Local lamellar structure in dense microemulsions

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The structure of the isotropic phase L_2 occurring in the ternary system sodium di-2-ethylhexylsulfosuccinate (AOT)–water–n-heptane is discussed on the basis of small-angle x-ray scattering data. Experimental results are not consistent with an ordered droplet phase but with a local lamellar structure.

Aerosol sodium di-2-ethylhexylsulfosuccinate (AOT) is an anionic surfactant with two aliphatic chains which gives rise to isotropic phases in ternary systems involving oil and water. Such systems are extensively studied for two main reasons: they are good models of microemulsions with only three constituents and they allow one to study chemical reactivity and polymerization in dispersed media. The L_2 isotropic phase (Fig. 1) is well known in dilute water-in-oil systems: A model of submicroscopic droplets of water, coated with the surfactant dipping in a continuous oil phase, is compatible with light, neutron and x-ray scattering results.[1-3] On the other hand, the structure of the L_2 phase in the concentrated zone with similar proportions of the various components is still debated. Experimental results obtained by small-angle neutron

scattering (SANS) seem to indicate that the droplet structure is maintained in the single-phase AOT–D_2O–n-decane microemulsions.[4]

In this Brief Report, we report small-angle x-ray scattering (SAXS) experiments, performed on AOT–H_2O–n-heptane microemulsions. It is shown that, in this system, the ordered droplet phase is not consistent with our experimental results. According to recent observations presented in a previous paper,[5] a local lamellar structure is proposed.

The boundary of the L_2 phase in the phase diagram of the ternary system AOT–water–n-heptane is known.[6] The lamellar phase D is approximately shown in Fig. 1. The three-component microemulsions are characterized by the molar ratio ω ($\omega =$ [water]/[AOT]) and the volume
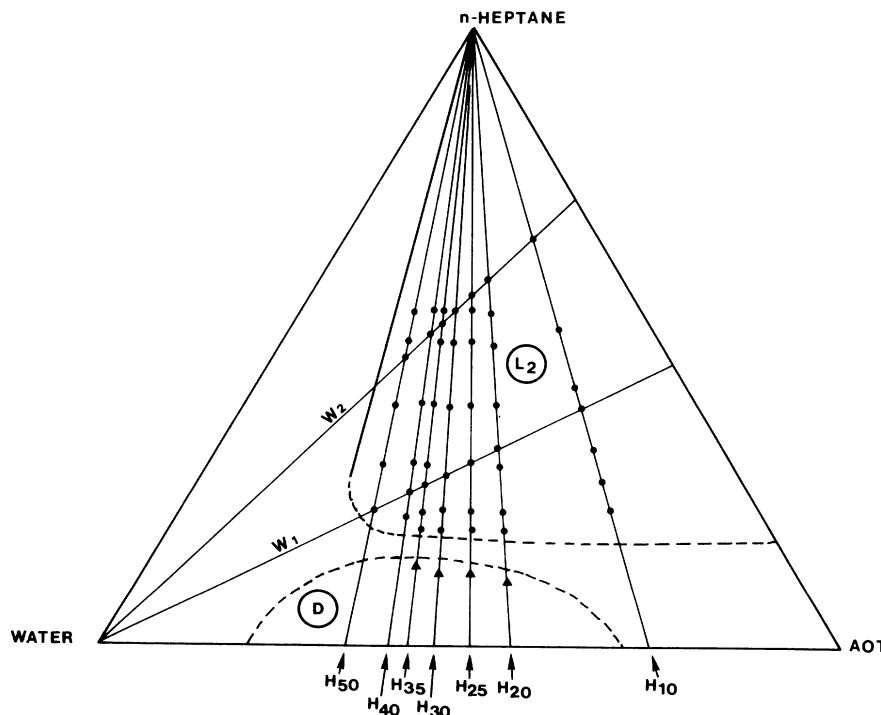

FIG. 1. Schematic representation of the isotropic (L_2) and lamellar (D) zones of the AOT–water–n-heptane system at 20 °C. The straight lines W (W_1 and W_2) and H_ω ($\omega = 10$–50) are, respectively, at constant [n-heptane]/[AOT] and [water]/[AOT] ratios.
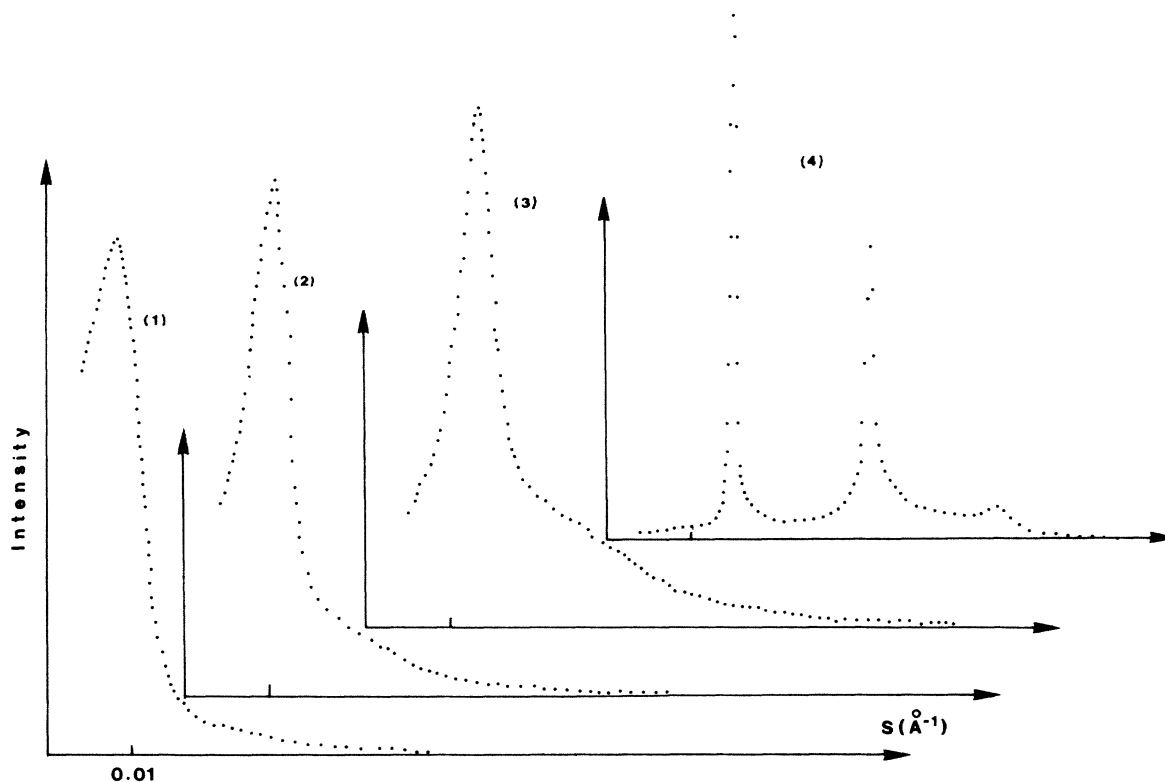

FIG. 2. Evolution of the scattering profile as a function of the volume fraction ϕ_o for the dilution line $H25$. (1) $\phi_o = 0.60$; (2) $\phi_o = 0.40$; (3) $\phi_o = 0.26$; (4) lamellar phase: $\phi_o = 0.14$.

fraction ϕ of one of the components (water or oil). The ω values are 10, 20, 25, 30, 35, 40, 50. All solutions which have the same ω value are on the straight line H_ω. For all the solutions of the L_2 phase the scattering pattern exhibits a pronounced maximum at $s = s_m$ (Fig. 2). $s = q/2\pi = 2\sin\theta/\lambda$ is the scattering vector, $\lambda = 1.54$ Å is the Cu $K\alpha_1$ wavelength, and 2θ is the angle between the scattered and the incident beam. On the dilution lines H_ω, s_m decreases when ϕ_o increases ($\phi_o = \phi_{oil}$) and on the dilution lines w_1 and w_2, a similar behavior is observed if now ϕ_w is varied ($\phi_w = \phi_{water}$). This maximum can be attributed to a repeat distance in the material. Indeed small-angle neutron scattering spectra obtained on single-phase AOT-D_2O-n-heptane microemulsions show that this maximum is not affected when the contrast is changed, especially with the mixture $H_2O + D_2O$ giving a shell effect on the scattering-length density function. This seems to indicate that the scattering profile is not due to the form factor of an object. On the other hand, if an increase of ϕ_o or ϕ_w leads to a dilution of objects, the position of a maximum related to the form factor would not change when the volume fraction of solvent is changed. The lamellar liquid-crystal phase was also investigated.

Figure 2 gives the angular distribution of the intensity scattered by this lamellar phase. Three well-defined peaks are observed. Their spacing (1:2:3) corresponds to the first-, second-, and third-order Bragg maxima characteristic of a lamellar structure. The main experimental result is that the maximum of the x-ray spectrum in the L_2 phase varies linearly (i) with ϕ_o, for a fixed value of ω

(line H_ω), (ii) with ϕ_w at fixed AOT-heptane ratio for $20 < \omega < 35$ (lines W). In Fig. 3, we have plotted the variation of the s_m as function of the degree dilution ϕ_o for each dilution line. They follow straight lines extrapolating down to zero for $\phi_o = 1$. In the same way, Fig. 4 gives $s_m = f(\phi_w)$; the extrapolated value at $s_m = 0$ is also $\phi_w = 1$.
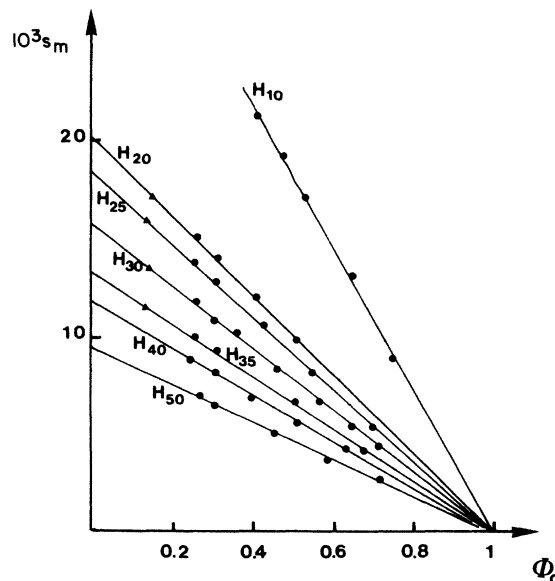

FIG. 3. SAXS peak position s_m vs ϕ_o where ϕ_o is the volume fraction of oil. H_ω refers to the lines drawn in Fig. 1.
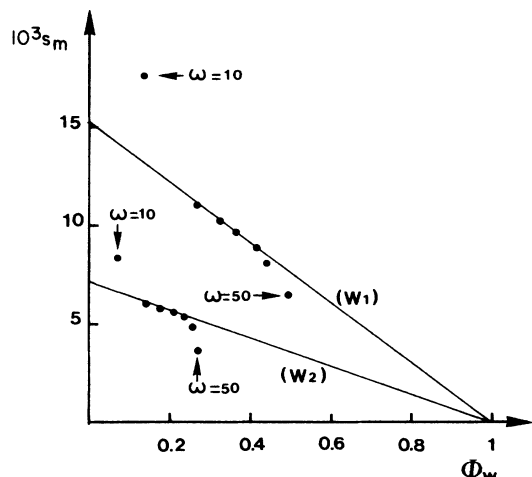
FIG. 4. SAXS peak position s_m vs ϕ_w where ϕ_w is the volume fraction of water. W_1 and W_2 refer to the lines drawn in Fig. 1.

These results are not consistent with an ordered droplet phase.[4] Indeed, in this case s_m is proportional to $\phi_{AOT}/(1 - \phi_{AOT})^{2/3}$ when $\phi_o/\phi_w = 1$. The same model gives, at fixed ω value, $s_m = k\phi_{AOT}^{1/3}$ where k is a constant which only depends on the lattice. It is obvious that our results do not verify this law.

On the other hand, the evolution of the repeat distance upon dilution seems to be in favor of a local lamellar structure. Let us first look at the evolution of this structure under dilution with water. We must have, in this hypothesis, an unidimensional expansion. Then, if d_1 is the thickness of a lamella (oil + surfactant) and d_{AOT} that of the surfactant for solution located on the dilution line W_1 (or W_2) the thickness d_1 of the lamellae must remain constant while the distance between these lamellae increases with the volume fraction of water (if a simple swelling behavior is assumed). Then owing to the unidimensional expansion, s_m verify the relation $s_m = (1 - \phi_w)/d_1$ with $d_1 = d_o + 2d_{AOT}$ which gives a linear variation of s_m with ϕ_w and $s_m = 0$ for $\phi_w = 1$. This linear behavior is experimentally observed. Table I summarizes the numerical results. The thicknesses d_o and d_{AOT} are calculated from the volume fractions of oil (ϕ_o^*) and of surfactant (ϕ_{AOT}^*) in the lamellae $d_o = d_1\phi_o^*$ and $d_{AOT} = d_1\phi_{AOT}^*/2$. The obtained value ($d_{AOT} \approx 13$ Å) is in good agreement with the calculated length of an AOT molecule which is in favor of our hypothesis. If one considers the dilution by oil (lines H_ω), d_2 is now the thickness of the lamella water + surfactant which for a given value of ω and in the case of a pure swelling, remains constant. Then, we can merely see the dilution of the lamellae by the oil. As done before we

can write $s_m = (1 - \phi_o)/d_2$ with $d_2 = d_w + 2d_{AOT}$. This linear behavior of $s_m(\phi_o)$ is followed by all the experimental points. Moreover, it must be pointed out that the experimental points obtained from the position of the diffraction peak in the true lamellar phase are in the continuity of those obtained in the L_2 phase (Fig. 3). If the thickness of the surfactant layer remains constant in all the L_2 phase, it is possible to calculate, from the value of d_2, the available area (σ) per polar head of AOT $\sigma \approx 44.7\omega/d_w$. Table II gives the main parameters of the L_2 phase obtained from this model. We can see that the area per polar head of surfactant remains about the same for $20 < \omega < 40$, which is in good agreement with results obtained in reverse micelles.[3] In the case of $\omega < 20$, because of an eventual incomplete hydration of the polar heads, the local lamellar model seems to be not completely adequate. Moreover, the high uncertainty on d_w value leads to anomalous area per polar head. The fact that the point corresponding to the extreme value ($\omega = 50$) is not on the straight line (Fig. 4) is not yet explained to read.

All these experimental evidences, (i) unidimensional expansion under dilution with water or oil, and (ii) continuity with the lamellar phase under dilution by oil, are in favor of a local lamellar structure without long-range translational and orientational orders. An estimate of the correlation length ratio in the lamellar liquid crystal and in L_2 can be obtained by comparison of the half widths of the diffractions peaks using Scherrer's formula for example. It is about ten times smaller in the L_2 phase. Then, the question which arises is how a lamellar structure can lose its orders? The answer can be obtained from theories based on fluctuations in smectic media.[7,8] Starting from the elastic free energy of a lamellar stacking,[9] involving the elastic constants k_c (the bending rigidity modulus of the surfactant film) and B (the compressibility of the layers) one obtains the orientational order given by[10-12]

$$\lim_{r \to \infty} \langle \,|\,\theta^2(r)\,|\,\rangle = (k_B T/2\pi k_c)[1 + \ln(\Lambda d^2/\pi a^2)] \,,$$

where $\theta(r)$ is the angle between the normal to the layers at $r = 0$ and at r, $\Lambda = d^{-1}(k_c/dB)$, d is the mean repeat distance, and a is a cutoff wave vector (about a molecular length). The expression shows that if k_c and/or B decrease $\langle \theta^2 \rangle$ increases. If it becomes larger than π the optical birefringence will disappear. On the other hand, it is predicted that the lamellar stacking must exhibit a quasi long-range translational order[7,11,12] with a correlation

TABLE I. d_{AOT} values obtained from the dilution lines W_1 and W_2.

Line	d_1 (Å)	ϕ_o^*	ϕ_{AOT}^*	d_o (Å)	d_{AOT} (Å)
W_1	64.5	0.60	0.40	39	12.9
W_2	140.8	0.185	0.815	114.5	13.0

TABLE II. Parameters of the L_2 phase assuming a local lamellar structure: For $20 \leq \omega \leq 40$ the available area per polar head of AOT remains constant ($\sigma = 37 \pm 3$ Å^2).

ω	d_2 (Å)	d_w (Å)	τ (Å^2)
10	30	4	> 100
20	49	23	39
25	54	28	40
30	63	37	37
35	71	45	35
40	79	53	34
50	102	76	30

function characterized by the exponent (Ref. 13) x $= \pi k_B T/2k_c$ which leads to a divergence of the scattered intensity at the Bragg reflection given in powder configuration[14] by $I(q) \propto (q - q_B)^{-(1-x)}$. If the exponent x is greater than 1, which can also be done if k_c and/or B are small, the singularity is replaced by a maximum only due to a classical interference function and always observed at such concentrations.

As a conclusion, we have here obtained a first strong evidence of a locally lamellar structure in a large range of the domain of stability of the microemulsion phase of the system AOT/water/heptane. The behavior of this phase under dilution can be explained in terms of low mechanical rigidity of the lamellar stacking. Usually, such a structure is not considered in microemulsion, where there is a small amount of surfactant, which seems to lead to, for instance, random microemulsions where water and oil are separated by a surfactant film. Here, the amount of surfactant is not negligible and this can explain the appearance of an intermediate structure between a lamellar liquid crystal (always present in these systems) and a random microemulsion.

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