Surfactant Curvilinear Diffusion in Giant Wormlike Micelles

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We present the first experimental measurements of surfactant curvilinear diffusion in giant wormlike micelles. The surfactant diffusion was monitored by pulsed field gradient NMR for various observation times t ranging from 0.020 to 1.5 s. The surfactant mean-square displacement was found to scale as $t^{1/2}$. A model of lateral diffusion along wormlike micellar aggregates with Gaussian statistics is found to describe the echo attenuation well. This type of diffusion is analogous to polymer segment diffusion in the tube-reptation model. [S0031-9007(98)06913-0]

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Several surfactants and lipids self-assemble in solution into very long wormlike micelles. These micellar solutions resemble in many ways polymer solutions, but there are also some particular differences (for a recent review, see Ref. [1]). The micellar contour length is not a constant but results from thermodynamic equilibrium and generally increases with the concentration. Because they are self-assembled aggregates of individual molecules, they also possess a finite lifetime, in contrast to polymer chains which are held together with covalent bonds. The micellar aggregates can break and recombine [2,3] and are therefore often referred to as "living polymers."

One micellar system which has been shown to contain giant wormlike micelles is the ternary lecithin/water/cyclohexane system, which has been studied extensively by Schurtenberger *et al.* [4–9]. Here, very long and flexible cylindrical reverse micelles are formed when a small amount of water, corresponding to 10 ± 4 water molecules per lecithin, is added to a solution of lecithin in cyclohexane (L_2 phase). This is an interesting model system since it is effectively nonionic, and Schurtenberger *et al.* have used this system to demonstrate the many similarities between such micellar solutions and classical polymer solutions. As we will see below, this system also appears to have unusually long micellar lifetimes which enable us to follow the surfactant curvilinear diffusion along the micellar contour in an NMR self-diffusion experiment. Most often, this is not possible due to a too rapid exchange of molecules between micelles and/or the influence of the reversible scission process [10–12].

In this paper we present lecithin self-diffusion data measured along a dilution line where the water-to-lecithin ratio was kept constant at 10 water molecules per lecithin. The micellar (lecithin plus water) volume fraction ϕ was varied in the range $0.038 \leq \phi \leq 0.24$. The lecithin self-diffusion was measured by pulsed field gradient (PFG) ^{1}H NMR experiments, on a Bruker DMX 200 instrument, applying the stimulated echo sequence with a phase cycling of 16 steps in order to isolate the desired echo. A stimulated echo sequence was used rather than the classical Hahn echo due to the rapid transverse relaxation of lecithin protons, which, in turn, is due to the slow reorientation of the very large lecithin aggregates. As a consequence, the time between the first two 90° pulses in the stimulated echo sequence was kept short and constant at 6 ms. The time between the second and third 90° pulse was varied between 14 and 1494 ms, corresponding to a variation of the gradient pulse separation between 20 and 1500 ms. The measurements were performed at fixed gradient pulse duration δ (3–5 ms) by varying the gradient magnitude G up to approximately 8 T/m. The echo attenuation was measured by recording the intensity of the trimethyl ammonium and terminal methyl protons in the spectra obtained by Fourier transform of the second half of the echo. A minor impurity, probably free fatty acids and lecithin monomers, gave a fast initial decay of the terminal methyl echo, and data were only collected after the complete relaxation of the impurity signal, where the echo attenuations of the terminal methyl and trimethyl ammonium signals were parallel. Experiments were performed for different values of t from 0.020 up to 1.5 s, hence, covering almost two decades in time. Soybean lecithin (Epicuron 200) was a generous gift of Lucas Meyer A.G. and was used without further purification. To minimize the intensity from the solvent protons we used perdeuterated cyclohexane purchased from Dr. Glaser, Basel, which was also used as received. Water was millipore filtered.

Within the short pulse limit ($\delta \ll t$), the normalized echo attenuation, $E(q,t)$, corresponds to the Fourier transform of the one-dimensional diffusion average propagator parallel to the applied magnetic field gradient (here, z direction). For a homogeneous and isotropic solution we may write [13]

$$E(q,t) = \int_{-\infty}^{\infty} dz\, P(z;t)\, \exp(iqz)\,. \tag{1}$$

Here, $q = \gamma G \delta$, where γ is the magnetogyric ratio of the nucleus (here, ^{1}H). The average diffusion propagator

$P(z;t)$ describes the probability that the molecule has diffused a distance z during a time t. In the PFG echo experiment the observation or diffusion time t is given by the time separation between the two gradient pulses. In a simple liquid, $P(z;t)$ is Gaussian,

$$P(z;t) = \frac{\exp(-z^2/4Dt)}{(4\pi Dt)^{1/2}}, \tag{2}$$

resulting in a Gaussian echo attenuation,

$$E(q,t) = \exp(-Dtq^2). \tag{3}$$

Experimental echo decays from two concentrations, $\phi = 0.054$ and 0.24, respectively, are shown in Fig. 1, plotted, as commonly done, on a semilogarithmic scale as $E(q,t)$ versus tq^2 (Stejskal-Tanner plot). Similar echo decays were observed at intermediate concentrations. As is seen, the data deviate significantly from a simple Gaussian diffusion behavior. In contrast to the prediction of Eq. (3), a straight line is not obtained in the Stejskal-Tanner plot and, moreover, we find a significant dependence on t.

When the average diffusion propagator which enters Eq. (1) is unknown, one can still determine the mean-square displacement $\langle z^2 \rangle$ from evaluating the initial slope of $E(q,t)$ when plotted as a function of q^2. In the limit of small q, we have

$$E(q,t) = \int_{-\infty}^{\infty} dz\, P(z;t)\left(1 - \frac{(qz)^2}{2}\right) = 1 - \frac{\langle z^2 \rangle q^2}{2}. \tag{4}$$

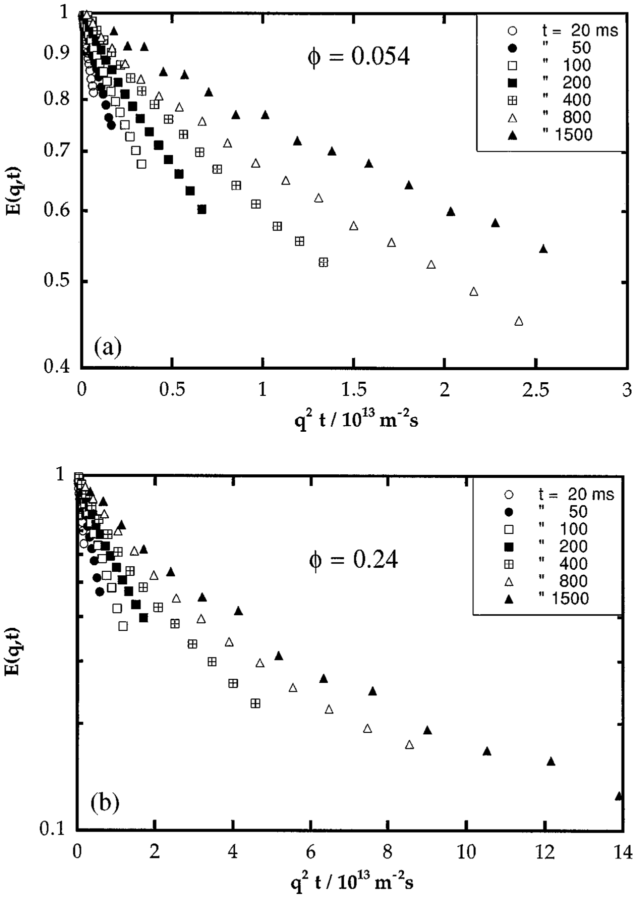

FIG. 1. Normalized echo attenuations from $\phi = 0.054$ (a) and $\phi = 0.24$ (b) measured at 25 °C plotted on a semilogarithmic scale as a function of $q^2 t$.

The mean-square displacement evaluated for some different concentrations is presented on a log-log scale as a function of t in Fig. 2. For ordinary free diffusion we have $\langle z^2 \rangle \sim t$. Here, however, we see a significantly different behavior, with $\langle z^2 \rangle$ rather scaling as $t^{1/2}$. As will be discussed below, this is the scaling expected if the diffusion mechanism observed corresponds to a lateral curvilinear diffusion along the micellar contour with Gaussian chain statistics. Such diffusion is analogous to the reptation diffusion of polymer chains in a tube, for times below the disentanglement time [14,15], where the reptation here is replaced by the lateral diffusion of surfactant monomers along the micellar contour. We also see in Fig. 2 that $\langle z^2 \rangle$ decreases slowly with increasing concentration. We will return to this observation below.

In a system of giant wormlike micelles the surfactant molecules are bound to the micelles, with a characteristic lifetime τ_1, where they are free to perform one-dimensional curvilinear diffusion along the micellar contour. If this lateral diffusion is the dominating mode of long range material transport, the average diffusion propagator $P(z;t)$ will be given by the one-dimensional lateral diffusion propagator $P_l(l;t)$, where l is a curvilinear distance along the micellar contour, modulated by a distribution function $\psi(z;l)$, describing the probability that a lateral displacement l corresponds to a displacement z in three-dimensional space. To sum up the contributions from all displacements, we integrate over all l to obtain

$$P(z;t) = \int_0^{\infty} dl\, P_l(l;t)\psi(z;l), \tag{5}$$

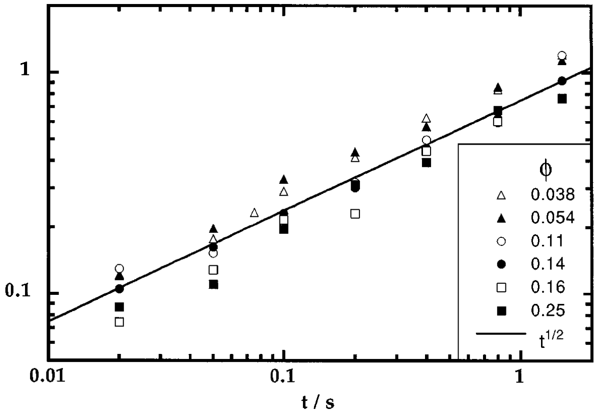

FIG. 2. Mean-square displacement $\langle z^2 \rangle$ as a function of the observation time. The different symbols correspond to different concentrations as indicated in the figure. The solid line shows the scaling $\langle z^2 \rangle \sim t^{1/2}$.

where we have assumed that the total contour length $L \gg \langle l^2 \rangle^{1/2}$ for the time window in our experiment (0.02–1.5 s), so that we can neglect end effects.

For the lateral diffusion we expect the usual one-dimensional diffusion propagator,

$$P_l(l;t) = \frac{\exp(-l^2/4D_l t)}{(\pi D_l t)^{1/2}}. \tag{6}$$

For the distribution function $\psi(z;l)$ we assume a Gaussian distribution (i.e., a Gaussian probability density for the end-to-end vector),

$$\psi(z;l) = \frac{\exp(-3z^2/4\lambda l)}{(4\pi\lambda l/3)^{1/2}}, \tag{7}$$

where λ is a characteristic step length which, for an isolated wormlike chain, could be identified with the persistence length. The second moment of the distribution function $\langle z^2 \rangle = 2\lambda l/3$ corresponds to the mean-square z projection of the end-to-end vector in the wormlike chain model in the limit $l/\lambda \to \infty$. The expression for the propagator obtained by combining Eqs. (5)–(7) is clearly non-Gaussian with a second moment given by [16]

$$\langle z^2 \rangle = \int_{-\infty}^{\infty} dz\, z^2 P(z;t) = \frac{4}{3}\lambda\left(\frac{D_l t}{\pi}\right)^{1/2}, \tag{8}$$

thus scaling as $t^{1/2}$ in accordance with the experimental observation (Fig. 2). The corresponding echo attenuation is given by

$$E(q,t) = \exp(x^2)\operatorname{erfc}\{x\}, \tag{9}$$

where

$$x = \frac{(D_l t)^{1/2}\lambda q^2}{3}. \tag{10}$$

This form of the echo attenuation, which has also been given by Fatkullin and Kimmich [17] in terms of the mean-square displacement, suggests that if the data are plotted, for example, as a function of $q^2 t^{1/2}$ all data points should fall on the same master curve. That this is indeed the case is demonstrated in Fig. 3, where the experimental data are replotted against $q^2 t^{1/2}$. Fits to the data, shown as solid lines, gave the values 1.05×10^{-13} and 9.1×10^{-14} m^2 s$^{-1/2}$ for $\phi = 0.054$ and 0.24, respectively, for the fitting parameter $D_l^{1/2}\lambda$.

As we saw in Fig. 2, there is only a weak concentration dependence of $\langle z^2 \rangle$. Using Eq. (8), the corresponding $D_l^{1/2}\lambda$ values were calculated and plotted in Fig. 4 as a function of ϕ. Assuming a power-law dependence, we find that $D_l^{1/2}\lambda$ scales as $\phi^{-0.24}$. This should be due predominantly to the concentration dependence of λ since we do not expect any significant concentration dependence of D_l in the present concentration range. Since we have approximately $\langle R_g^2 \rangle \sim \langle R^2 \rangle \sim \lambda$, where R_g is the radius of gyration and R is the end-to-end distance, we expect $\phi^{-0.24}$ to describe the concentration dependence of the effective micellar or chain dimension. In fact, the exponent -0.24 is very similar to the value -0.25 reported by Daoud *et al.* [18] for the concentration dependence of the radius of gyration of polystyrene in CS$_2$ and predicted by theory for polymers in good solvent [19]. It is also consistent with the related scaling $\phi^{-0.70}$ reported by Schurtenberger and Cavaco [5,7,8] for the correlation length and confirms the striking similarity between this micellar system and classical polymer solutions.

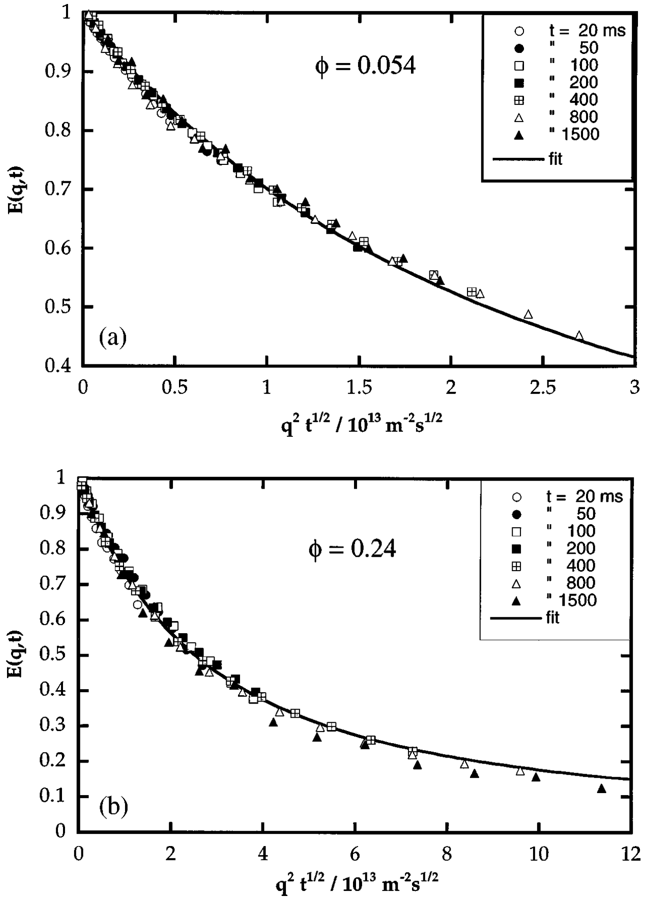

FIG. 3. Normalized echo attenuations from $\phi = 0.054$ (a) and $\phi = 0.24$ (b) measured at 25 °C plotted as a function of $q^2 t^{1/2}$. The solid lines are the best fits of Eqs. (9) and (10) to the data.

Unfortunately, there is at present too large uncertainty in D_l to make a reliable estimate of λ. In bilayers formed in the lamellar phase of the binary water-lecithin system, the lateral diffusion coefficient of lecithin is approximately 2×10^{-12} m^2 s^{-1} at room temperature [20]. If we calculate λ using this value for D_l we obtain λ values of the order of 700 Å which probably is a strong overestimate. From accurate small-angle neutron scattering studies on the same system, Schurtenberger *et al.* have persistence length $\lambda = 150$ Å [21]. In the present system, where the lecithin monolayer is swollen by cyclohexane, we expect D_l to be significantly higher than in the oil-free lamellar phase, possibly about 10^{-11} m^2 s^{-1}, as it has been measured recently in a bicontinuous microemulsion

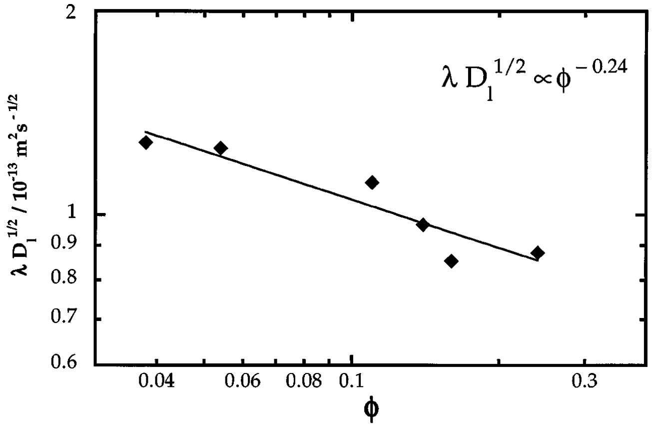

FIG. 4. Log-log plot of the concentration dependence of the parameter $D_l^{1/2}\lambda$, calculated from fitting Eq. (8) to the mean-square displacement data of Fig. 2. The solid line is a power-law fit to the data yielding $D_l^{1/2}\lambda = 6.1 \times 10^{-14}\phi^{-0.24}$ m^2 s$^{-1/2}$.

[22]. However, further discussion of this topic has to await an accurate determination of D_l.

From the observation of pure curvilinear diffusion up to an observation time of 1.5 s, a number of conclusions can be drawn. (i) The micellar contour lengths have to be very long. In the analysis of the experimental results we see no signs of end effects. This implies that the micellar contour length must be much longer than $\langle l^2 \rangle^{1/2}$ for the longest observation time 1.5 s. With this observation time and $D_l = 10^{-12}$ m^2 s^{-1} we have $\langle l^2 \rangle^{1/2} = 2$ μm. Thus, the micellar contour lengths have to be much longer than micrometers. (ii) The characteristic time for breaking the micelles also has to be very long. This is consistent with recent shear experiments, where a shear induced nematic phase needs several minutes to relax back to the liquid phase [23]. (iii) The micelles do not form branches, in which case we should have observed a simple Gaussian surfactant diffusion. (iv) The surfactant molecular lifetime in the micelle is longer than 1.5 s. When the lifetime is shorter than the experimental observation time the surfactant samples several micellar coils during the observation time. Keeping the analogy with polymer reptation, an exchange between micelles corresponds to tube renewal, and we would expect $\langle z^2 \rangle \sim t$ for the long time diffusion behavior. This is, in fact, the case for the water diffusion in the present system [24], which shows a simple Gaussian diffusion with a time independent diffusion coefficient. The much shorter lifetime of the water molecules makes them visit a large number of micelles on the experimental time scale.

In summary, we have presented, for the first time, experimental self-diffusion data from a wormlike micellar system which, in full consistency, can be interpreted in terms of pure curvilinear diffusion along the micellar contour. From the analysis, it also follows that the micellar contour lengths are much longer than 2 μm; in other words, they are giant wormlike objects.

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