

Thermal Fluctuations of Surfactant Films in Micellar and Microemulsion Systems

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Thermal fluctuations produce large undulations in surfactant layers when their bending elastic modulus is comparable to kT . We have studied long cylindrical micelles that become wormlike and lamellae that become spongelike due to these thermal fluctuations. We show that both structural and dynamic properties are strongly affected by the undulations.

Introduction

When dissolved in water or oil, surfactant molecules self-associate to form mono- or bilayers. Since the layers can have different spontaneous curvatures, the microstructures observed are extremely varied: spherical, tubular, or disklike micelles, lamellae, etc. We will be concerned in this paper with layers of small spontaneous curvature and investigate systems of long cylindrical micelles and lamellae. In these microstructures, the role of the bending elastic constant of the surfactant layer is very important. If the layer is stiff, cylindrical micelles form hexagonal phases when concentrated; lamellae order into lamellar phases. If the layer is flexible, micelles have wormlike shapes and entangle when concentrated, forming viscoelastic polymer-like semidilute solutions;¹ the lamellae do not exhibit long-range order either, and form spongelike phases.²

In this paper we present the results of experiments done with wormlike micelles and spongelike (bicontinuous) microemulsions. We have studied the self-diffusion of micelles with a photobleaching technique, and we present data supporting the polymer analogy. However, the micelles being transient aggregates, the self-diffusion process is a combination of reptation like with polymers and breakage of the micelles. In the case of spongelike microemulsions, we have been able to measure the bending elastic constant by studying the amplitude of the thermal fluctuations of the surfactant layers with ellipsometry. We present a correlation between the persistence length of the layers calculated from these data and the characteristic size in the microemulsion as determined with neutron scattering experiments.

Theoretical Background

The bending elasticity of surfactant layers per unit area is according to Helfrich³

$$F = \frac{1}{2}K(C_1 + C_2 - C_0)^2 + \bar{K}C_1C_2 \quad (1)$$

where K and \bar{K} are respectively the splay and saddle-splay bending elastic constants and C_1 and C_2 are the local principal curvatures of the layer and C_0 its spontaneous curvature. K and \bar{K} scale like energies. When they are comparable to kT , the thermal fluctuations strongly distort the layers. The competition between bending and thermal energy can be expressed in terms of the persistence

length. When C_0 is small, but nonzero, long micelles can be formed. The persistence length ξ is the average length of the straight portions of the micelles; micelles longer than ξ are wormlike. This definition of ξ is entirely analogous to the persistence length of polymers.⁴ Using eq 1, one can calculate⁵

$$\xi = a \frac{K}{kT} \quad (2)$$

where a is a molecular length.

When C_0 is about zero, the surfactant layers are locally flat. The persistence length is here the distance above which the correlations between the orientations of the normals to the layers are lost²

$$\xi = a \exp(2\pi K/kT) \quad (3)$$

At scales shorter than ξ , the lamellae are flat; at scales larger than ξ , they appear strongly wrinkled. The variation of the persistence length with K is different in eqs 2 and 3 because in the first case one deals with linear aggregates, whereas in the second the aggregates are two-dimensional. In the two calculations the second elastic constant \bar{K} was made equal to zero. We will come back to this point later.

Wormlike Micelles

The persistence length of long micelles is very difficult to determine experimentally. In ideal cases, when very long micelles form at very low surfactant concentration, ξ can be determined by neutron scattering experiments.⁶ In our systems (cetyltrimethylammonium bromide, CTAB, in potassium bromide aqueous solutions), the micelle length is not long enough in the dilute regime to allow determination of ξ in this way. However, the semidilute solutions can be well described in terms of flexible entangled polymers,⁷ and we will assume that in this regime, the micellar length is larger than ξ .

We have measured the self-diffusion coefficient D_S of the micelles by incorporating a fluorescent tracer into the micelles and using a fluorescence recovery after a fringe pattern photobleaching technique.⁸ The results are shown in Figure 1. In the semidilute regime D_S is a power function of the surfactant concentration, as in flexible polymers.

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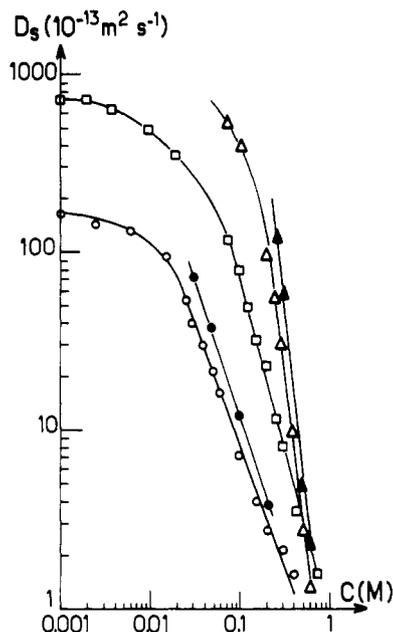


Figure 1. Self-diffusion coefficient versus CTAB concentration. The slopes of the linear portions are (open circles, 0.25 M KBr, 30 °C) 1.4, (filled circles, 0.25 M, 35 °C) 1.57, (squares, 0.1 M, 30 °C) 2, (open triangles, 0.05 M, 30 °C) 4.4, and (filled triangles, 0.05 M, 35 °C) 4.6. Reprinted with permission from ref 8. Copyright 1988 American Institute of Physics.

The polymer behavior was explained by de Gennes, assuming that the diffusion of a given chain is a reptation process within tubes formed by the other chains.⁴ This leads to

$$D_s \sim C^{-7/4} N^{-2} \quad (4)$$

where C is the concentration and N is the chain length in monomer units. In the case of micelles, N depends on concentration. Classical models give a polydisperse size distribution centered on a mean value N_0 , such as $N_0 \sim C^{1/2}$. This results in a *mean* diffusion coefficient

$$D_s \sim C^{-11/4} \quad (5)$$

Due to the polydispersity, one should observe in the fluorescence recovery signal a superposition of the exponential contributions of the different diffusion coefficients. The experiments show that this is the case in the dilute region (left points of the curves, Figure 1), but that the signal becomes exponential in the semidilute region although the polydispersity is larger. This paradox was explained by Cates by taking into account the micellar breakage events in the diffusion process. When the reptation time t_r is longer than the micelle average lifetime t_b , the diffusion process is a combination of breakage and reptation. It can be described by a *single* diffusion coefficient⁹

$$D_s \sim C^{-19/12} \quad (6)$$

The experimental slopes (Figure 1) are all larger, except the slope for the largest KBr concentration. The dependence of the slope on salinity was explained by Safran and co-workers:¹⁰ when the salinity is small, the ionic strength of the solution varies with surfactant concentration, and the growth law is modified (in Cates' model $N \sim C^{1/2}$). We have made experiments with CTAB at larger salinities

Table I. Measured and Renormalized Bending Elastic Moduli, Calculated Persistence Length, and Measured Characteristic Sizes for Nonionic Spongellike Microemulsions^a

system	measured $K(l)/kT$	scale $l, \text{\AA}$	renormalized $K(a)/kT$	$\xi, \text{\AA}$	$d, \text{\AA}$
C_8E_3	0.31	36	0.35	50	58
$C_{10}E_4$	0.51	12	0.76	188	187

^a Data from ref 13. We have taken $a = 7.5 \text{\AA}$.

and with wormlike micelles in organic solvents without salt (lecithin + variable traces of water in isooctane).¹¹ With these systems, we find $D_s \sim C^{-\alpha}$ with $\alpha = -1.35 \pm 0.05$, in reasonable agreement with Cates' predictions.

Spongellike Microemulsions

We have studied ternary mixtures water-alkane-nonionic surfactant (C_nE_m , n , alkyl; m , ethylene oxide). The spontaneous curvature of the surfactant layer vanishes in a temperature range depending on n , m , and the alkane chain length. We have studied C_8E_3 with decane and $C_{10}E_4$ with octane in order to set this temperature close to 25 °C.

We have measured the bending elastic constant of the surfactant layer by studying the thermal fluctuations of the layer at the interface between oil and water phases (these phases being saturated in surfactant monomers, but containing no aggregates).¹² The oil-water interfacial tension γ is ultralow because of the high surface pressure surfactant monolayer that forms at the interface. The amplitude of the thermal fluctuations at the interface is then large and depends on both γ and K .¹² The measured values are given in Table I, together with the persistence length calculated from

$$\xi = 2.117a \exp(3.254K(a)/kT) \quad (7)$$

taking into account the renormalization with scale of the bending constant.¹²

The structure of the microemulsions was studied by small-angle neutron scattering.¹³ The characteristic distances between oil and water microdomains were deduced from the positions of the scattering peaks by

$$d = \pi/q_{\max}$$

where q_{\max} is the scattering peak position in Fourier space. The values of d are reported in Table I.

There is a remarkable correlation between d and ξ . This is as predicted by theory^{2,14} and as observed in many other experimental systems.¹⁵ The spongellike microemulsions are therefore not completely random in the sense that the mean distance between oil and water microdomains is not arbitrary; it is fixed in average to a value close to the persistence length of the surfactant layer. The Gaussian or saddle splay bending constant \bar{K} is usually neglected but may have an important contribution to the persistence length.¹⁶ This problem is currently under investigation. In particular, at the temperatures where C_0 is nonzero and where microemulsion droplets are formed, the droplet polydispersity and the interfacial tension¹⁵ between the microemulsion and excess oil or water depend on K and \bar{K}

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in a different way. Due to the ellipsometry signal being independent of \bar{K} , combined interfacial and bulk structure experiments will be undertaken to clarify the issue.

Conclusion

We have studied surfactant systems where the spontaneous curvature of the surfactant layer is small and its bending elastic modulus is close to kT . In the case of polymer-like micelles, we have shown that the dynamic properties are very similar to those of entangled flexible polymers although the relaxation processes are faster due

to micelle breakage and recombination. In the case of spongelike microemulsions, we have studied their structural properties and shown that they are not completely random, in the sense that the mean distance between oil and water microdomains is close to the persistence length of the surfactant layer. The interplay between bending and thermal energies thus plays a very important role in these systems, affecting both their structural and dynamic properties.

Registry No. CTAB, 57-09-0; C_8E_3 , 19327-38-9; $C_{10}E_4$, 5703-94-6; KBr, 7758-02-3; decane, 124-18-5; octane, 111-65-9.