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Defects and curvatures of the interfaces in the « birefringent microemulsions » (*)

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Résumé. — L'état local dans le film interfacial de nouvelles phases qui ressemblent aux microémulsions, a été étudié par marquage de spin. Ces systèmes sont des phases lamellaires ayant des propriétés particulières associées au mécanisme de formation des microémulsions : 1) la présence de défauts très courbés pourrait être une étape de la rupture du film et 2) les ondulations à grande échelle des lamelles, dont l'amplitude augmente avec le taux de gonflement, prouvent la flexibilité du film, théoriquement prévue par ailleurs.

Abstract. — The local state in the interfacial film of new phases resembling microemulsions was studied by spin-labelling techniques. These systems are lamellar phases with unusual characteristics which might be correlated to the mechanisms of microemulsion formation. These are : 1) the presence of highly curved local defects which may be a necessary step for the rupture of the interfacial film, and 2) large scale undulations of the lamellae, the amplitudes of which increase with the swelling of the phase, which indicate the interfacial flexibility theoretically predicted.

In the past few years much interest has been shown in lyotropic systems containing the immiscible liquids oil and water [1]. Usually one of two things happens : either the oil and water regions organize themselves into periodic arrays (based on lamellae or rods or more complex objects) or they form fluid, isotropic dispersions, called microemulsions [2].

In a previous paper [3], we presented a preliminary study of new phases which appear at cosurfactant concentrations of 50 to 80 % of that needed to form a microemulsion, and which exhibit features of both extremes : they resemble microemulsions in their transparency and chemical composition, yet their optical birefringence indicates an organized structure.

In the preliminary experiments, characteristic optical textures and X-ray diffraction diagrams were observed only for mixtures of very low oil content. The present experiments which were performed on systems with minimum amounts of cosurfactant (corresponding to the bottom of the phase domain) give rise to classical lamellar optical textures when the samples are planar (Fig. 1A). X-ray diffraction peaks, corresponding to spacings of up to 150 angström units are observed over a wide range of oil-water compositions.

We present here new results concerning the local state in the interfacial film as reflected in the

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Fig. 1. — (a) Optical aspect of a sample (0.4 g SDS, 1 ml H_2O , 4 ml C_6H_{12} , 0.43 ml P_1OH) observed between crossed polarisers in a flat glass cell (0.1 mm thick). The drawing (b) represents the distribution of the constituents in such a phase. Note that the interfacial film contains both SDS and 1-pentanol.

electron resonance spectra of spin labelled amphiphiles [4]. It was already observed in reference [3] that these phases exhibit larger order parameters ($S = 0.46$) [5] than the corresponding microemulsions ($S = 0.32$) [6, 7]. In the present study, these phases are investigated in more detail, with the object of following the events which occur in the interfacial film before the microemulsion appears.

1. Experimental. — These phases are typically prepared from 400 mg of sodium dodecyl-sulfate (SDS-1.39 mmole), 1 ml of water, 0 to 8 ml of C_6H_{12} and the minimum of 1-pentanol (P_1OH) needed to obtain a clear birefringent system (volumic fraction $\text{C}_6\text{H}_{12} + \text{P}_1\text{OH}/\text{water}$: from 0.37 to 8.70). The spin labelled amphiphile 1 which resides exclusively in the interfacial film [8] is used at a molar concentration of 0.1 % of that of the SDS. Samples were observed in glass containers of different geometries as shown in figure 2 : sample A is a thin film (0.1 mm)

Fig. 2. — Various types of sample holder. The orientation of the smectic layers is represented schematically in each case.

of planar symmetry oriented throughout its volume by the glass slides as indicated by its homeotropic aspect; sample B is obtained by injecting into the bulb the minimum amount of the phase needed to produce an oriented thin film of spherical symmetry; in sample C where the large bulb (4 mm in diameter) is filled up with the phase, the bulk is only partially oriented by the glass surface.

Syntheses of the spectra were performed following classical procedures [9] on a HP 9825 computer.

2. Results. — Figure 3 shows typical spectra of these phases in spherical conditions. The spectrum of sample B is very similar to the widely studied powder spectrum of the L_α phase of phospholipids [5]. However, the spectrum of sample C shows, in addition to a component indicative of lamellae (L), three small lines (M) which correspond to almost completely averaged motion in the time scale of the experiment (10^{-8} s).

A second problem arises from the analysis of the spectra from sample A. If the A type samples were perfectly oriented by glass surfaces, the molecules being perpendicular to the smectic layers, the maximum and minimum experimental splittings of the lines measured as a function of the static magnetic field orientation would give the $T'_\parallel$ and $T'_\perp$ parameters of the averaged hyperfine tensor. These parameters and the corresponding linewidths would be identical to the parameters needed to synthesize the B « powder spectrum ». This identity was not found here.

These two points are discussed, in turn, below.

Fig. 3. — Comparison of the spectra of samples B and C. L refers to the lamellar powder spectrum; the M_1 , M_2 and M_3 arrows indicate the three components of M.

3. Discussion. — 3.1 THE M SPECTRUM IS DUE TO HIGHLY CURVED LOCAL DEFECTS IN THE LAMELLAE. — The M spectrum in figure 3 (reflecting fast label reorientation) might be attributed to the coexistence of lamellar and micellar phases in the sample. This possibility is excluded by the fact that samples of identical composition (e.g. B and C) exhibit different relative intensities of the M spectrum. Moreover M is not observed for the thin planar A sample. M is thus clearly a manifestation of the core volume of the C type sample, which is not oriented by the glass surface and contains regions where the molecules undergo a fast reorientation. Highly curved regions may induce such an effect by means of fast lateral diffusion (Fig. 4b). Such a process

Fig. 4. — Influence of the curvature radius on the spin labelled molecule disorientation by the lateral diffusion process over a time τ_c .

has been invoked previously in studies on the curved film in hexagonal phases [10, 11]. We propose that highly curved regions exist also in the present lamellar phases. If one infers the pure M spectrum by subtracting the lamellar L spectrum, the correlation time is found to be several nanoseconds. A reasonable value for the lateral diffusion coefficient is several millionths of a cm^2/s [10, 12]. These considerations lead to a calculated radius of curvature of a few tens of angström units (below the repeat distance of the lamellae). Such a low radius of curvature must correspond to very local defects. In order to propose models for these defects, several facts must be taken into account. Let us recall [3] that the internal phase organization is easily disrupted : stirring decreases the birefringence and transforms the two line D_2O NMR powder spectrum into a narrow averaged spectrum. This proves that the disorientation of D_2O occurs in less than 10^{-3} s. If the D_2O diffusion coefficient parallel to the lamellae is taken to be equal to 10^{-5} cm^2/s , then the organization has been disrupted at a scale smaller than one micron. Moreover birefringence and NMR powder spectrum are restored, whilst the M spectrum disappears with time. These results indicate that all these defects cost little energy to form. We propose that they could be the ends of layers or lamellae defects such as pores. Helfrich has recently discussed the existence of defects in amphiphilic bilayers [13] and has suggested that the B and C phases described by Eckwall [1], where the interfacial film is also a mixture of two amphiphiles, are lamellar phases with a significant concentration of pores in the lamellae. Whatever the precise model may be, the experimental facts demonstrate how exceptionally easy the rupture and reconstitution of the interfacial film is in these systems.

Another interesting aspect of these defects is that their number increases with the amount of cosurfactant, i.e. their number increases as the microemulsion region is approached.

3.2 THE INTERFACIAL FILM IS FLEXIBLE. — Figure 5 (a) shows the experimental spectrum of sample A when the magnetic field is applied perpendicularly to the glass plates, which corresponds to the maximum splitting of the lines. This is to be compared to the spectrum (b) which is expected on theoretical grounds from the parameters of the corresponding powder spectrum. There is disagreement in two respects : in the experimental spectrum (a), the splitting $T''_{\parallel}$ is smaller and the linewidths are larger than predicted. Conversely, $T''_{\perp}$ is larger than predicted. This effect increases with the oil concentration in the phase, i.e. as the separation of the water layers increases (Fig. 1b).

Such a discrepancy has also been observed in thermotropic [14] and lyotropic [15] systems. It indicates that a significant fraction of the molecules are not aligned parallel to the magnetic

Fig. 5. — Comparison of the sample A spectrum (a) with the magnetic field corresponding to the maximum lines splitting ($2 T'_{||}$) with the corresponding theoretical spectrum (b) which gives $2 T'_{||}$. The arrows indicate a small contribution of the molecules oriented by the small sides of the cell. Their splitting gives $2 T'_{\perp}$.

field. Two different geometrical models were used to explain these differences. The « tilt » model, where the molecules form a well-defined angle with the smectic layers normal, leads to a decreased order parameter but unmodified linewidths. This model has been verified for thermotropic smectics B and C. The second model which allows a continuous angular spread of molecules around a mean orientation, modifies both splittings and linewidths. It corresponds to smooth undulations of the lamellae in the oriented sample (Fig. 4a). The table shows that it is possible to predict the experimental splittings and linewidths by introducing a static angular spread θ_0 ; θ_0 increases with the swelling of the oil layer. By taking the same value as above for the lateral diffusion coefficient and noting that these curvatures appear as « static effects » (the relaxation time is greater than 10^{-7} s), the corresponding radius is calculated to be of the order of several thousands of angström units.

Table. — Variation of the spread angle θ_0 with the oil content expressed as the volumic fraction $\Phi = C_6H_{12} + P_1OH/\text{water}$.

Φ	Oriented spectra								θ_0 (degree)
	Experimental			Calculated					
	splitting (Gauss) $T'_{\parallel G}$	order para- meter S	width of 3rd line l_{3G}	<i>without</i> θ_0 : fitting parameters of the powder spectrum			<i>with</i> θ_0		
				$T'_{\parallel G}$	S	l_{3G}	$T'_{\parallel G}$	l_{3G}	
0.37	22.84	0.44	2.5	22.75	0.42	2	22.75	2	< 3
1.35	22.15	0.41	3.125	22.75	0.43	2.8	22.25	3	19
2.31	22.06	0.41	2.95	22.63	0.42	2.9	22	3.1	20
4.43	22	0.40	3.375	23	0.43	3	21.88	3.7	27
8.70	21.73	0.38	3.5	22.81	0.43	3	21.75	3.8	27

4. **Conclusions.** — As noted in a previous preliminary communication [3], the phases which precede microemulsions are lamellar phases with unusual characteristics.

The studies of the local states presented here show that, even when oriented by external forces,

the interfacial film exhibits large scale curvature. Such undulations in lamellae have been investigated theoretically [16] and could inhibit the formation of well-organized lamellae. In addition, these lamellar phases exhibit highly curved local defects.

The various types of experiments prove that these two features are characteristic of being in the vicinity of the microemulsion phase. The importance of the interface flexibility in the microemulsion formation has been emphasized recently [17]. The presence of defects associated with a lack of continuity in the lamellae, which was predicted by Helfrich, may be a necessary step for the rupture of the interfacial film before the formation of microemulsions.

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