First Observation of the Undulation Mode in Birefringent Microemulsions by Quasielastic Light Scattering

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Lamellar systems which are close to microemulsions in the phase diagram are observed for the first time by quasielastic light scattering. The observed hydrodynamical mode is attributed to the collective undulations of the lamellae and allows us to determine the rigidity constant of the interfacial film. The results emphasize the role of the cosurfactant (alcohol) in the transition from organized phases (lamellar and birefringent) towards isotropic phases (droplet microemulsions).

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Microemulsions have raised a great deal of interest for now nearly ten years because of their practical implications and their puzzling physical properties. Their phase diagram reveals an extraordinary polymorphism (liquid crystal phases, critical points).[1] Recently, it has been emphasized[2] that the existence of very curved phases like the droplet microemulsions may be due to the high flexibility of the interfacial film, flexibility enhanced by the cosurfactant. The persistence length of the film is proportional to $\exp(K)$ where K is the rigidity constant of the film (the curvature energy per unit area is $\frac{1}{2}K/R^2$ with R the radius of curvature of the film) so that a very small lowering of K would decrease drastically the persistence length of the film towards a very curved phase. In a previous paper,[3] the lamellar phases which are close to microemulsions in the phase diagram were investigated by the local technique of spin labeling. These phases are obtained with a lower amount of cosurfactant (alcohol) than needed to get the isotropic phase of droplets.[4] They are characterized by a large reticular distance d, the repeat distance of the lamellae (up to several hundreds of angstroms), due to the swelling by oil. Their structure is extremely labile and is easily destroyed through a gentle stirring. We have named them "birefringent microemulsions." Our experiments revealed unusual features of the spectra which are due to smooth undulations of the lamellae [3]; these undulations have been shown to be thermal fluctuations of the normals of the lamellae and their amplitude is determined by the competition between the high flexibility of the interfacial film and the interactions between two adjacent lamellae.[5] The technique of spin labeling is not sensitive when the characteristic time of the dynamics is longer than 10^{-6} s and so these undulations have been described as being static. In order to investigate the dynamic nature of the phenomenon a quasielastic light-scattering experiment has been performed.

The samples [sodium dodecylsulfate (SDS), 1-pentanol (Serlabo), cyclohexane (Merck, Uvasol), and tridistilled water] were oriented by heating (up to around 75 °C) in parallel-wall glass containers (0.1 mm path length, 2 mm width, and around 5 cm length) sealed in order to avoid evaporation. Both the influence of the ratio of oil to water (swelling) and of the cosurfactant have been investigated. The compositions of the samples are given in Tables I and II.

We are interested in out-of-reference-plane fluctuations of the lamellae and so the scattering vector $\mathbf{q}$ has to be parallel to the layers. The power of the incident laser beam (ionized krypton, wavelength 5309 Å) was limited to a few tenths of a milliwatt in order to avoid convection inside the sample which would destroy the lamellar order. The autocorrelation function of the scattered intensity was analyzed for a scattering angle between 9° and 60°. In the small-angle limit, the detection of the scattered signal was hindered by the presence of the incident beam, and in the large-angle

TABLE I. Study of the swelling ratio.

Oil/water	2	4	8
Sodium dodecylsulfate (g)	0.4	0.4	0.4
Tridistilled water (ml)	1	1	1
1-pentanol (cosurfactant) (ml)	0.32	0.43	0.72
1-pentanol required to obtain a microemulsion (ml)	0.69	1	1.6
Calculated reticular distance d (Å)	120	200	360

TABLE II. Study of the influence of the cosurfactant.

Oil/water ratio	1-pentanol (ml)
4	0.43 (minimum)
4	0.47
4	0.63
4	0.78

limit, we were not able to record a dynamic signal (recall that the scattered intensity in the case of smectics decreases when q is increased[6]). This corresponds to q^{-1} between 845 and 5345 Å. Instrumental limitations do not allow us to investigate hydrodynamical modes whose frequencies are greater than 10^4 Hz. The dynamic/static signal ratio is small and decreases strongly with the swelling of the phases. Although the orientation of the samples was carefully checked to be homeotropic before the scattering experiment, we attribute this small ratio to the presence of textural defects induced by the manipulation of the samples to settle them in the spectrometer, and this more likely for the very swollen samples which are very fluid.

We present here a summary of theoretical predictions of hydrodynamical modes in the case where the scattering vector lies in the plane of the lamellae. Most of the theories[7] deal with phospholipidic systems (surfactant bilayer plus water, which is the interlayer solvent). In our systems, we have considered the bilayer (surfactant plus cosurfactant) swollen by water as analogous to the phospholipidic bilayer where the interlayer solvent is cyclohexane. For each prediction, the mean frequency of the mode is indicated in order to check if this mode can be observed with our experimental setup. This mean frequency (ω_t) is computed with the following values: $q = 68\,000$ cm^{-1}, $K = 10^{-14}$ erg,[5] $d = 200$ Å, and $\eta = \eta(C_6H_{12}) = 10^{-2}$ P. The origin of the modulation of the scattered light is also discussed.

Free film fluctuation[8] *[Fig. 1(a)].*—This mode is observable if $qd > 1$. The dispersion equation is

$$\omega = i(K/2\eta)q^3 \quad (\omega_c \approx 160\ \mathrm{s}^{-1}),$$

and the light modulation is due to the local density variation (the indices of water and cyclohexane are different). The value of ω_c indicates that this mode must be easily observable by quasielastic light scattering. In our case, the lamellar phases have correlated layers (and thus, not free), so that the fluctuation modes must be mainly collective modes. But for the samples with a large oil/water ratio the condition $qd > 1$ is not far from being satisfied and this free film mode has to be considered.

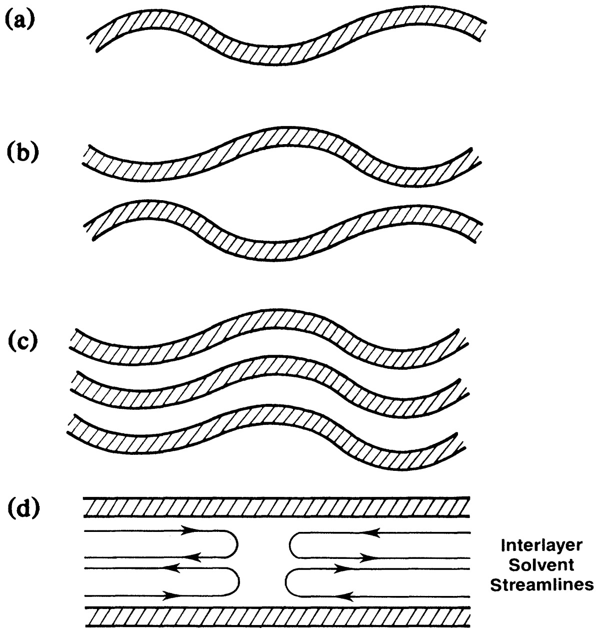

FIG. 1. Slow modes in lamellar systems. (a) Free film, (b) peristaltic, (c) pure undulation, and (d) slip.

Peristaltic mode[8] *[Fig. 1(b)].*—This mode is observable when $qd < 1$. The dispersion equation is

$$\omega = i\frac{Kd^3}{24\eta}q^6 \quad (\omega_c \approx 0.03\ \mathrm{s}^{-1}),$$

and the light modulation is also due to the local density variation. ω_c is a very low frequency which cannot be easily detected by quasielastic light scattering. It is, however, hard to imagine such modes in long-range lamellar order systems.

Pure undulation mode[6,7] *[Fig. 1(c)].*—The dispersion relation is

$$\omega = i(K/\eta d)q^2 \quad (\omega_c \approx 2300\ \mathrm{s}^{-1}).$$

This mode has already been observed in thermotropic smectics[9] and in this case, the modulation of the light was induced by the modulation of the birefringence of the liquid crystal molecules. As a consequence, the scattered light was polarized. In our case, we think that this mode could be induced by a local variation of the density.

Simple shearing mode[6,7].—This mode is the same as the one in viscous isotropic fluids. We have

$$\omega = i(\eta/\rho)q^2$$

which leads to

$$\omega_c \approx 4.6\times 10^7\ \mathrm{s}^{-1} \quad (\rho \approx 1\ \mathrm{g/cm^3}).$$

This frequency is very high and cannot be recorded by our experimental setup.

Slip mode[7] *[Fig. 1(d)].*—The physical process which gives rise to this mode is the coupling of a viscous fluid with an elastic medium (the swollen bilayer). The optical-index modulation is due in this case to the fluctuation of the local surfactant density in the film which must lead to tiny scattering intensities. The dispersion equation is

$$\omega = i\mu D q^2,$$

where μ is a slipping coefficient which reflects the coupling between surfactant motions and interlayer solvent ones and D is a compressibility coefficient. $\mu = d^2/12\eta$ and $D = \chi c \Sigma_0^2$ where Σ_0 is the mean polar head surface of the surfactant, c the surfactant concentration (molecules/cm^3), and χ the compressibility coefficient of the film [the energy of compression per surfactant is $\frac{1}{2}\chi(\Sigma - \Sigma_0)^2$]. We evaluate χ by assuming that it is proportional to K. As $\chi = 10^{16}$ cgs units (Ref. 7) and $K = 2\times 10^{-12}$ erg[10] for lecithin systems, we find $\chi = 10^{14}$ cgs units. Taking $\Sigma_0 = 60$ Å^2 and $c = 1.7\times 10^{20}$ molecules/cm^3, we get $\omega_c \approx 93\,000$ s^{-1}. This frequency is higher than one would expect from a pure undulation mode and should not be observed with our experimental setup. Notice that this mode has already been observed in lecithin systems.[11]

So, with the existing theories, we expect to obtain mainly the pure undulation mode.

For all the studied samples, the autocorrelation function of the scattered intensity fits a single exponential reasonably well [$\propto \exp(-t/\tau)$]. Because of the very low signal-to-noise ratio, the results are analyzed as an heterodyne modulation (the signal beats with the noise) except for one large-angle experiment where the sample was defect free. We find by plotting all our results $\tau^{-1} = f(q)$ logarithmically that the correlation time τ is proportional to q^{-2} which allows us to say that the main contribution comes from the undulation mode. However, a small deviation for small q could indicate in this case a slower mode. No polarization effects have been noticed and we have not observed edge effects like in thermotropic smectics[7] when the inverse modulus of the scattering vector is comparable to the reticular distance of the sample, and this may be due to the high flexibility which hinders the propagation of such effects through the samples.

(I) *Effect of swelling.*—The results curves are shown on Fig. 2 where the error bars represent the statistical errors of the fit of the experimental spectra to the exponential law. The results are gathered in the following table

Oil/water	$K/\eta d$ (cgs units)	d (Å)	K (erg)
2	2.6×10^{-7}	120	$(3.1 \pm 0.5)\times 10^{-15}$
4	9.2×10^{-8}	200	$(1.9 \pm 0.3)\times 10^{-15}$
8	3×10^{-0}	360	10^{-16}

The viscosity constant used is that of cyclohexane (0.01 P) and the recticular distance is computed from the volumes of water and oil and from a mean polar head area of 60 Å^2 per surfactant molecule. The incertitude of the determination of K comes from the incertitude of the least-squares fit to the lines.

Two points should be noted:

(i) We had previously shown that the rigidity constant K only depends on the chemical composition of the film which is the same for all the above samples. The values of K are roughly the same for the samples with an oil-to-water ratio of 2 and 4, but for the more swollen sample, K is lower by one order of magnitude. But remember that for this sample, the very high fluidity must lead to the presence of textural defects; in fact the static scattering is predominant and gives a very poor signal/noise ratio and thus a difficult analysis of the spectra.

(ii) The values obtained for K are in good agree-

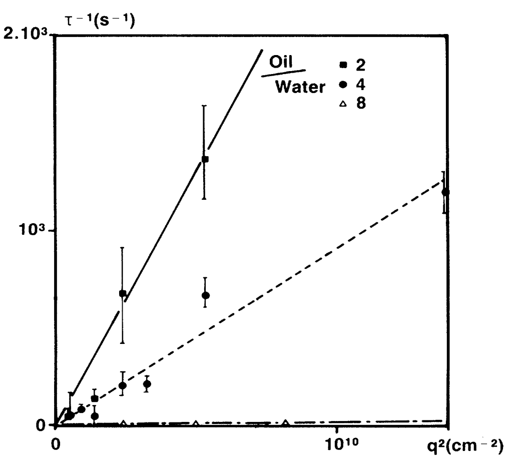

FIG. 2. Effect of swelling: inverse correlation time vs q^2.

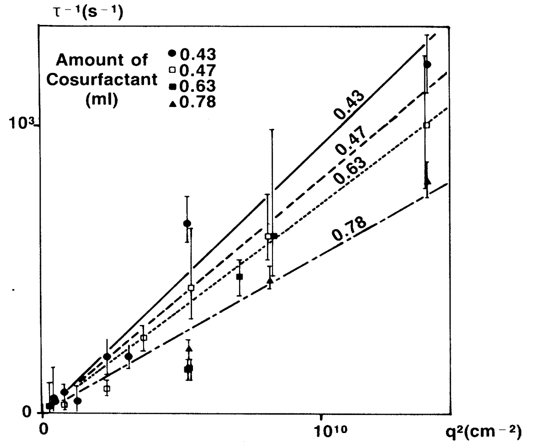

FIG. 3. Effect of the cosurfactant: inverse correlation time vs q^2. The oil/water ratio is 4.

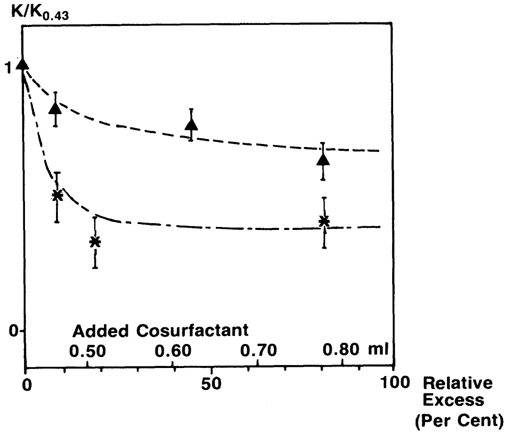

FIG. 4. Relative variation of the rigidity with respect to added cosurfactant. Triangles are quasielastic light-scattering experiments and asterisks are previous results obtained by spin-labeling experiments (Ref. 3).

ment with those obtained by spin labeling[5] where for the sample with a oil/water ratio of 4, $K = 6.4 \times 10^{-15}$ erg from investigation of the temperature behavior and $K = 2.3 \times 10^{-14}$ erg from investigation of the effect of swelling. This low flexibility is to be compared to the one of lecithin lamellar systems ($K_{\text{lec}} = 2 \times 10^{-12}$ erg[10]). If the results are analyzed according to the slip mode which also scales with q^2, the width of the "free" layer of solvent between lamellae is around 13 Å, which is not compatible with our very swollen phases.

(II) *Effect of the cosurfactant.*—Several samples with increasing quantities of cosurfactant have been studied. The smallest amount of cosurfactant is the minimum needed to obtain a lamellar phase. The results are shown in Fig. 3. The reticular distance does not change because of the low quantity of cosurfactant added with respect to the volume of the whole sample and thus the slopes of the curves are proportional to the constant of rigidity of the film. Figure 4 shows that the rigidity constant of the interfacial film is lowered by the addition of cosurfactant. The results of the spin-labeling experiments are also plotted on the same figure and emphasize the same effect.

Quasielastic light scattering has allowed us to observe the slow dynamics of the flexible interfacial films of "birefringent microemulsions." The rigidity constant determined by analysis of the dynamics according to the undulation mode is particularly low with respect to the much-studied lecithin systems, depends only on the chemical composition of the film, and is lowered by the adding of cosurfactant as seen by spin labeling; this therefore may explain the transition towards isotropic structures.

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