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Note

Effect of a neutral water-soluble polymer on the lamellar phase of a zwitterionic surfactant system

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Abstract

We have studied the effect of adding a water-soluble polymers (PEG) to the lamellar phases of the ternary system tetradecyldimethylaminoxide (C_{14}DMAO)–hexanol–water. The results of Freeze-Fracture Electron Microscopy (FFEM) and Small Angle X-ray Scattering (SAXS) experiments show that the addition of the polymer induces the spontaneous formation of highly monodisperse multilayered vesicles above a threshold polymer concentration.

Keywords: Surfactant; Polymer; Zwitterionic; Lamellar; Vesicle

1. Introduction

The interaction of polymers with surfactant bilayers or monolayers give rise to a wealth of interesting phenomena [1–4]. The mixed polymer–surfactant systems have properties differing from those of the pure components due to the complexation of the polymer with the surfactant.

It has been observed that anionic surfactants have a higher affinity for neutral polymers than cationic ones [2]. On the other hand, the interaction between neutral polymers and non-ionic surfactants seems to be weaker, at least in the micellar surfactant phase [1,2]. In this case, the nature of the surfactant headgroup as well as the structure and size of the micelles formed are important factors determining the interaction pattern.

In literature there are few reports on the interaction between micelles of nonionic surfactants and neutral polymers. Using dynamic light scattering (DLS) and fluorescence quenching experiments, Feitosa et al. have shown that $C_{12}E_5$ form complexes with Polyethylene oxide (PEO) of high molecular weight [5]. In addition, the same group has shown that $C_{12}E_8$ also forms complexes when mixed in solution with low molecular weight polyethylene glycol (PEG) [6]. Note that the polar head of the nonionic surfactants of the family C_nE_m is composed of the same monomer as PEG or PEO.

Some groups have studied the interaction between polymers and surfactant bilayer phases. Most of the interest has been devoted to the interaction between neutral polymers and the lamellar phases of ionic surfactants. For instance, it has been shown that large amounts of PEG can be solubilized in the lamellar phase of an anionic surfactant (SDS) [7–9]; the added polymer causes a reduction in the swelling of the phase and produces a phase separation between two lamellar phases [7]. On the other hand, polyvinylpyrrolidone (PVP) has been incorporated in the lamellar phase of a cationic surfactant (CPCl) [10–13]. The polymer modifies the texture of the lamellar phase, inducing the proliferation of closed domains embedded in the lamellar structure [12]. Although many properties of these neutral polymer–ionic surfactant systems are known, there is still

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a lack of information on the interaction between water-soluble polymers and lamellar phases of non-ionic or zwitterionic surfactants.

In this paper, we report on the effect of adding the water-soluble polymer polyethylene glycol (PEG) to the lamellar phase of a zwitterionic surfactant system: tetradecyldimethylaminoxide–hexanol–water. Our aim was to understand the effect of the polymer on the lamellar region of the phase diagram and to investigate whether it can induce new bilayer structures. In fact, as we shall show, the polymer induce the spontaneous formation of highly monodisperse multilayered vesicles.

The paper is divided as follows. In Section 2 we briefly describe the experimental methods. In Section 3 we present and discuss our experimental results and in Section 4 we draw conclusions.

2. Experimental

2.1. Materials

Tetradecyldimethyl aminoxide or C_{14}DMAO was a gift from the Hoffmann group in Bayreuth. The surfactant was recrystallized twice. C_{14}DMAO is a zwitterionic surfactant. In our experimental conditions (basic pH) it behaves like a non-ionic surfactant. Hexanol and PEG were obtained from Aldrich and used without further purification. The polymer molecular weight was 20000 g/mol; its hydrodynamic radius, as measured by dynamic light scattering, is 27 ± 2 Å. Ultrapure millipore water was used.

2.2. Sample preparation

The lamellar phases were prepared according to the phase diagram reported by Hoffmann et al. [14]. C_{14}DMAO was dissolved either in pure water (polymer-free samples) or in a polymer solution of the required concentration. Then hexanol was added while the samples were gently stirred. The mixtures were kept at 24 °C. In the experiments reported here, the bilayer volume fraction was varied between $\phi = 0.1$ and 0.3 and the C_{14}DMAO–hexanol mass ratio was $r = 0.85$. The polymer concentration was varied between 0 and 10 g/l.

2.3. Phase structure characterization

The samples were equilibrated several days before examination. Observation between crossed polarizers allowed the identification of anisotropic samples (lamellar phases). The lamellar structure was checked with Small-Angle X-ray Scattering (SAXS) and Freeze-Fracture Electron Microscopy (FFEM) experiments. In the first technique, we used a Rigaku rotating anode source that produces the Cu $K\alpha$ lines (1.54 Å) with a fine focus (1×0.1 mm). The output was collimated by a gold-plated quartz mirror. The linear detector, with 512 channels, was placed 81 cm from the sample position. The resolution of the direct beam was measured to be $\Delta q = 0.0017$ Å^{-1} full width at half maximum. For the FFEM experiments, a thin layer of the sample (20–30 μm) was placed on a thin copper holder and then rapidly quenched in liquid propane. The frozen sample was fractured at −125 °C, in a vacuum better than 10^{-6} Torr, in a Balzers freeze-etching unit. The replication was done using unidirectional shadowing at an angle of 35°, with platinum–carbon. The replicas were washed with organic solvents and distilled water and were observed in a Philips 301 electron microscope.

3. Results and discussion

C_{14}DMAO is a zwitterionic surfactant and its phase diagram has been characterized by Hoffmann et al. [14]. When diluted in water, an increasing amount of a cosurfactant (in general a short-chain alcohol, e.g., hexanol) produces a series of well defined phases: spherical micelles, cylindrical micelles, flat bilayers (lamellar phase) and multiple-connected bilayers (sponge phase). The lamellar phase is stable in a broad volume fraction range of surfactant, resulting in a large variation of the interbilayer mean distance, typically between 100 and 1000 Å. The bilayer thickness is 23.8 Å, as measured by SAXS experiments [20].

We have examined the effect of solubilizing PEG, an uncharged water-soluble polymer, in the lamellar phase of the C_{14}DMAO–hexanol–water system. In Fig. 1a, we show a freeze-fracture electron microscopy (FFEM) picture of the polymer-free lamellar phase with bilayer volume fraction $\phi = 0.2$. Parallel ondulating layers are clearly observed in the whole visual field; in some regions they have an slight tendency to bend, a typical texture of these phases. The parallel bilayers give rise to a well-defined Bragg peak in the small-angle X-ray scattering (SAXS) spectrum (Fig. 2). This peak is visible for sufficiently high concentrations, i.e., for those samples where it is not hidden by the strong signal at very small angles. This intense small-angle signal arises presumably from the large-scale inhomogeneities and the structural defects observed in the FFEM picture. From the peak position in the scattering spectra, $q_{\max}$, we can deduce the mean interbilayer distance by the Bragg relation $d = 2\pi/q_{\max}$; for the free-polymer lamellar phase of Fig. 1a, $d = 114 \pm 3$ Å. Note that the size of the polymer is smaller than the interbilayer distance in the lamellar phase. The ratio of the polymer radius to the water layer thickness is $r/d_w \sim 0.3$.

The effect of adding PEG ($M_w = 20000$ g/mol) to the lamellar phase can be summarized as follows. For bilayer volume fractions between 0.1 and 0.3, relatively small amounts (up to a concentration of the order of 1 g/l) of polymer can be solubilized without changing the physical characteristics of the phase. The samples remain optically birefringent and the SAXS spectra still give a single Bragg peak whose main features (position, width) are not appreciably modified. However, after a polymer concentration of about 1 g/l (which depends only slightly on the surfactant volume fraction), the samples become progressively more and more turbid and later a white, "milky" phase appears. Finally, a macroscopic phase separation occurs: the "milky" and viscous liquid (upper layer) coexists with a transparent isotropic one (lower layer), as shown in the first tube of Fig. 3.

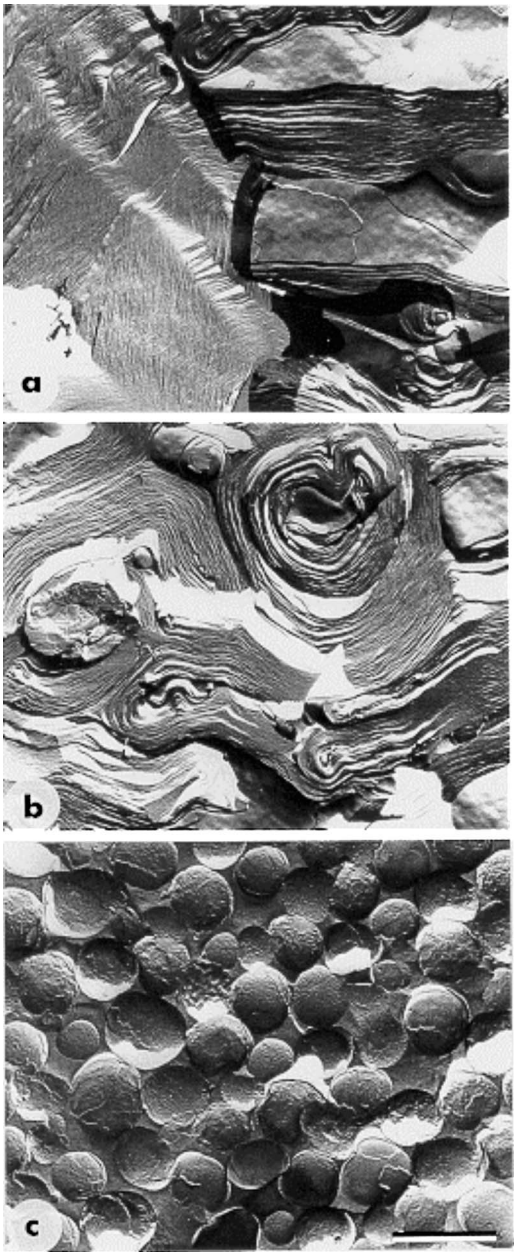

Fig. 1. Efect of the PEG concentration on the lamellar phase. (a) Polymer-free lamellar phase. (b) Lamellar phase where the polymer concentration is 1 g/l. (c) Multilayered vesicles obtained with a polymer concentration of 5 g/l. In all cases, the bilayer volume fraction is 0.2. The length scale is the same in the three pictures; the bar in (c) represents 1 μm.

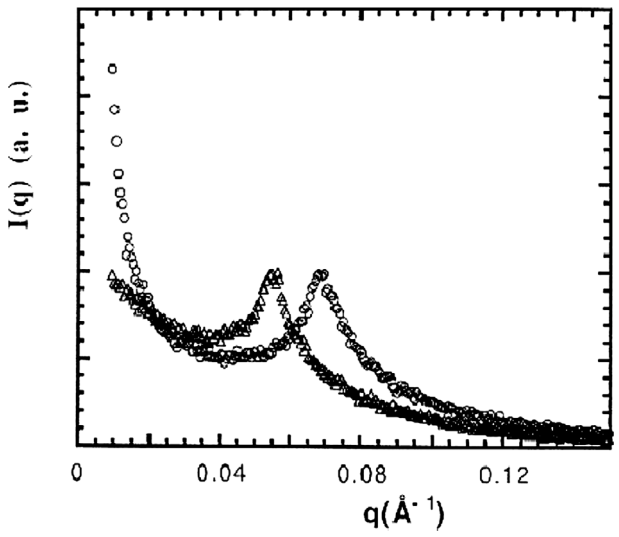

Fig. 2. SAXS spectra of the polymer-free lamellar phase (△) and of the vesicular phase (○) of Fig. 1. In both cases the bilayer volume fraction is $\phi = 0.2$.

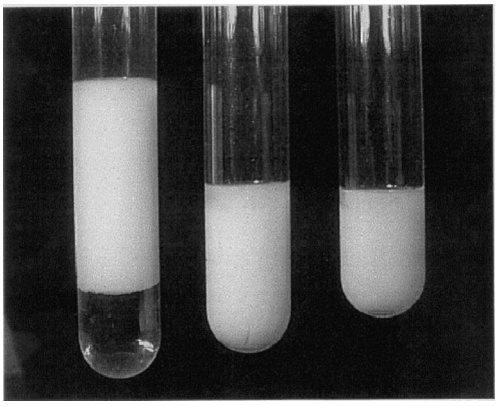

Fig. 3. Three samples showing the vesicular phase, which appears white because its aggregates scatter light strongly. From left to right, the surfactant volume fractions are: 0.1 (in this sample the vesicular phase coexists with the isotropic, transparent phase), 0.2 and 0.3. The PEG concentration is 2 g/l in each sample.

The isotropic phase does not scatter X-rays appreciably, thus no structural information about this phase can be extracted from SAXS experiments. On the other hand, the SAXS spectra of the "milky" phase display a Bragg peak, thus revealing a multilayered structrure. A typical spectrum is also shown in Fig. 2. In fact, the SAXS spectra of the "milky" phases are qualitatively very similar to those of the polymer-free lamellar phases, the only difference being an important shift in the peak position and a strong increase in the small-angle scattering signal; the Bragg relation ($d = 2\pi/q_{\max}$) for the milky phase of Fig. 2 gives an interbilayer distance, $d = 92 \pm 2$ Å, smaller than that of the original lamellar phase. In this case, the ratio of the polymer radius to the water layer thickness is a little bit higher: $r/d_w \sim 0.4$. For all the bilayer volume fractions studied, we obtain similar results: d decreases appreciably when the "milky" phase appears, whereas it remains constant, within experimental error, for polymer concentrations smaller than 1 g/l.

The white colour of the "milky" liquid indicates that it is formed by large aggregates which scatter strongly light. In order to elucidate their large-scale structure, which is out of the range of the SAXS experiments, we used FFEM. Fig. 1c shows a micrograph of the "milky" phase where the PEG concentration is 5 g/l; the bilayer volume fraction is $\phi = 0.2$. We see that the strong light scattering is due to a very compact array of nearly monodisperse vesicles; their size is of the order of 1 μm. In addition, for some spherical vesicles the fracturing process reveals several concentric layers (Fig. 1c), thus it is clear that the vesicles are multilayered, in agreement with the observed Bragg peak.

Global packing constraints of the vesicle array explain the decrease in the interbilayer distance when the lamellar phase–vesicular phase transformation occurs. In fact, the maximum possible volume fraction occupied by packed spheres is that of a face-centered cubic arrangement ($\phi_{\text{sph}} = 0.74$). On the other hand, the swelling law for a lamellar phase links the interbilayer distance d with the bilayer volume fraction ϕ, $\phi = \delta/d$, where δ is the bilayer thickness. As the vesicles are multilayered, and assuming a face-centered structure, a straightforward calculation shows that the interbilayer distance in the vesicular phase should be $d_{\text{v}} = 0.74 d_{\text{l}}$, where d_{l} is the interbilayer distance in the lamellar phase. This simple result, which at first approximation neglects curvature of the vesicles, predicts $d_{\text{v}} = 84.36 \pm 2$ Å, for the vesicular phase, in reasonable agreement with the experimental value.

Note that the change in the interbilayer spacing d on adding PEG could be an osmotic dehydration of the bilayers, as has been observed in several systems [18]. However, this effect is observed when the polymer is excluded from the bilayers. In that case, an osmotic imbalance between the hydration layer of the membranes and the bulk polymer solution is created, thus causing a partial dehydration of the surfactant headgroups. A related effect has been widely used in order to measure interbilayer forces by equilibrating a lamellar phase with an external polymer solution [19]. We can discard such an effect in our system because PEG is solubilized in the aqueous phase, even in the interbilayer space, and no osmotic gradient is created.

The observed vesicular aggregates appear progressively on addition of PEG to the lamellar phase. This effect explains the increase in the turbidity of our samples. In Fig. 1b we show a FFEM picture of a polymer-containing lamellar phase before phase separation; a few closed aggregates are already present at this polymer concentration (1 g/l). These results are somehow similar to those reported by Bouglet et al. for the PVP–CPCl system [12]. In this case, Cryo-TEM experiments show that the water-soluble polymer induces the proliferation of polydisperse ovoid objects (spherulites) embedded in the lamellar matrix. However, in our PEG–C_{14}DMAO system, the final vesicular phase is remarkably monodisperse (Fig. 1c).

It is also interesting to note the analogies between our results and those found in the ternary system DMPC–pentanol–water, where PEG with a lipid anchor was added [15,16]. In this case, the addition to a lamellar phase of small amounts of the polymer induces the formation of a highly viscoelastic hydrogel, composed of interconnected spherulites of high membrane curvature. The electron microscopy observations are consistent with a model where the PEG-lipid diffuses in the plane of the membrane and seggregates into curved regions thus stabilizing spherulites [16]. This analogy supports the idea that, even if our polymer does not have a hydrophobic anchor, it adsorbs onto the bilayers and stabilizes the highly-curved vesicles by a similar mechanism.

In order to understand the role of the polymer and the mechanism of the lamellae–vesicle transition, note that the bilayer topology changes drastically. This behaviour can be explained in terms of the Gaussian bending rigidity, a parameter which plays a relevant role in transformations involving topology. The elastic energy (per unit area) describing any curved bilayer can be written as [21]:

$$E = \frac{1}{2} K \left(\frac{1}{R_1} + \frac{1}{R_2} \right)^2 + \tilde{K} \left(\frac{1}{R_1 R_2} \right), \tag{1}$$

where R_1 and R_2 are the principal radii of curvature of the surface at any point. K is the bilayer mean bending rigidity; its value controls sinusoidal-like thermal undulations. $\tilde{K}$ is the bilayer Gaussian bending rigidity. When $\tilde{K}$ is large and negative, Eq. (1) is minimized when R_1 and R_2 have small values and the same sign; closed aggregates, like vesicles, are stable in the system. On the other hand, when $\tilde{K}$ is positive, the bending energy is minimized when R_1 and R_2 have opposite signs, and bicontinuous or sponge-like structures are prefered. At this stage of our work, we can speculate that adsorption of the polymer onto the surfactant bilayers decreases $\tilde{K}$, until it reaches a large negative value, thus stabilizing the mutilayered vesicles shown in Fig. 1c. Adsorption of the polymer is consistent with preliminary Dynamic Light Scattering (DLS) and Fluorescence Recovery after Pattern Photobleaching (FRAPP) measurements which show that PEG forms complexes with C_{14}DMAO micelles [17].

Note that the vesicular phase produced by adding PEG to the C_{14}DMAO lamellar phase is stable over a long period of time; samples prepared by this method preserve their physical properties for at least six months.

4. Concluding remarks

We have studied the effect of adding a water-soluble polymer to the lamellar phases of the ternary system tetradecyldimethylaminoxide (C_{14}DMAO)–hexanol–water. FFEM and SAXS experiments show that the addition of the polymer triggers the transformation of the lamellar phase into a vesicular phase. The polymer is solubilized in the water domains of the phase and adsorbs onto the surfactant bilayers thus stabilizing aggregates of high curvature. More experiments are necessary in order to have a better understanding of the interaction responsible of this effect. For this goal, it will be useful to study a less complex system: the micellar phase of the same surfactant, where no cosurfactant is added to the system. On the other hand, preliminary DLS and FRAPP results show that PEG and the C_{14}DMAO bilayers interact strongly also at much lower cosurfactant contents. A future challenge will be to understand the exact nature of the polymer–surfactant interaction and to determine the factors governing the size and monodispersity of the multilamellar vesicles.

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