

Effect of polymer on the elasticity of surfactant membranes: A light scattering studyRamón Iñiguez-Palomares, Heriberto Acuña-Campa, and Amir Maldonado
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We have performed a dynamic light-scattering (DLS) investigation of the effect of a water-soluble polymer, polyethylene glycol (PEG), on the bending elastic modulus κ of surfactant membranes. The polymer, in concentrations ranging from 0 to 8 g/L (0 to 0.4 mM), was incorporated into the solvent of sponge phases of the sodium dodecyl sulfate (SDS)-hexanol-brine system. PEG adsorbs into the SDS membranes. The correlation functions of the polymer-doped sponge phases displayed a stretched-exponential decay, appropriately described by the Zilman-Granek (Z-G) theory for fluctuating membranes. The dynamics of the surfactant bilayers was slowed down by the addition of the polymer: Increasing PEG concentrations increase the DLS relaxation times. From the Z-G model we extracted the membrane-bending elastic modulus, as a function of polymer concentration, $C_{\text{PEG}} = \kappa$ increases with C_{PEG} , a behavior opposite to that expected from available models for the interaction between fluid membranes and adsorbing polymers. Our results suggest that the polymer penetrates to some extent the surfactant bilayers.

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I. INTRODUCTION

Surfactants in solution give rise to different equilibrium phases [1], depending on the values of the physicochemical variables (concentration, temperature, concentration of additives, etc.). There are two basic local structures: micelles (spherical or cylindrical) and bilayers (membranes). In both cases the hydrophobic tail of the surfactant molecule avoids water contact by hiding in the interior of the structure.

Bilayers in aqueous solutions are formed by two surfactant monolayers facing each other through their hydrophobic moieties. At a larger scale, surfactant bilayers can adopt several configurations. Two of the most common are the so-called lamellar [2] and sponge phases [3]. In the first case, the membranes arrange in a parallel stack of fluctuating bilayers separated by solvent; the system is characterized by the interbilayer distance d and the bilayer thickness δ , related through the surfactant volume fraction ϕ by the classical dilution law $\phi = \delta/d$.

On the other hand, the sponge phase (Fig. 1) is a disordered array of bilayers continually connected in the three dimensions; this phase can be pictured as a structure containing pores or passages separating two equivalent volumes of solvent. A characteristic distance d is measured in appropriate static scattering experiments; it can be interpreted as a mean interbilayer distance or as the mean diameter of the pores in the structure. In the sponge phase, d is also related to the bilayer thickness by the dilution law: $\phi = \alpha\delta/d$, where α depends on the topology of the phase and has a value near to 1.5.

It is interesting to study and understand the properties of lamellar or sponge phases doped with polymers of different chemical characteristics: water-soluble, nonadsorbing polymers, adsorbing polymers, or amphiphilic polymers. The interaction between surfactant structures and polymers is of interest because of the applications of the mixed systems. Surfactants are relevant in detergency, wetting, foaming, or emulsification, while polymers are usually added to control

the viscosity of the solutions. The phase behavior as well as the physical properties of these systems strongly depend on the polymer-membrane interactions. In the literature there are several reports, both experimental [4–20] and theoretical [21–25], on the effect of polymers on lamellar or sponge phases.

For instance, in a previous work, it has been shown that the addition of polyethylene glycol (PEG) to the lamellar or sponge phase of the sodium dodecyl sulfate (SDS)-hexanol-brine system produces the appearance of a vesicular phase in coexistence with excess solvent [20]. The actual mechanism of this transformation is not completely understood so far, but one can argue that the polymer modifies the Gaussian elastic constant of the surfactant bilayers and thus triggers a topological phase transformation. In order to obtain a better insight into the mechanism of the reported lamellar (sponge)-vesicular transformation, it is interesting to study the elastic properties of the membranes of this system, as a function of polymer concentration.

In this context, we have carried out a systematic light-scattering study of the effect of increasing concentrations of PEG on the bending elastic modulus of SDS-hexanol-brine sponge phases. The experimental results are reported in this paper. The aim is to understand the effect of the polymer on the elastic properties of the surfactant membranes.

The paper is organized as follows. In the next section we provide a brief theoretical as well as experimental background to our work. In Sec. III we give the details of our experiments. In Sec. IV we present and discuss our results. Finally, in Sec. V we draw conclusions of our investigation. In the supplementary material, we present related experimental results obtained for our system [40].

II. BACKGROUND**A. Bilayer elastic constants**

The elastic properties of surfactant membranes can be described by the bending elastic modulus κ and the Gaussian

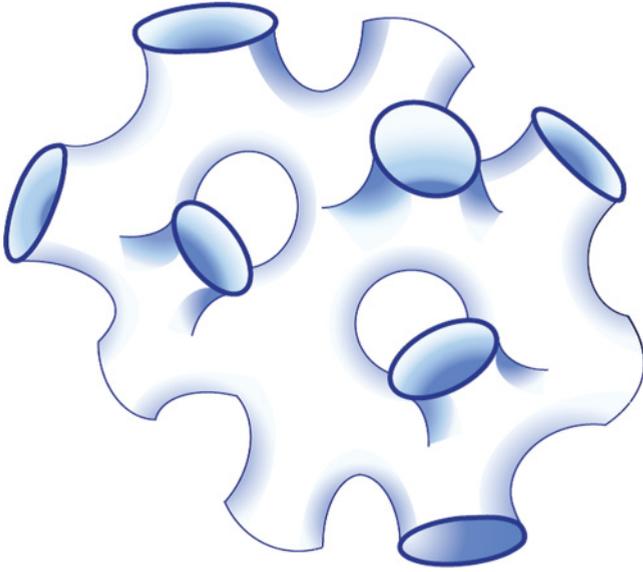


FIG. 1. (Color online) Schematic representation of a sponge phase. The local structure is a surfactant bilayer. This bilayer is connected in space in a complex three-dimensional structure, separating two equivalent volumes of solvent.

elastic modulus $\tilde{\kappa}$, defined in the Helfrich elastic energy [26] (per unit area):

$$E = \frac{1}{2}\kappa \left(\frac{1}{R_1} + \frac{1}{R_2} - \frac{2}{R_0} \right)^2 + \tilde{\kappa} \frac{1}{R_1 R_2}, \quad (1)$$

where R_1 and R_2 are the principal curvature radii in each point of the membrane, and R_0 is the spontaneous curvature radius. The bending modulus κ determines the amplitude of thermal bending fluctuations of the membrane. Flexible membranes have low κ values (of the order of $k_B T$); rigid membranes, like those formed with phospholipids, have higher κ values, of the order of tens of $k_B T$. This elastic modulus has thus a direct influence on the dynamics of surfactant bilayers. On the other hand, the Gaussian modulus $\tilde{\kappa}$ controls topology transformations. Depending on its value, flat (lamellar phase), saddlelike (sponge phase), or closed (vesicles) topologies can be stable. However, for a fixed topology the Gaussian term of the elastic energy is a constant and can be neglected.

When a polymer interacts with the membranes of a surfactant system, it modifies their physical properties. Theoretical studies have predicted that an adsorbing polymer modifies the bending elastic modulus of the bilayers. For instance, Brooks *et al.* have shown that κ decreases in the cases of both weak and strong adsorption [21]. From an experimental point of view, the most studied system is the one where bilayers of the anionic surfactant SDS interact with the water-soluble, neutral polymer PEG. Several groups have shown that PEG binds to the SDS bilayers and micelles [14,27–29].

Maugé and Bellocq have studied the effect of both adsorbed and anchored polymers on the SDS-hexanol-brine sponge phases [4]. As adsorbing polymer, they have used PEG of molecular weight 20,000. The solvent is an aqueous solution with 30% of glycerol. This additive is commonly used as a cryoprotectant in freeze-fracture experiments in order to prevent the formation of ice crystals. Under these

conditions, they find that it is possible to solubilize up to 50 g/L of PEG without changing the sponge bilayer structure. Furthermore, the modifications of the phase diagram in this system suggest that PEG increases the Gaussian curvature modulus of the membranes, an opposite effect to that observed in the SDS-hexanol-brine system without glycerol [20].

The effect of adding PEG to SDS bilayer phases depends on physicochemical variables such as the salt concentration in the solvent. For instance, it has been shown that in the absence of salt it is possible to solubilize large amounts of PEG in SDS lamellar phases, without disturbing the bilayer structure [4]. However, if the electrostatic interactions are screened by adding salt to the system, the lamellar and sponge phases are no longer stable after a relatively moderate PEG concentration; instead, a phase separation occurs, where the bilayers adopt a vesicular structure and expel excess solvent [20]. This transition is not observed if the electrostatic interactions are not screened. The actual mechanism of the lamellar (or sponge)-vesicular transformation is not fully understood so far. However, one can argue that the polymer modifies the elastic moduli of the membranes, thus triggering the observed topological modification. This is one reason why it is relevant to measure the elastic constants of polymer-doped membrane phases.

B. Zilman-Granek theory

There are several ways to assess the elastic properties of surfactant bilayers. In the case of dilute lamellar or sponge phases, dynamic light scattering (DLS) is a well-suited tool to measure the bending elastic modulus κ . In a DLS experiment, one measures the normalized autocorrelation function of light scattered by the sample at a certain angle:

$$g^{(2)}(q,t) = \frac{\langle I(q,0)I(q,t) \rangle}{\langle I^2(q,0) \rangle}. \quad (2)$$

The corresponding correlation function of the scattered electric field $\vec{E}(q,t)$, $g^{(1)}(q,t) = \langle \vec{E}^*(q,0)\vec{E}(q,t) \rangle / \langle |\vec{E}(q,0)|^2 \rangle$, is obtained via the Siegert relation: $g^{(2)}(q,t) = 1 + b|g^{(1)}(q,t)|^2$, where b is an experimental constant of the order of unity and the angular brackets mean an equilibrium ensemble average that is obtained as a time average from the experimental data. In this equations $I(q,t)$ is the light intensity arriving at the detector. Here $q \equiv \frac{4\pi n}{\lambda} \sin \frac{\theta}{2}$ is the wave number, n the refractive index of the medium, λ the wavelength of the light, and θ the scattering angle; $g^{(1)}(q,t)$ is proportional to the dynamic structure factor, $g^{(1)}(q,t) \sim S(q,t)$.

The correlation of the scattered light decays with time accordingly to the dynamics of the sample. In most diluted colloidal systems the decay of $g^{(1)}(q,t)$ is described by exponential functions. However, in the case of dilute sponge phases, the correlation functions differ from single exponentials. In fact, they are well described by stretched exponentials [4,30]:

$$g^{(1)}(q,t) \sim \exp[-(\Gamma t)^\beta]. \quad (3)$$

In this equation $\Gamma = \frac{1}{\tau}$ is the relaxation frequency, τ the relaxation time, and β the stretching exponent.

Zilman and Granek have developed a theory [31,32] that has been successful in describing DLS experiments in dilute sponge [4,30] and lamellar [5–7,33] phases, as well as in

microemulsions [34] and even in vesicular structures [35]. In their theory they consider the scattering of light by pieces of membrane of size ξ . These membranes undergo thermal fluctuations whose amplitude is related to the bending modulus of the bilayer: κ . After doing some approximations and taking an angle average to take into account the isotropy of the phase, they found that $g^{(1)}(q,t)$ decays in time as a stretched exponential [Eq. (3)]. The stretching exponent is found to be $\beta = 2/3$. Moreover, the relaxation frequency scales with the third power of the wave number: $\Gamma = m q^3$. The slope in this equation contains the bending elastic modulus of the membrane:

$$m = 0.025 \gamma_k \left(\frac{K_B T}{\kappa} \right)^{\frac{1}{2}} \frac{K_B T}{\eta}. \quad (4)$$

In this equation, γ_k is a constant approaching unity, K_B the Boltzmann constant, T temperature, and η the solvent viscosity.

These equations are the basis for the measurement of κ in sponge phases with the DLS technique. In a typical experiment, the correlation functions for several scattering angles are measured and fitted to stretched exponentials [Eq. (3)]. Then, the relaxation frequency Γ is plotted as a function of q^3 . The bending elastic modulus is obtained from the slopes [Eq. (4)] resulting from linear fits to the Γ versus q^3 curves.

III. MATERIALS AND METHODS

The sponge phases were prepared in the system SDS-hexanol-brine. The solvent was a 170 mM NaCl solution. SDS (99% purity), hexanol (99% purity), and NaCl were purchased from Sigma-Aldrich and used as received. Ultrapure water from a Milli Q system (Millipore) was used to prepare the brine solutions. To the solvent of the samples, polyethylene glycol (PEG, Mw = 20 000) was added in concentrations ranging from 0 to 0.4 mM (8 g/L). PEG was purchased from Sigma-Aldrich and used as received.

The samples were prepared by weighing appropriate amounts of the components. The membrane volume fraction in the samples was ~ 0.02 . The surfactant/cosurfactant mass ratio was $m_{\text{SDS}}/m_{\text{hex}} = 0.455$. The cosurfactant (hexanol) penetrates the surfactant membrane; its concentration determines whether the lamellar (lower hexanol contents) or the sponge phase (higher hexanol contents) are stable. PEG was incorporated in the brine solutions in the appropriate concentrations. The samples (50 ml total volume) were prepared in pyrex bottles. They were homogenized with a magnetic stirrer for 1 hour, while observing them between crossed polarizers in order to look for flow birefringence (Fig. 2). The samples were allowed to stabilize for several months. Some experiments were also performed with “fresh” samples (2 weeks after sample preparation) in order to test for reproducibility. For the sake of comparison, some experiments were also performed with lamellar phases, where the SDS/hexanol mass ratio was 0.55. However, these experiments did not produce reproducible results, probably due to local alignment inside the samples. The bilayer thickness of the membranes δ was determined by small-angle x-ray scattering (SAXS)

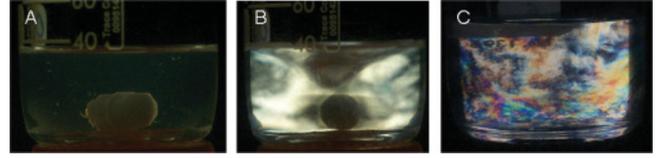


FIG. 2. (Color online) Illustration of flow birefringence in our system. (a) At rest, the sponge phase is isotropic, and thus no light is transmitted. (b) When a shear stress is applied (with a magnetic stirrer), the bilayers are locally aligned, and the phase becomes birefringent. For the sake of comparison, we show the birefringence of a lamellar phase at rest (c). All samples are observed between crossed polarizers. A white light source illuminates the samples from behind the first polarizer.

experiments in the lamellar phase: $\delta \approx 20 \text{ \AA}$ (Fig. S1 in Ref. [40]).

The DLS experiments were performed with a BI-9000AT Digital Brookhaven correlator. The used laser has a 25 mW power at 633 nm. Correlation functions were collected for nine equally spaced angles, from 40° to 120° . This range is equivalent to wave numbers q from 9.06×10^6 to $2.29 \times 10^7 \text{ m}^{-1}$. All the experiments were carried out at room temperature (24°C). The experimental correlation functions were fitted to the Zilman-Granek theory. From the fits, the parameters Γ (inverse of relaxation time) and β (stretching exponent) were obtained. Γ was plotted as a function of q^3 ; from the slopes of these curves, the mean elastic modulus of the membranes was obtained, using Eq. (4). In addition, we have performed a CONTIN analysis of the DLS data in order to know the distribution functions of relaxation times and compare the results with those of the Zilman-Granek theory.

The viscosity of the brine and polymer solutions were measured using an Ubbelohde viscosity meter immersed in a thermal, circulating water bath. The measurements were made at 24°C ; eight repetitions were made in order to obtain the average viscosity for each concentration.

IV. RESULTS AND DISCUSSION

All the samples prepared with PEG/brine solutions have the macroscopic characteristics of a sponge phase. They have low viscosity and are isotropic, as observed between crossed polarizers. Furthermore, when sheared, flow birefringence is clearly observed (Fig. 2), indicating that under flow the originally disordered membranes locally align in an anisotropic structure. This behavior is typical of a sponge phase.

The scattering correlation functions cannot be fitted with single exponential functions like most of diluted colloidal suspensions. In fact, the measured correlation functions are very well fitted by stretched exponential functions, in excellent agreement with the Zilman-Granek prediction for dilute membrane phases [31,32] and with previous experimental results for sponge phases [4,30]. For illustrative purposes, in Fig. 3 we present three correlation functions, with their corresponding theoretical fits [Eq. (3)], for sponge phases with polymer concentration $C_{\text{PEG}} = 1 \text{ g/L}$; the scattering angles for these curves are 40° , 80° , and 120° . Similar, qualitative results have been obtained for the other angles and polymer concentrations. Furthermore, the stretching exponential for all

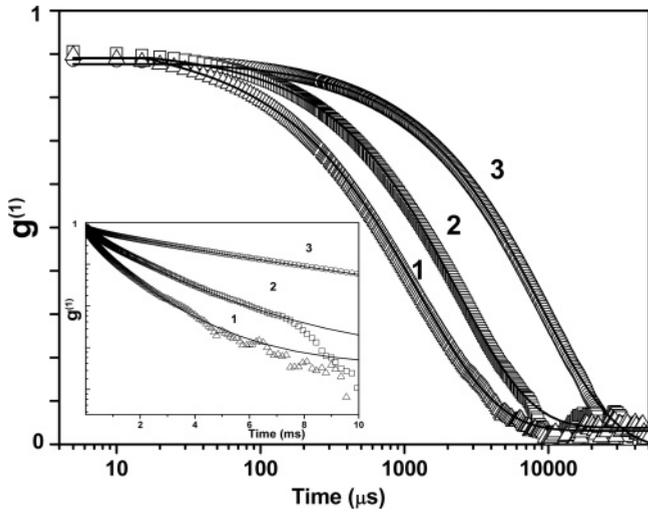


FIG. 3. Light-scattering correlation functions for a sponge phase with a PEG concentration $C_{\text{PEG}} = 1$ g/L, for three scattering angles: (1) 120° , (2) 80° , and (3) 40° . The curves are the best fits to the Zilman-Granek theory.

our samples is in the range 0.7–0.8, slightly higher than the theoretical predicted value ($\beta = 2/3$) but in full agreement with previous experimental results [4,30]. This is a further indication that our phases have the sponge structure.

From the fits to the electric field correlation functions, $g^{(1)}(t)$, we have obtained the relaxation times. Our results show that for a given angle this time increases when the polymer concentration increases. In Fig. 4 we show this behavior for some scattering angles. The increase in the relaxation times means that the addition of PEG slows the microscopic dynamics of the membrane phases.

In the framework of the Zilman-Granek theory, the inverse of the relaxation time, $1/\tau$, also called the relaxation frequency,

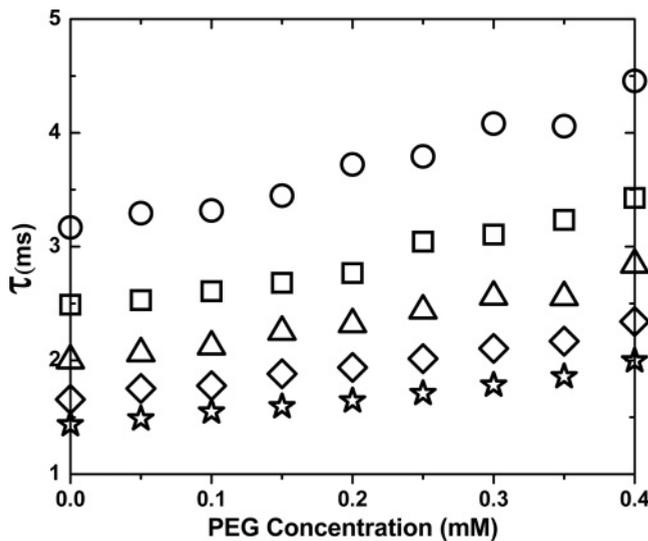


FIG. 4. Scattering relaxation times at 70° (circles), 80° (squares), 90° (triangles), 100° (diamonds), and 110° (stars) for the sponge phases, as a function of polymer concentration. Increasing the polymer concentration increases the relaxation time.

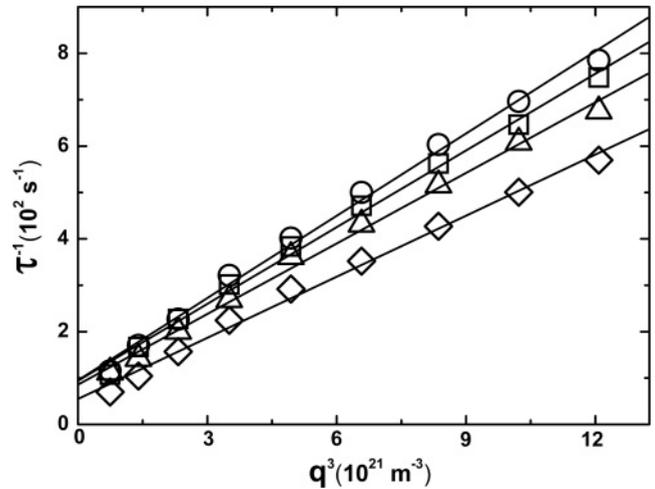


FIG. 5. Γ vs q^3 curves for sponge phases with different polymer content: 0 g/L (circles), 2 g/L (squares), 4 g/L (triangles), and 8 g/L (diamonds). The lines are fits to linear equations. Note that the slope decreases with polymer concentration.

scales as q^3 . This behavior is observed for all the scattering angles and polymer concentrations, as shown in Fig. 5.

Before proceeding further in the discussion of the Zilman-Granek results, it is worth mentioning that we have performed a CONTIN analysis of the DLS data. This procedure is well suited for samples presenting polydispersity or multiple decay times. In fact, the structure of the sponge phase is so complex that one could expect additional modes, such as a collective “breathing” mode of the phase; the decay time of this mode would be larger than that predicted by the Zilman-Granek theory. However, the distribution functions of decay times revealed by the CONTIN analysis (Fig. S5 in Ref. [40]) reveal no slow mode in either of our samples. In fact, the main peak found by the CONTIN procedure agrees remarkably well with the decay times obtained with a fit to Eq. (3).

There is a systematic behavior of the slopes of the experimental curves obtained from the Zilman-Granek theory (Fig. 5): The more concentrated the polymer in the solvent, the smaller the slope in the $1/\tau$ vs q^3 curve. This is expected if the polymer slows down the dynamics of the membranes. We have fitted the $1/\tau$ versus q^3 curves for all polymer concentrations. As observed in Fig. 5, the first two points, corresponding to the scattering angles 40° and 50° , slightly deviate from the expected linear behavior. We attribute this deviation to the fact that these points are the most separated from the range of validity of the Zilman-Granek theory, i.e., $\xi q \gg 1$. However, we have taken into account all the points in the theoretical fits to the data of Fig. 5. We have estimated the experimental error associated with neglecting these points to be of the order of 5% (Fig. S2 in Ref. [40]). This error slightly modifies the obtained values of κ but does not change the qualitative behavior with increasing polymer concentrations.

From the fitted slopes of the curves of Fig. 5, we can obtain the membrane mean bending modulus κ . The results are shown in Fig. 6. For the calculation, we have used a constant viscosity: that of the brine solution, 0.98 ± 0.008 cp. We use this value because, as we explain in the following paragraphs, PEG binds to the surfactant bilayers, and thus we consider the solvent as

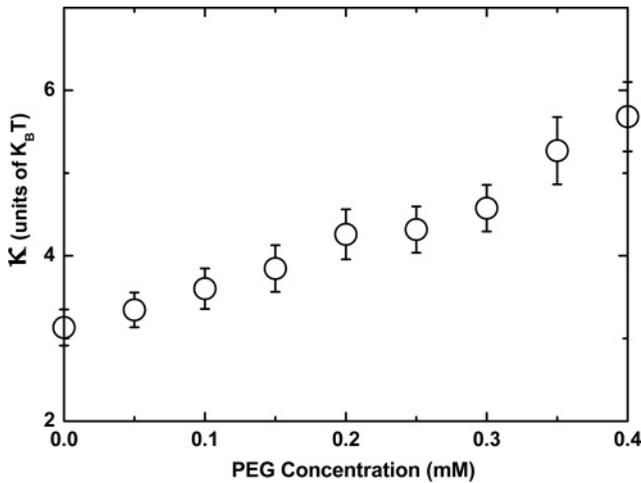


FIG. 6. Bending elastic modulus of the sponge phases, as a function of polymer concentration. κ systematically increases with polymer concentration, indicating that PEG stiffens the surfactant bilayers.

the brine solution. This choice is very important. Since κ scales as $1/\eta^2$, the bending modulus is very sensitive to the value of the solvent viscosity. We discuss this point below.

In Fig. 6 we see that the polymer increases the rigidity of the membranes, thus reducing their thermal fluctuations. For a polymer-free sponge phase, we obtain a value of $\kappa = 3.13 \pm 0.22 k_B T$, in very good agreement with previous results on similar systems [4,30,36]. When polymer is added to the sponge phase, the bending modulus increases and reaches a value of $\kappa = 5.68 \pm 0.42 k_B T$, for the highest polymer concentration. The slower dynamics (with polymer addition) in the relaxation times of Fig. 4 is due to this increase in the membrane rigidity.

It is interesting to compare our results to those reported in Ref. [4]. The system studied there is very similar to ours, except for the fact that the brine solution is prepared with a water (70%)-glycerol (30%) mixture. In that case, the DLS experiments also show that the reduced relaxation frequency $\Gamma^* = \Gamma_q/q^3$ decreases by the addition of PEG. This behavior qualitatively agrees with our measurements, depicted in Fig. 5. However, the obtained bending modulus decreases from $3.1 k_B T$ (for a polymer-free sponge phase) to $1.7 k_B T$ ($C_{\text{PEG}} = 50 \text{ g/L}$) [4]. The reasons for the discrepancy with our results could be related to the presence of glycerol in the system of reference [4]. In fact, several physical properties of the lyotropic phases are modified by the addition of this alcohol. For instance, we have found that this additive slightly modifies the phase boundaries in our system. Furthermore, PEG solubility is also affected by the presence of glycerol. In a previous work, we have found that, in the absence of glycerol, only relatively small amounts of PEG ($\leq 9 \text{ g/L}$) can be solubilized in the sponge phases [20]. However, in the presence of glycerol, larger quantities of PEG (at least up to $C_{\text{PEG}} = 50 \text{ g/L}$) can be solubilized [4]. Finally, PEG increases the Gaussian elastic modulus of glycerol-containing sponge phases [4], while it decreases the same modulus when no glycerol is added to the solvent [20]. Thus, glycerol might be responsible for the quantitative differences between our results (Fig. 6) and those

of Ref. [4]. Note that another source of difference could be the value used in Eq. (4) for the solvent viscosity. In fact, the relaxation frequency is related to η and κ by

$$\Gamma^* \equiv \frac{\Gamma_q}{q^3} = \frac{1}{\eta} \frac{1}{\sqrt{\kappa}} \quad (5)$$

The decrease in Γ^* depicted in Fig. 5 (and observed in Ref. [4]) can be due either to an increase in κ or to an increase in the solvent viscosity (or both). In our case we used a constant solvent viscosity, assuming that the polymer completely binds to the surfactant bilayers.

The choice of a constant viscosity for the calculation of the elastic modulus is based on the plausible assumption that the polymer adsorbs onto the surfactant bilayers. The adsorption of PEG to SDS bilayers or monolayers has been reported several times in the literature [14,27–29]. So, one expects that the increasing amount of PEG in our system incorporates into the membranes of the SDS sponge phases, leaving as solvent the brine solution. Thus, the value of η in Eq. (4) is that of the brine solution. If this were not the case, the viscosity used to calculate κ should be that of a PEG-containing brine solution. We have measured that viscosity, as a function of polymer concentration (Fig. S3 in Ref. [40]). If we take into account the viscosity of brine solutions with increasing PEG concentrations (no adsorbed polymer), the calculated κ values depend only slightly on polymer concentration (see Fig. S4 in Ref. [40]). However, we can rule out this effect since, as we have pointed out, the adsorption of PEG to SDS has been established in the literature [14,27–29].

Finally, note that the measured increase in κ (Fig. 6) is not expected from the available theories on the effect of adsorbing polymers on the elasticity of surfactant bilayers [21]. Indeed, the theoretical prediction is a decrease in the bending modulus when polymer is adsorbed onto the surfactant membrane [21]. This fact seems to indicate that our experimental system does not meet the theoretical assumptions of the model. The strongest assumption in the theory of reference [21] is the homogeneous, nonpenetrating adsorption of the polymer onto the surfactant membranes. However, different experimental techniques show that PEG has a nonnegligible degree of penetration in surfactant micelles and membranes [28,37–39]. This might lead to an internal rearrangement in the membrane structure and to additional contributions to the adsorption energy, not taken into account in the theory. On the other hand, the adsorption of PEG could also lead to a local disturbance of the membrane composition. Indeed, with the used surfactant-to-cosurfactant mass ratio ($m_{\text{SDS}}/m_{\text{hex}} = 0.455$), there are approximately six hexanol molecules per SDS molecule in the bilayer. The homogeneous distribution of these species in the membrane surface gives rise to the properties of the polymer-free sponge phase. When PEG is adsorbed into the bilayers, it might interact in different ways with hexanol and SDS. This could lead to a local redistribution of these molecules around the PEG binding sites, locally changing the SDS/hexanol molar ratio. As the properties of the sponge phase depend on this ratio, this effect could lead to a modification of parameters such as observed variation of the elastic bending constant of the membrane. However, further experiments are required to clarify this point.

V. CONCLUSIONS

The adsorbing polymer PEG has been solubilized in the sponge phases of the SDS-hexanol-brine system. Polymer concentrations of up to 0.4 mM can be added to the phases without modification of their macroscopic characteristics. In order to study the elastic properties of polymer-containing sponge phases, we have performed DLS experiments. The decay of the DLS correlation functions is well described by the Zilman-Granek theory for all polymer concentrations, as expected for dilute membrane phases.

The decay times agree with the main peak of a CONTIN analysis of the DLS data. The main effect of the polymer is to increase the DLS relaxation times of the sponge phases, due to an increase in the bending elastic modulus κ of the membranes. The observed behavior is not predicted by available theories for the effect of adsorbing polymers on the elastic properties

of surfactant bilayers. This discrepancy is probably due to a complex adsorption mechanism, involving penetration of the polymer into the membrane and a possible local redistribution of the molecular species (SDS and hexanol) in the bilayer. Neither effect is taken into account by the available theories. Further experiments and computer simulations are needed in order to have a better insight into these effects.

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 - [40] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevE.84.011604> for additional figures.