

Letters

Surfactant Self-Diffusion in L_3 Phases

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In order to distinguish between two structural models of the L_3 phase, we have performed fringe pattern photobleaching experiments, determining the surfactant self-diffusion coefficient. The results rule out the isolated disk structure and are consistent with interconnected bilayers.

Introduction

Surfactant molecules self-associate in water to form a variety of structures¹ including micelles (L_1 phases) and flat bilayers (lamellar or L_α phases). When the micelles are cylindrical and parallel to each other, they form hexagonal (H) phases; when the lamellae are curved but interconnected, they form cubic (Q) phases. In some cases, isotropic phases (L_3) exhibiting strong flow birefringence are observed.^{2,3} Light and neutron scattering experiments as well as electrical birefringence and rheological experiments can be interpreted by assuming either of two different types of structures:

One structure is spongelike, made of randomly connected bilayers, locally similar to a bicontinuous cubic phase, but showing no long-range order.^{4,5} A recent model proposes that the sponge phase forms upon dilution of a lamellar phase, the basic idea being that the ordered phase melts at some stage into a more disordered one.⁶ Another model suggests that the sponge phase forms upon changing the

Gaussian curvature of the surfactant bilayers.⁷ A bilayer consists of two associated monolayers. When the spontaneous curvature, C_0 , of the monolayers is about zero, a lamellar structure is favored. But if the monolayer is slightly bent, a "frustration" arises. When C_0 is positive, i.e. when the monolayer is curved toward water, the bilayers break and small micelles are formed. When C_0 is negative, the frustration can be released by the formation of saddle-splay regions where the Gaussian curvature of the bilayer is negative. This leads to ordered cubic or disordered spongelike phases.

Another structure consists of isolated disks.⁸ In order to account for the experimental features, the disk diameter must remain equal to the mean disk spacing. This implies that the size of the disks increases linearly with the dilution degree $\phi - 1$, ϕ being the bilayer volume fraction. A theoretical model accounts for this structure, showing that it is possible to compensate the curvature energy of the disk borders by their dispersion entropy.⁹

The striking difference between the two types of structures is their connectivity. In order to distinguish between them, experimental techniques probing this connectivity should be used. Electrical conductivity has been used in oil-water surfactant mixtures, where the bilayers are made of surfactant and water, and the solvent is the oil phase: in these L_3 phases, the bilayers are clearly interconnected.⁵ In most known L_3 phases, the solvent is

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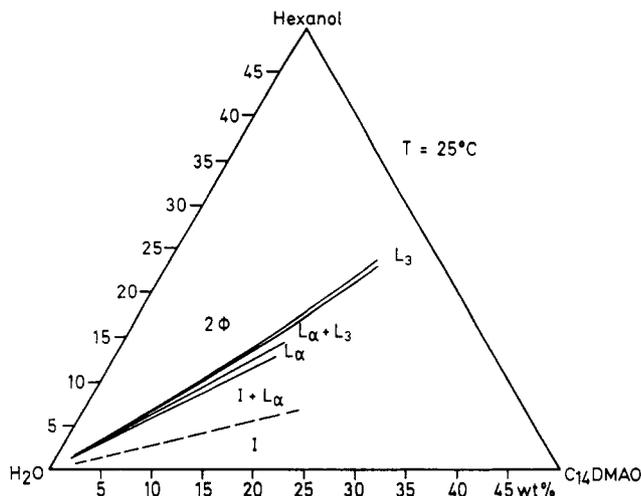


Figure 1. Phase diagram of the system C_{14} DMAO/hexanol/water at 25 °C.

water and the electrical conductivity is no longer a probe of the bilayer connectivity. NMR spin-echo techniques allow the determination of the surfactant self-diffusion coefficient D . If the surfactant forms isolated disks, D is the diffusion coefficient of these objects. If the surfactant forms connected layers, D is close to the two-dimensional diffusion coefficient of the surfactant, i.e. to the value measured in lamellar phases D_α ; due to obstruction effects, one expects $D = 2/3 D_\alpha$.¹⁰ This simple analysis presupposes that the surfactant remains trapped in the layers and does not exchange with the solvent. Such exchange has been observed in a spongelike microemulsion phase where the surfactant diffusion coefficient D was found to be 5 times larger than the diffusion coefficient of a probe better embedded in the surfactant layer.¹¹

In order to resolve the present issue without any ambiguity, we performed fluorescence recovery after fringe pattern photobleaching experiments (FRAPP) to measure the diffusion coefficient of a fluorescent amphiphilic probe embedded in the surfactant layers. In this experiment, we can vary the chain length of the probe and change its residence time in the layer. If D does not depend on the chain length, this means that the fraction of time spent by the probe in the solvent is negligible, and the straightforward analysis holds.

Experimental Section

The samples are mixtures of water, 1-hexanol, and *n*-tetradecyltrimethylamine oxide (C_{14} DMAO). The surfactant is obtained from Hoechst and purified as described previously.¹² The phase diagram is represented in Figure 1. The L_3 phase exists over a narrow range of alcohol to surfactant ratios for surfactant concentrations varying by more than an order of magnitude (50–800 mM). The solvent is pure water. The bilayer volume fraction is $\phi = 10^{-3}C(M_s + nM_a)$, where C is the surfactant molar concentration, M_s and M_a are the surfactant and alcohol molecular weights, and n is the ratio of alcohol to surfactant number of molecules (here $n \sim 2$).

The FRAPP experiments have been done on several samples for surfactant concentrations ranging between 50 and 600 mM. Details on the experimental procedure can be found elsewhere.¹³ The fluorescent recovery curves are exponential in all cases. The

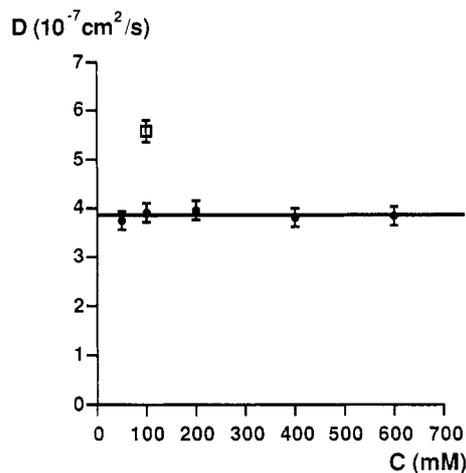


Figure 2. Self-diffusion coefficient D versus surfactant concentration C : square, L_α phase; circles: L_3 phase; the straight line represents the mean value of $D = (3.86 \pm 0.08 \times 10^{-7} \text{ cm}^2/\text{s})$.

decay times τ are inversely proportional to the square of the fringe spacing i in the range $5 < i < 100 \mu\text{m}$. This allows us to deduce the diffusion coefficient D : $\tau = i^2/4\pi^2 D$. The measured values are given in Figure 2.

Discussion

The measured $D = (3.86 \pm 0.08) \times 10^{-7} \text{ cm}^2/\text{s}$ does not depend on the surfactant concentration. This is consistent with the existence of interconnected bilayers. In the case of disks, D should be inversely proportional to their diameter d , and not too much dependent on the disk concentration.¹⁴ This implies that D should be about proportional to ϕ ; this is clearly not the case. Moreover, the measured diffusion coefficient is comparable to the one measured in cubic phases¹⁵ and does not correspond to objects of the size of disks.

In order to confirm this result, we have measured D in the nearby lamellar phase for $c = 100 \text{ mM}$. The L_α phase has been oriented by repeated temperature cycles in a thin glass cell.¹⁶ The value of D in the direction parallel to the lamellae is given in Figure 2. The value of D in the direction perpendicular to the lamellae is a factor 100 times smaller, confirming the good quality of the achieved orientation. $D_\alpha/D = 1.45 \pm 0.07$ in agreement with the theory,¹⁰ assuming that the phase consists of interconnected bilayers.

In this experiment, we have used two different lengths of the aliphatic chain of the fluorescein probe, 16 and 18 carbon atoms. This changes the residence time of the probe in the surfactant layer by at least an order of magnitude.¹⁷ The measured diffusion coefficient was the same for the two probes used, confirming that the time spent by the probe in the solvent is negligible.

Due to the limited spatial scale probed during the experiments, the present experiments demonstrate that the layers are interconnected over a scale equal to i_{max} , i.e. $100 \mu\text{m}$, which is much larger than the estimated size of the disks. Let us note that FRAPP experiments allows one to probe the connectivity over a scale larger than NMR spin echo, where the time scale is shorter, of the order of

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10 ms; with $D = 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, the probed scale is only of the order of $1 \mu\text{m}$.

One may finally wonder about the role of the finite lifetime of the disks. If they break and recombine on a time scale shorter than the time needed by the probe to reach the end of a disk, the discontinuous structure will behave as if it were connected on a large scale. In systems of giant micelles, that behave like "living" polymers, this has not been observed, because the micelle lifetime is too long, $\sim 1 \text{ ms}$.¹³ Here, in order to observe such an effect, the lifetime must be shorter than about $1 \mu\text{s}$ at large concentrations ($\phi \sim 0.4$, $d \sim 100 \text{ \AA}$) and $100 \mu\text{s}$ at small concentrations ($\phi \sim 0.05$, $d \sim 1000 \text{ \AA}$),¹² which seems very unlikely. In the framework of the interpretation of the phase in term of disks, the disk lifetime should be larger than the rotational time measured in electrical birefringence experiments: $\sim 1 \mu\text{s}$ for $\phi \sim 0.4$.¹² The lifetime is expected to be proportional to $\exp(E/kT)$, where E is an activation energy, of the order of $m kT$, m being the number of monomers exposed to water after the breakage of the disk.¹⁸ It should therefore increase by an enormous factor when the disk diameter increases and be much larger than $100 \mu\text{s}$ for $d \sim 1000 \text{ \AA}$. The crossover between the behavior of "living" disks and permanent disks would be crossed at some point in our experiments. Therefore, our

results can definitely not be explained within the framework of the disk model.

The structure of the studied L_3 phase is therefore likely to be made of randomly interconnected bilayers, the present experiments excluding the isolated disk structure. The phase diagram (Figure 1) indicates that the L_3 phase is not obtained by dilution of the L_α phase, but rather by adding alcohol to the bilayers, i.e. by changing the spontaneous curvature of the individual surfactant monolayers. This is in favor of the important role of the Gaussian curvature and of the formation of saddle splay structures in these systems. A recent theoretical model suggests sponge phases and disk phases in the same phase diagram.¹⁹ It is possible that by decreasing the bilayer border energy, one could stabilize pores in the bilayers and end by breaking the structure as first proposed by Miller et al.⁹ Interesting transitions between symmetric and asymmetric sponge phases and disk phases are then predicted. We are currently investigating the phase diagrams of amine oxide surfactants to look for this type of transition.²⁰

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Registry No. C_{14} DMAO, 3332-27-2; 1-hexanol, 111-27-3.

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