apart from its neighbour :

$$F_{\text{st}} = c_0 \frac{1}{d^2} \frac{(k_B T)^2}{\kappa} \quad (3.9)$$

with  $c_0$  of the order of unity [12].

As already pointed out by de Gennes and Taupin [33], the Laudau coefficient  $r_0$  appearing in (3.7) is the second derivative of the potential of interaction between the membranes.

For large enough lamellar periods ( $d > 40 \text{ \AA}$  in all our experiments) the van der Waals attraction and the hydration forces are negligible. In the case of pure water dilution, electrostatic interaction prevails and  $r_0$  is calculated from reference [32] :

$$r_{0 \text{ elec}} = \frac{\pi k_B T}{L_B} \left( \frac{1}{(d - \delta)^3} - \frac{3 \Sigma}{\pi L_B (d - \delta)^4} \right) \quad (3.10)$$

in which  $L_B$  is the Bjerrum length ( $L_B \approx 7 \text{ \AA}$ ),  $\delta$  the thickness of the membrane and  $\Sigma$  the area per polar head of surfactant ( $\Sigma \approx a^2$ ). Note that the actual separation ( $d - \delta$ ) of the surfaces of the bilayers is used instead of  $d$ . Values of  $\delta$  and  $\Sigma$  will be determined in section 4.

For brine or oil dilution, steric repulsion predominates. A singular steric interaction cannot be differentiated but the simple Gaussian model of equation (3.7) allows an easy calculation of the free energy per unit area of film :

$$\frac{\Delta F(r_0, \kappa)}{L^2} = \frac{k_B T}{8} \left( \frac{r_0}{\kappa} \right)^2 \quad (3.11)$$

Identifying this result to Helfrich's formula (3.8) and correcting for the thickness  $\delta$  of the membrane gives the value of  $r_0$  for steric repulsion :

$$r_{0\text{st}} = \frac{(8 c_0)^2 (k_B T)^2}{(d - \delta)^4 \kappa} \quad (3.12)$$

Depending on the sample, (3.10) or (3.12) will be used in (3.8) to calculate  $\langle (\nabla_{\perp} u_i)^2 \rangle$ . The contributions of  $\tilde{u}$  and  $u_i$  are not coupled at Gaussian order since they have different  $q_{\perp}$  wavevectors. They can therefore be added for completeness and the order parameter  $S_F$  reads :

$$S_F \approx \frac{1}{2} \left( \frac{3}{1 + \langle (\nabla_{\perp} \tilde{u})^2 \rangle + \langle (\nabla_{\perp} u_i)^2 \rangle} - 1 \right). \quad (3.13)$$

The cut off length  $L_1$  (of order  $d$ ), appearing in equation (3.5), can be estimated more accurately as the mean distance between two contacts of two neighbouring membranes or equivalently as the size of a free membrane that would have a mean square amplitude of fluctuation of  $(d/2)^2$ , i.e.  $L_1^2 \sim d^2 (\kappa/k_B T)$ .

The bending elastic constant  $K$  is simply

$$K = \frac{\kappa}{d} \quad (3.14)$$

whereas the bulk compressional elastic modulus  $\bar{B}$  is estimated from the electrostatic potential in the case of pure water dilution :

$$\bar{B}_{\text{elec}} = d \left( \frac{d^2 V(r)}{dr^2} \right)_{r=d-\delta} = \frac{\pi k_B T d}{2 L_B (d - \delta)^3} \quad (3.15)$$

and, from reference [12], in the case of brine or oil dilution :

$$\bar{B}_{\text{st}} = 6 c_0 \frac{(k_B T)^2}{\kappa} \frac{1}{(d - \delta)^3}. \quad (3.16)$$

Equations (3.2), (3.5), (3.8) and (3.13) will be used in the next section to fit the observed quadrupolar splitting,  $\Delta\nu_Q$ , with equations (3.10) and (3.15) for pure water dilution lines and equations (3.12) and (3.16) for brine dilutions lines.

At this point of the discussion, we know how to express the quadrupolar splitting  $\Delta\nu_Q$  as a function of the three order parameters  $S_I$ ,  $S_M$  and  $S_F$ . Moreover, we can link  $S_F$  to the repeat distance of the bilayers, which depends on the volume fraction of membrane  $\Phi_M$ , and to the bending elastic modulus  $\kappa$ . The other two order parameters  $S_I$  and  $S_M$  are strongly dependent on the internal properties of the film, i.e. bilayer thickness and area per polar head. The constant value of the bilayer thickness, as measured by X-ray diffraction

(see next section) or by  $^2\text{H}$ -NMR with perdeuterated SDS in the same systems [34], suggests that the product  $S_1 S_M$  remains constant upon dilution. We have actually checked that it does, by measuring the bending modulus  $\kappa$  for different positions of the C-D bond either on the surfactant or on the cosurfactant molecules as will be shown in the next section.

#### 4. Results.

In all the following experiments, we have made the assumption that all the alcohols are entirely located in the membranes, which is quite reasonable for long chain alcohols. The evolutions of the quadrupolar splittings are fitted by a mean square method which enables to determine three parameters : the bending modulus  $\kappa$ , the constant  $\Delta\nu_0$  term (corresponding to  $3/4 A_Q S_1 S_M$ ) and the bilayer thickness  $\delta$ . The comparison between  $\delta$  values extracted independently from the fits and from X-ray diffraction experiments constitutes an important checking of the method. We have found in all data treatment a good agreement between both techniques, within 10 % error.

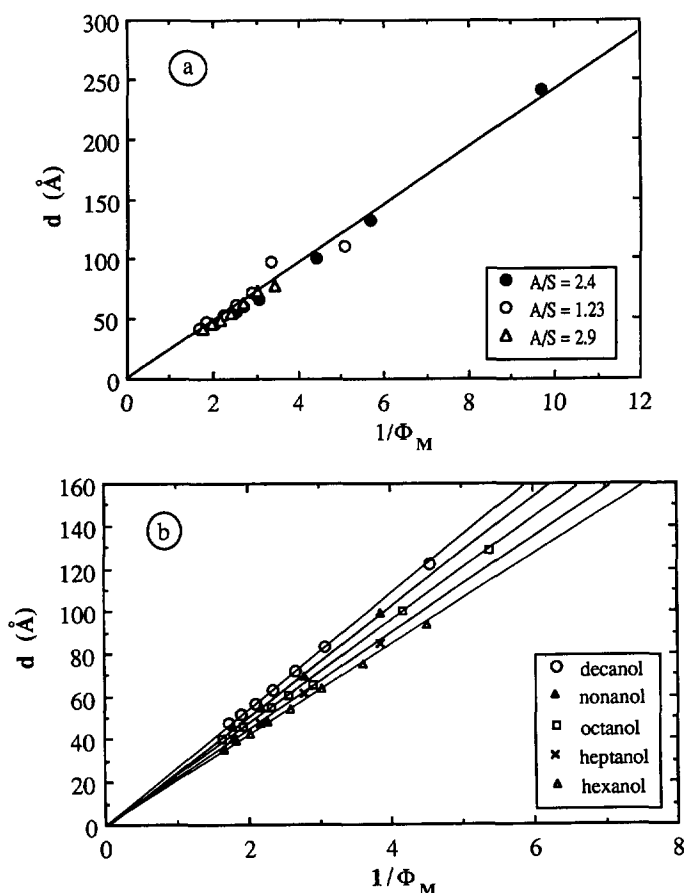


Fig. 4. — Bilayer thickness measurements by X-ray diffraction experiments : plot of the repeat distance ( $d$ ) versus the inverse of the membrane volume fraction ( $\Phi_M$ ). a) Effect of the membrane composition in the water/SDS/octanol system : three different molar ratios were investigated, leading to the same value of the bilayer thickness :  $\delta = 24 \pm 0.5 \text{ \AA}$ . b) Effect of the alcohol chain length in water/SDS/alcohol systems. Experiments were carried out at the same molar ratio  $A/S = 2.4$ , leading to different values of the bilayer thickness :  $\delta = 21.0 \pm 0.5 \text{ \AA}$  for the hexanol,  $\delta = 22.4 \pm 0.5 \text{ \AA}$  for the heptanol,  $\delta = 24.0 \pm 0.5 \text{ \AA}$  for the octanol,  $\delta = 25.6 \pm 0.5 \text{ \AA}$  for the nonanol and  $\delta = 27.5 \pm 0.5 \text{ \AA}$  for the decanol system.

**4.1 BILAYER THICKNESS AND AREA PER POLAR HEAD MEASUREMENTS.** — As we can see in equations (3.10), (3.12), (3.15) and (3.16), it is fundamental to control both the distance separating the bilayers and the area per polar head  $\Sigma$ . These informations can be obtained from small angle X-ray diffraction experiments on dilution lines in the  $L_\alpha$  phase.

The repeat distance  $d$  of a stack of lamellae of thickness  $\delta$  can be connected to the membrane volume fraction  $\Phi_M$  by the relation  $d = \delta/\Phi_M$  (this relation is purely geometrical and does not take into account the excess area related to the undulations of the film) [17]. The repeat distance  $d$ , obtained from the position of the Bragg peak, is plotted against  $1/\Phi_M$  in figure 4 for different systems. The thickness  $\delta$  of the bilayers can be obtained from the slope of the lines. In figure 4a, we examine the effects of the alcohol/surfactant (A/S) molar ratio in the water/SDS/octanol system. The linear dependance observed in the three experiments for the various A/S ratios (1.23, 2.40 and 2.90) suggests that the surfactant-cosurfactant bilayers at fixed composition do not change significantly upon dilution: we found  $\delta = 24.0 \pm 0.5 \text{ \AA}$ . In figure 4b, we examine the effect of alcohol chain length in water/SDS/alcohol systems at molar ratio A/S = 2.4, with the following alcohols: hexanol, heptanol, octanol, nonanol and decanol. We found  $\delta = 21.0 \pm 0.5 \text{ \AA}$  for hexanol,  $\delta = 22.4 \pm 0.5 \text{ \AA}$  for heptanol,  $\delta = 25.6 \pm 0.5 \text{ \AA}$  for nonanol and  $\delta = 27.5 \pm 0.5 \text{ \AA}$  for the decanol system.

The average area per polar head  $\Sigma$  has been defined as follows:  $\Sigma = \Sigma_S + A/S \times \Sigma_A$ , where  $\Sigma_S$  is the area per polar head of surfactant, A/S is the molar alcohol/surfactant ratio and  $\Sigma_A$  is the area per polar head of alcohol. We have obtained the area per polar head values from X-ray diffraction experiments (Fig. 4), from a simple geometric model based on the conservation of the molar volume: we found  $\Sigma_S \approx 36 \pm 3 \text{ \AA}^2$  and  $\Sigma_A \approx 25 \pm 3 \text{ \AA}^2$  in all the systems investigated.

**4.2 INVARIANCE OF THE INTRAMOLECULAR AND MOLECULAR ORDER PARAMETERS.** — Figures 5 and 6 show the evolution of the quadrupolar splitting along a dilution line as a function of the distance between bilayers, for different deuterated species and positions.

Data reported in figure 5 concern  $\alpha$ -deuterated SDS and hexanol in the water/SDS/hexanol system (A/S = 2.8). In this figure, we can note that the model (solid line) accurately fits the results. Moreover  $\kappa$  values, as determined by the fit, are the same for the two  $\alpha$ -deuterated molecules: we find  $\kappa = 1.4 \pm 0.5 k_B T$ .

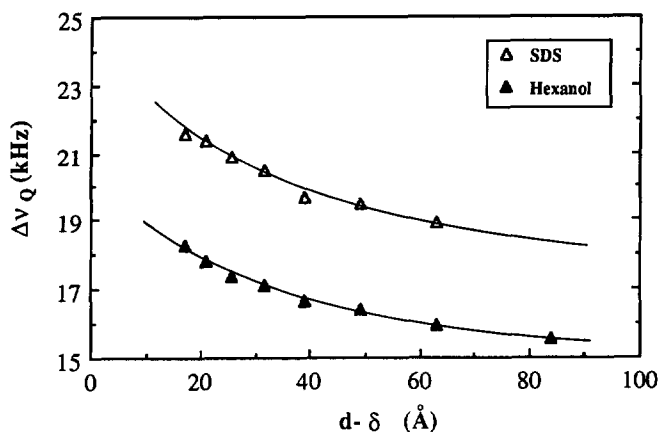


Fig. 5. —  $\Delta\nu_Q$  versus  $(d - \delta)$  for the line A/S = 2.8 in the water/SDS/hexanol system. The solid triangles are for  $\alpha$ -labelled hexanol and the open triangles for  $\alpha$ -labelled SDS. The solid lines are fits by equations (3.2, 3.5, 3.8 and 3.13) yielding  $\kappa = 1.4 \pm 0.5 kT$  for the two labelled species.

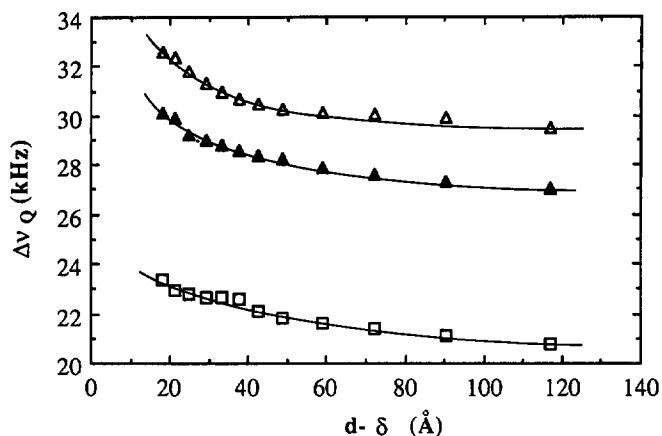


Fig. 6. —  $\Delta\nu_Q$  versus  $(d - \delta)$  for the line  $A/S = 2.4$  in the water perdeuterated SDS-hexanol system.  $\square$ ,  $\Delta$ ,  $\blacktriangle$  correspond to the data obtained for the positions 1, 3 and 6 respectively from the polar head of perdeuterated SDS. The solid lines are fitted by equations (3.2, 3.5, 3.8, 3.13). Best-fit curves lead to  $\kappa = 2.6 \pm 0.5 kT$  for the three labelled positions.

In figure 6, positions 1, 3 and 5 (positions from the polar head) of perdeuterated SDS in the water/SDS/octanol system ( $A/S = 2.4$ ) are fitted (the attribution of labelled positions comes from Ref. [34]). We can see again that the best-fit curves (solid line) are in good agreement with the experimental results and that the value of  $\kappa$  does not depend on the labelled position whatever the composition: we found  $\kappa = 2.6 \pm 0.5 k_B T$ .

As the molecular and intramolecular order parameters depend both on the geometry of the molecule and on the position of the deuterium nucleus, the same values of  $\kappa$  found for the different species and positions verify the invariance of the product  $S_I S_M$  along the dilution. The invariance of  $\kappa$  along the dilution will be discussed later.

**4.3 EFFECT OF THE AMOUNT OF COSURFACTANT IN THE MEMBRANE.** — We have studied the effect of the amount of alcohol in the membrane of the water/SDS/octanol system. The following compositions, expressed as molar ratios, were investigated:  $A/S = 1.23, 1.50, 1.78, 2.40, 2.60$  and  $2.90$ . Figure 7 represents the evolution of the quadrupolar splitting versus the water fraction (expressed in wt%) for three different membrane compositions:  $A/S = 2.4, 2.6$  and  $2.9$ . As we can see in the figures, a break can be observed (indicated by an arrow), separating the  $L_\alpha$  phase into two different regions (see phase diagram in Fig. 1). A more detailed study, using transmission electron microscopy, has shown that the change in the behavior of  $\Delta\nu_Q$  versus  $\Phi_M$  corresponds to the appearance in the dilute part of the  $L_\alpha$  phase of a domain of textural defects of the lamellar phase, referred to as spherulites [35].

The existence of these defects, appearing at high solvent dilutions for high alcohol contents (72 wt% water for  $A/S = 2.90$ ) and at low dilutions for alcohol poor membranes (see Fig. 1), introduces various problems in the determination of  $\kappa$ :

i) the theoretical model has been established for planar membranes and not for spherical surfaces like in spherulites (we cannot take into account the change of topology corresponding to the appearance of spherical structures). Nevertheless, we can make the assumption that the spherulites are big enough to be compared to a polycrystalline  $L_\alpha$  phase and determine values of  $\kappa$  in this region;

ii) moreover, the spherulites may possess rotational and diffusional motions that have not been integrated in the model. The occurrence of these motions may explain a further decrease of the quadrupolar splitting, as shown in the figure 7.

Thus, two fits have been performed, one corresponding to the data strictly obtained in the lamellar region, the second one corresponding to the entire dilution, i.e. covering both regions

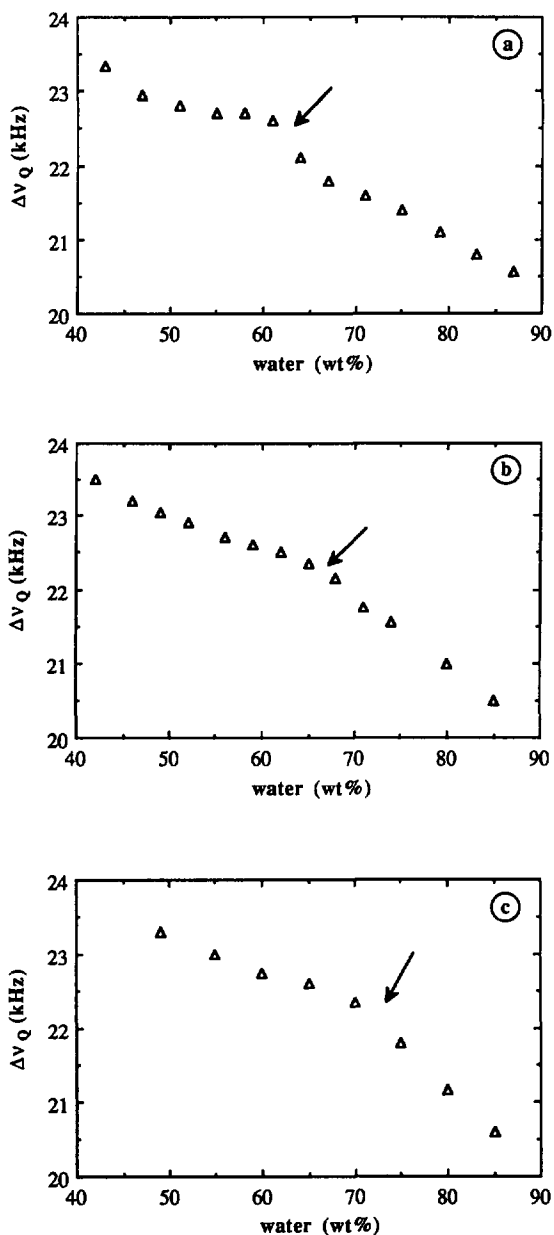


Fig. 7. —  $\Delta\nu_Q$  as a function of the water weight percentage for the water/SDS/octanol system with different A/S molar ratios : a) A/S = 2.4, b) A/S = 2.6, c) A/S = 2.9. Two different behaviors can be distinguished in the dilution line : note the break marked by arrows which shifts to higher water content as A/S increases.

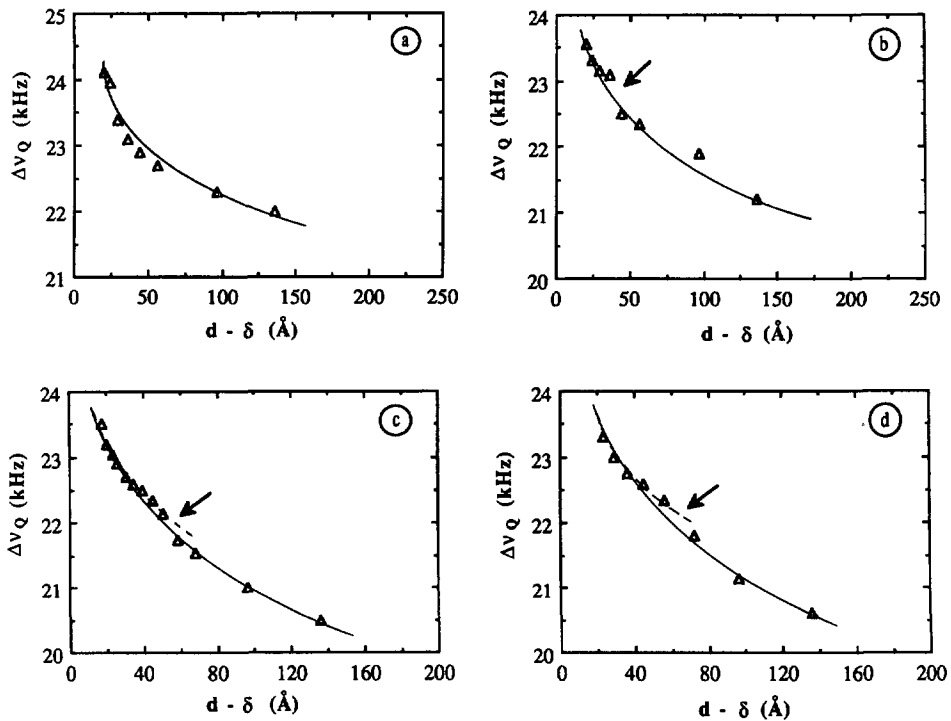


Fig. 8. —  $\Delta\nu_Q$  versus  $(d - \delta)$  for the water/SDS/octanol system measured along the four dilution lines defined by a)  $A/S = 1.8$ ; b)  $A/S = 2.4$ ; c)  $A/S = 2.6$  and d)  $A/S = 2.9$ . The arrow shows the position of the break better seen in figure 7. In c and d the dashed lines are the fits of the data obtained in the concentrated region. In a-d the solid lines are the fits of the entire dilution line. Results are given in tables I and II.

Table I. —  $\kappa$  values resulting from the fits of  $\Delta\nu_Q$  versus  $(d - \delta)$  in figures 8c and 8d.

$A/S$ (molar)	$\kappa(k_B T)$ , region L	$\kappa(k_B T)$ , region L+S
2.60	$2.74 \pm 0.5$	$2.28 \pm 0.5$
2.90	$2.23 \pm 0.5$	$2.15 \pm 0.5$

Table II. —  $\kappa$  values as a function of the octanol/SDS ratio.

$A/S$ (molar)	$\kappa(k_B T)$
1.23	$5.80 \pm 1.0$
1.50	$5.20 \pm 1.0$
1.78	$3.28 \pm 0.75$
2.40	$2.90 \pm 0.5$
2.60	$2.28 \pm 0.5$
2.90	$2.15 \pm 0.5$

(Figs. 8c and 8d, Tab. I). The values of the bending modulus were similar as reported in table I, the fit of the entire dilution line leading to a small reduction in  $\kappa$  values evaluated to be of the order of  $\pm 0.5 k_B T$ . From this control, we have fitted the entire experimental curves for all the systems studied (Figs. 8a to 8d), knowing that the error in the measurement of the bending modulus strongly depends on the amount of spherulites in the phase, i.e. on the  $A/S$  ratio, the error in  $\kappa$  measurements will be more important for low  $A/S$  ratios,  $\kappa$  values for  $A/S = 1.8$  and  $2.4$  should be considered as rough estimates. The results are given in table II and figure 8.

**4.4 EFFECT OF THE ALCOHOL CHAIN LENGTH.** — We have studied five different electrostatic systems containing hexanol, heptanol, octanol, nonanol and decanol. We have carried out all the experiments with samples having the same molar ratio  $A/S = 2.4$ . Figure 9 shows that the fits are in good agreement with the data. The bending rigidity  $\kappa$  is found to depend significantly on the alcohol,  $\kappa$  increases with the alcohol chain length : we found  $\kappa = 1.3 \pm 0.5 k_B T$  for hexanol,  $\kappa = 1.9 \pm 0.5 k_B T$  for heptanol,  $\kappa = 2.9 \pm 0.5 k_B T$  for octanol,  $\kappa = 4.4 \pm 0.5 k_B T$  for nonanol and  $\kappa = 13.0 \pm 0.5 k_B T$  for decanol (Tab. III).

**4.5 ADDITION OF SALT.** — Three series of samples containing hexanol, octanol and nonanol were prepared with brine (NaCl, 20 g/l) instead of pure water. The lamellar phase of salted

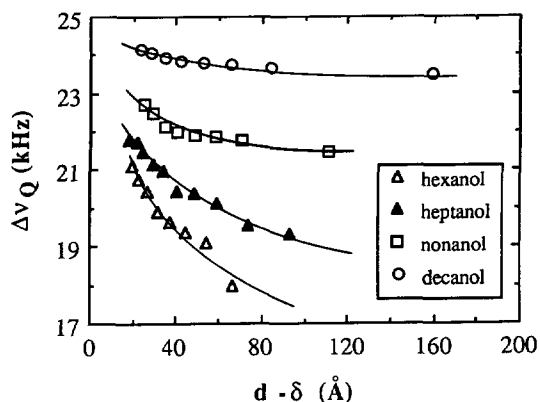


Fig. 9. —  $\Delta\nu_Q$  versus  $(d - \delta)$  for four water/SDS/alcohol systems. In each case, measurements have been performed along the dilution line  $A/S = 2.4$ . The solid lines are fits by equations (3.2, 3.5, 3.8, 3.13). Results are given in table III.

Table III. —  $\kappa$  values as a function of alcohol chain length ( $A/S = 2.4$  systems).

Alcohol	$\kappa(k_B T)$ in pure water	$\kappa(k_B T)$ in brine
hexanol	$1.30 \pm 0.5$	$1.10 \pm 0.5$
heptanol	$1.90 \pm 0.5$	
octanol	$2.90 \pm 0.5$	$3.20 \pm 0.5$
nonanol	$4.40 \pm 0.5$	$4.20 \pm 0.5$
décanol	$13.0 \pm 0.5$	

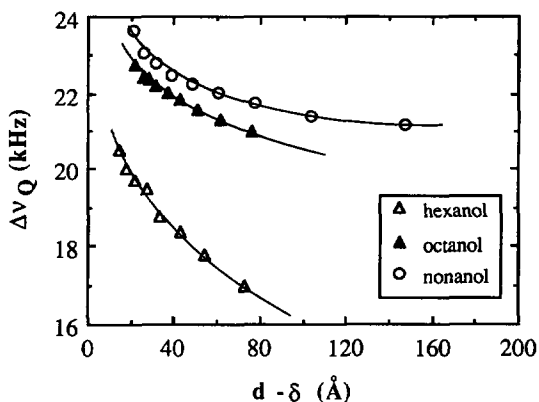


Fig. 10. —  $\Delta\nu_Q$  versus  $(d - \delta)$  for three brine/SDS/alcohol systems. The sodium chloride concentration in water is 20 g/l. The solid lines are fits by equations (3.2, 3.5, 3.8, 3.13). Results are given in table III.

systems is constituted of two zones : a very important region of spherulites [5], found for the low  $A/S$  ratios, and a lamellar region containing a small amount of defects. As the separation between the two zones corresponds approximatively to a dilution line, we have studied systems exclusively located in the region without spherulites, with the following  $A/S$  ratios for the different alcohols :  $A/S = 2.60$  for octanol and  $A/S = 2.65$  for nonanol. Figure 10 shows the experimental data. As argued above, the electrostatic interactions between the membranes are now screened and the steric repulsion predominates. Again, the theoretical curves fit remarkably well the experimental points and we found approximately the same value of the bending modulus  $\kappa$  (Tab. III) with brine and pure water.

## 5. Discussion.

From the above, it is clear that the analysis of the evolution of the  $^2\text{H}$ -NMR quadrupolar splittings with dilution of the lamellar phases provides a new and independent measurement of the collective fluctuations of the films. The analysis is performed in the frame of a realistic model where two basic assumptions have to be fulfilled :

i) internal molecular motions (angles  $\theta_1$  and  $\theta_M$ ) and collective fluctuations of the films (angle  $\theta_F$ ) must be uncorrelated (Eq. (3.3)). This is fulfilled here since collective motions are known to occur at much slower time scales than molecular motions. Typical time scales have been shown to be  $10^{-6}$ - $10^{-1}$  s and  $10^{-8}$  s, respectively [28] ;

ii) the internal properties of the film (intra and intermolecular ordering) remain unchanged upon swelling.

This assumption appears to be true if one considers that the present values agree very well with the bending rigidity measurements (Tabs. I and II) on the same systems reported earlier [20]. In addition, the fluctuations of the different labelled species (alcohol and surfactant) have been measured independently. The fits with the theoretical formulae are also totally independant.  $S_M S_I$  order parameters are different but the values of the bending modulus obtained from the two species *are the same* as expected from the model. This result is important for the verification of the assumptions made about the invariance of the molecular and intramolecular order parameters upon swelling. One other important verification of the validity of the model is the bilayer thickness measurement : we can use the fit to determine the value of  $\delta$  from the equations (3.10), (3.12), (3.15) and (3.16). The similar values of  $\delta$

measured by this way and by X-ray diffraction constitutes an important argument in favor of the validity of the model.

Note however that the second assumption may be questionable : several authors have shown that the electrostatic contribution to the bending rigidity  $\kappa$  depends on the interlayer spacing ( $d - \delta$ ) [35, 36]. Following Pincus *et al.* [36], our experiments are in the Gouy-Chapman regime for pure water dilution  $\lambda_D > d > \lambda_{GC}$  ( $\lambda_D$  is the Debye screening length and  $\lambda_{GC}$  the Gouy-Chapman length that characterizes the surface charge) and in the « intermediate » regime ( $d > \lambda_D > \lambda_{GC}$ ) when salt is added. A linear dependance of  $\kappa/k_B T$  with  $d$  is expected in the former case only [37] :

$$\frac{\kappa}{k_B T} = C \frac{(d - \delta)}{L_B} \quad (5.1)$$

with a proportionality constant  $C$  of about 0.12.

The corresponding variation of  $\kappa/k_B T$  in our range of dilution would then be of about 1 (from 0.34 to 1.36), which is not negligible. Thus, the experimental curves have also been fitted with the variable bending modulus of equation (5.1) plus a constant part from non electrostatic origin as follows :  $\kappa/k_B T = \kappa_M + \kappa_{el}(d - \delta)/L_B$ , where  $\kappa_{el}$  corresponds to the electrostatic contribution to the bending elasticity and  $\kappa_M$  corresponds to the non electrostatic (mechanical) contribution to the bending elasticity. The correction is found to be small ;  $\kappa_{el}$  is close to zero in all the cases. However, the possible presence of traces of ionic impurities in the surfactant may drive the system into the intermediate regime. Moreover, the values of  $\kappa$  measured in brine and in pure water are very close, which suggests that the electrostatic contribution to the bending modulus is very small. We shall therefore assume a constant value of  $\kappa/k_B T$  with dilution in the following and consider a possible variation as a small perturbation. This may not hold of course for larger ranges of dilution.

The effects of the membrane composition have been studied, through the variation of either the amount of alcohol in the membrane or the alcohol chain length. We have observed a decrease of  $\kappa$  when the amount of alcohol in the membrane increases and an increase of  $\kappa$  with the increase in the alcohol chain length (Figs. 11, 12). We can compare these results to theoretical studies. As Szleifer *et al.* pointed out [38], the mean bending modulus  $\kappa$  can be connected to the bilayer thickness  $\delta$  and to the area per polar head of surfactant  $\Sigma$ , as follows :

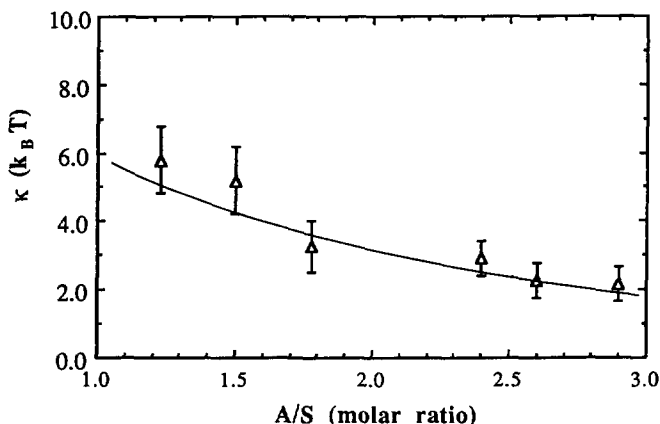


Fig. 11. —  $\kappa$  versus the A/S ratio for the SDS/octanol water system. The solid line follows a  $1/\Sigma$  law.

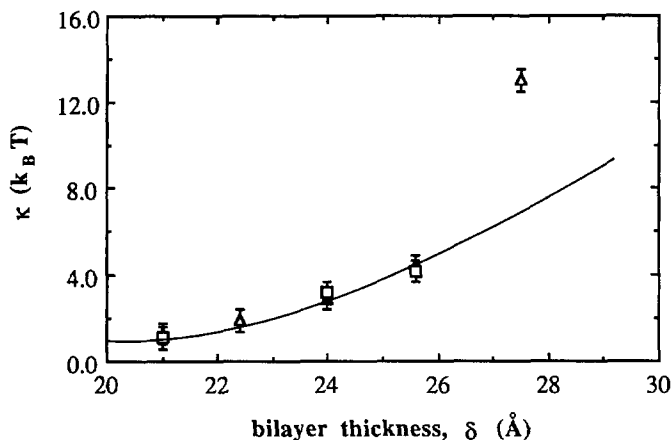


Fig. 12. —  $\kappa$  as a function of the membrane thickness  $\delta$  for the SDS/alcohol/water systems for five varying alcohol chain lengths (hexanol to decanol).  $\square$  and  $\triangle$  correspond respectively to brine and pure water systems. The solid line follows a  $\delta^3$  law which may be expected from elasticity theory (Ref. [38]).

$\kappa \propto \delta^n / \Sigma^p$ , where  $n$  and  $p$  are numerical coefficients,  $n \approx 2-3$  and  $p \approx 5$ . For a given film composition, we can define a global area per surfactant, including the area of the alcohol molecules associated to a surfactant molecule. When the  $A/S$  ratio increases, this mean area per surfactant increases, leading to a decrease of  $\kappa$ , as experimentally observed. In figure 11, we plot  $\kappa$  and  $1/\Sigma$  as a function of  $A/S$  for the octanol system. As we see, our results give an unambiguous trend in the correlation of  $\kappa$  with the inverse of the area  $\Sigma$ .

Figure 12 shows the evolution of  $\kappa$  as a function of the alcohol chain length, represented there by the bilayer thickness, as previously measured by X-ray diffraction. The curve corresponds to  $\kappa = \delta^n$ , with  $n = 3$ . We can note a very good agreement between our results and the theoretical study of Szleifer *et al.*, excepted for the SDS/decanol/water system. An important discrepancy between the theory and the experience for this system can not be explained until we carry out the same study on  $L_\alpha$  phase with alcohols longer than C10, which only appears at higher temperatures. Our results can also be compared to those obtained by Roux *et al.* [20] with X-ray experiments in the same systems : their results showed a step in  $\kappa$  value between heptanol and octanol what could not be theoretically explained by Szleifer's model, whereas our results show a continuous evolution of the bending modulus, which is much closer to the theory.

## 6. Conclusion.

The present paper shows that the  $^2\text{H-NMR}$  technique can be used to study the fluctuations of the film in lyotropic lamellar phases. The statistics of the undulations of the films depends on the intrinsic properties of the films (curvature energy) but also on the long range film-film interactions that stabilize the lamellar structure. The  $^2\text{H-NMR}$  spectra give a valuable information on the angular fluctuations of the molecules that form the membranes. A simple mean field theory was developed to establish a relationship between these fluctuations (or more precisely the measured quadrupolar splitting) and the bending rigidity,  $\kappa$ , of the films.

The bending modulus  $\kappa$  is found to be an intrinsic characteristic of the film, insensitive to the nature of the interactions between the films (electrostatic or steric), but very sensitive to the composition of the film. Our results show unambiguously that  $\kappa$  is controlled by the thickness

of the membrane and the polar head area of the surfactant. The main effects of replacing surfactant by alcohol is a thinning of the membrane and an increase of  $\Sigma$ , both leading to a reduction in  $\kappa$ .

When the nature of the alcohol is changed,  $\kappa$  increases with the length of the alkyl chain.

Unlike other experimental methods of determination of the bending modulus  $\kappa$  (dynamic light scattering [7, 11], optical microscopy on giant vesicles [39], Landau-Peierls effect by high resolution X-ray scattering [10] or EPR measurements [8]), the proposed method is simple. The lamellar samples need not to be oriented. The repetition of the measurements over a large series of samples of different compositions or at different temperatures is fairly easy.

Comparison with the EPR method deserves a comment : both techniques indeed allow to obtain the angular undulations of the membrane surface but they differ in the way this information is obtained. The EPR lineshape must be simulated by introducing the hyperfine splitting (measured on spectra), the linewidth, the molecular order parameter and the angular spread which may be related to membrane undulations. Angular undulations are directly obtained from the quadrupolar splitting which is easily measured on NMR spectra. Therefore, the NMR approach is more direct than the EPR approach. In addition, the use of perdeuterated samples allowed to prove the underlying hypothesis for both techniques : the characteristic time for membrane undulations is much larger than that of molecular motions and as a consequence, both dynamical contributions to spectra can be separated.

This method is however limited to those lamellar phases that can be swollen with a solvent since a plot of the quadrupolar splitting *versus* lamellar period is required. Extremely diluted (hyperswollen) lamellar phases may give a very weak NMR signal. In this case, the signal would be improved by the use of oriented samples. A study of the variation of the bending modulus with dilution is possible if a theoretical scaling behaviour is available. Among other limitations, we can mention the applicability to flexible membranes only ( $\kappa \leq 10\text{-}15 k_B T$ ) and the need of deuterium-labelled molecules (although deuterium labelling is useful to study the behaviour of one particular species in the phase).

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