Surface Self-Diffusion in L_3 Phases

A. Maldonado,* W. Urbach, and D. Langevin†

Laboratoire de Physique Statistique de l'Ecole Normale Supérieure (associé aux universités Paris VI & VII et URA CNRS 1306), 24 rue Lhomond, 75231 Paris Cedex, France

Received: December 10, 1996; In Final Form: March 21, 1997[⊗]

The self-diffusion coefficient of amphiphilic probes in the L_3 phases of a surfactant system has been measured by fringe pattern photobleaching (FRAPP) experiments. The variation of the diffusion coefficients with the surfactant volume fraction is in agreement with a model for diffusion in cubic phases, which allows to determine approximately the topology of the phases. The observed variation of the diffusion coefficients with the probe lengths agrees with the free-area model for surfactant diffusion.

I. Introduction

Surfactant systems show a great variety of thermodynamic phases as the physicochemical conditions for the aggregation of their amphiphilic molecules are changed. In the case of surfactant−water systems, one can find phases with very different structural properties: simple aggregates such as spherical or cylindrical micelles; vesicles, where a bilayer encloses a volume of solvent; and more complex and continuous bilayer structures such as cubic, lamellar, and L_3 phases. The latter, also called sponge phase,[1−5] is formed by a disordered but connected array of bilayers that divides space into two independent solvent regions. Its structure has been very well characterized by small-angle X-ray and neutron scattering[2,3] as well as by freeze-fracture electron microscopy.[4,5] Macroscopically, it presents some interesting properties such as a very low viscosity and, in the dilute regime, flow birefringence.

Self-diffusion experiments (NMR, FRAPP, etc.) have been extensively used to investigate the physics of amphiphilic systems. For instance, the study of lateral diffusion of lipids and proteins in lipid bilayers has allowed a better understanding of membrane fluidity, a crucial property in some biological processes such as the electron-transfer chain of the inner mitochondrial membrane or the hormone signal transduction.[6] On the other hand, the analysis of self-diffusion data of amphiphiles and macromolecules such as polymers and proteins in monolayers at the air/water interface provides information about the monolayer dynamics, complementary to that obtained by other techniques such as surface light scattering or electrocapillary wave diffraction.[7] Another example of the utility of this kind of experimental approach, which permits the connectivity of complex surfactant phases to be tested, is the determinant role played by self-diffusion measurements to rule out a disklike structure for the L_3 phase and to establish its now well-confirmed continuous bilayer structure.[8,9]

In a previous work,[9] the self-diffusion coefficient of surface active molecules in the L_3 phase of a ternary system formed by water, hexanol, and zwitterionic surfactant (tetradecyldimethylamine oxide or C_{14}DMAO) has been measured in order to elucidate the microscopic structure of the phases. A rather constant diffusion coefficient was found, in agreement with a connected bilayer structure. Nevertheless, some questions were raised regarding the concentrated regime behavior and the effect of the size of the diffusing molecule on its motion.

The aim of the present work is to provide a more systematic study of the system in order to clarify these questions. The diffusing probes used in this work are fluorescein derivatives, modified in such a way that they have a hydrophobic tail which ensures their permanence in the bilayers of the phase. Whereas the diffusion coefficient of large integral membrane proteins in lipid bilayers shows a weak dependence upon the diffusing particle size as predicted by hydrodynamic theories,[10] for small amphiphilic molecules a substantial variation with the molecular weight has been found.[6] In the present work, we compare the diffusion coefficient of three amphiphilic molecules that differ only by the number of carbons in their hydrophobic tail and with another molecule of the same nature but displaying a double aliphatic chain.

In the next section, we give a brief theoretical background for self-diffusion in L_3 phases. In particular, we describe several numerical and analytical predictions for cubic phases as applied to L_3 phases, and furthermore we discuss facts of the free-area model for diffusion in liquid membranes. In section III we give experimental details of the work, and in section IV we present our results and their analysis.

II. Theoretical Section

Self-Diffusion in L_3 Phases. The L_3 or sponge phase is encountered in nonionic[3] and ionic[11] surfactant−water binary systems as well as in nonionic surfactant−alcohol−water[5] and ionic surfactant−alcohol−brine ternary systems.[12] Generally, the sponge phase is found in phase diagram regions close to a lamellar phase, and in some cases, both phases can be swollen almost to the same extent.[13]

Two complementary models have been proposed to account for the structural properties of the L_3 phase.

The random surface model[14] is able to predict some of the main characteristics of phase diagrams presenting lamellar and L_3 phases; it focuses mainly on the thermal fluctuations of the bilayers and describes the L_3 complexity by considering a highly randomized network of nonintersecting surfaces lying in a cubic lattice. The free energies are easy to compute, and the phase behavior can be related to the elasticity modulus of mean curvature of the bilayers K, the main prediction being that for large values of K as compared to k_BT the lamellar phase is stable, while for smaller K the lamellar to L_3 transition takes place (k_B is the Boltzmann's constant and T the temperature).

In the second model,[15] the lamellar to L_3 transition is related to the obvious difference in the topology between both phases and which is therefore controlled by the elasticity modulus of Gaussian curvature K. Smaller values of K will favor lamellar

† Actual address: Centre de Recherche Paul Pascal, Avenue A. Schweitzer, 33600 Pessac, France.

⊗ Abstract published in *Advance ACS Abstracts,* May 1, 1997.

S1089-5647(96)04039-4 CCC: $14.00

phases while higher values will produce complex topologies such as that of the L_3 phase. In fact, it can be shown that K for a bilayer is proportional to the spontaneous curvature c_0 of the constituent monolayers. Addition of a cosurfactant to a binary system modifies the spontaneous curvature of the monolayers. Changing c_0 will lead to variations in K and consequently the changes in topology that induce the lamellar to L_3 transition in our system.

Since the bilayers that form the L_3 phase are very disordered, the task of describing the diffusion of particles in its interior is very difficult. Nevertheless, model systems can be found in order to make theoretical predictions, which must be interpreted carefully when analyzing the L_3 phase. One such model system describes cubic phases, where the surfactant bilayers form a periodic structure with cubic symmetry. Anderson et al.[16] have provided a useful theoretical framework for the interpretation of self-diffusion measurements in cubic phases. Their results can be also applied to the geometrically more disordered but topologicaly related L_3 phase. Such identification is justified because the cubic and the L_3 phases have a very similar structure: they are locally formed by bilayers that are highly connected and divide space into two solvent regions, the main difference being the lack of long-range order in the L_3 phase, which can be pictured as a disordered or melted cubic phase. In fact, the similarity between these two phases has been quantified for the case of solvent and surfactant self-diffusion, where a certain continuity has been reported for the diffusion coefficients as one crosses the L_3-cubic transition.[8]

In this theoretical approach,[16] the geometrical obstruction factor β for the surfactant self-diffusion is computed by a two-dimensional finite element method, considering the surfactant molecules confined to a minimal surface which defines the cubic array of bilayers. In fact, this approach remains valid along any of the constant mean curvature structures, also called H surfaces, which are generalizations of minimal surfaces.[17,18] These surfaces are periodic in three dimensions, free of self-intersections, and divide space into two interpenetrating multiply connected regions. Several families of these structures are known, differing with respect to symmetry, topology, and local geometry.

At low surfactant concentrations, the variation of the self-diffusion coefficient D with the bilayer volume fraction ϕ can be written as

$$\beta = D/D_0 = \alpha + b\phi^2 \tag{1}$$

The value $\alpha = {}^2/_3$ in eq 1 is exact provided that diffusion takes place in a minimal surface of cubic symmetry, but experimental effects (like solvation) may modify it. The parameter b depends on the topology of the surface and has to be computed for every particular case. D_0 is the lateral diffusion coefficient in a plane bilayer.

Free-Area Model. Several models can describe the diffusive motion of a probe confined to a membrane as a function of its geometrical shape and size. The hydrodynamic-based models[19] are in good agreement with experiments only in the case when the hydrodynamic limit is valid, that is, when the diffusing particle is large compared to the molecules forming the membrane. Such is the case for membrane protein diffusion in lipid bilayers.[20] In our system, the size of the diffusing particles is comparable to that of the surfactant molecules in the bilayers; therefore, we have to use a microscopic model to describe their motion.

One of these theories, the free-area model, has been successfully used to describe the diffusion of lipids in bilayers[6] and of surface-active molecules in monolayers.[7] Although it may exist as a formal distinction between the monolayer and the bilayer case, it has been shown that in both cases the probe diffusion is based on the same molecular mechanism.[21] In its usual form,[22] the free-area model describes the diffusion of a particle as a three-step process: (1) density fluctuations in the membrane create a local free area in the neighborhood of the diffusing probe; (2) if the free area is large enough, the probe moves into this hole; and (3) the free area disappears as the surfactant molecules fill the void behind the probe. The repetition of this process gives the Brownian trajectory of the particle. Cohen et al.[23] have shown how this process can be quantitatively described by statistical thermodynamics and kinetic theory arguments for three-dimensional liquids. The same kind of ideas can be applied to two-dimensional liquid membranes, treating the diffusing probes as hard-disk-like particles. First of all, one has to compute the probability $P(a)$ of finding a free area in the membrane exceeding some value a^*, which can be written as

$$P(a^*) = \exp\left(-\frac{\gamma a^*}{af}\right) \tag{2}$$

where γ is a numerical factor, introduced to correct for overlap of the free areas (it lies between 0.5 and 1; if there is not such overlap $\gamma = 1$), and a_f is the mean free area per surfactant molecule. Now, from kinetic theory we can express the diffusion coefficient of monodisperse hard-disk particles moving in a plane with a mean free area per particle a as

$$D_a = gd(a)\, v \tag{3}$$

where g is a geometric factor, d the diameter of the available area to every hard-disk diffusing particle in the liquid matrix, and v the gas kinetic velocity of the probe. In a surfactant system, the diffusing hard-disk probe does not find a constant but a fluctuating mean free area in its surroundings. One can suppose that the contribution of one particle to the diffusion coefficient is zero unless it finds a free area large enough to jump into it. In other words, the diffusion coefficient of the probes that have a free area a in its surroundings is

$$D_a = \begin{cases} 0 & \text{if } a < a^* \\ D_{a^*} = gd^* v & \text{if } a > a^* \end{cases} \tag{4}$$

where a^* is related to the hard-disk cross section of the probe. If D_a varies slowly with a, its value can be approximated by D_{a^*}. In eq 4, d^* is the mean diameter of the available area to the diffusing particle, and it is of order of the molecular diameter of the surfactant molecules in the membrane. Then it can be easily shown[21] that the average diffusion coefficient is

$$D = D_{a^*}P(a^*) = gd^* v \exp(-\gamma a^*/a_f) \tag{5}$$

The kinetic velocity can be written as $v = (2k_BT/m)^{1/2}$ where k_B is Boltzmann's constant, T the temperature, and m the mass of the diffusing particle. Then

$$D = gd^*\left(\frac{2k_BT}{m}\right)^{1/2} \exp\left(-\frac{\gamma a^*}{a_f}\right) \tag{6}$$

To allow quantitative predictions from this equation, it is important to keep in mind which parameters refer to membrane properties and which ones refer to the moving probe characteristics. In this respect the most important facts are that a^* and m are respectively the hard-disk cross section and the mass of the probes while a_f is the free area per surfactant molecule. Thus, the effect of the geometrical dimensions of the probe on its diffusion is taken into account by a^* and m. A simplification can be done if one compares results for diffusion of particles with the same hard-disk cross section but different mass. In

this case, if diffusion occurs in the same membrane, we can obtain from eq 6

$$D\sqrt{m} = c \tag{7}$$

where c is a constant that depends on the membrane properties and on the diameter of the diffusing particles.

III. Experimental Section

Materials and Methods. Zwitterionic surfactant tetradecyldimethylamine oxide (C_{14}DMAO)[13,24] was obtained from Fluka and recrystallized twice; its cmc at 20 °C is 0.14 mM, and its density in the bilayer form is 0.891 g/mL. Hexanol was purchased from Merck and used as received. The water used as solvent was purified in a Millipore system.

Linear 5-(*N*-dodecanoylamino)fluorescein, 5-(*N*-hexadecanoylamino)fluorescein, and 5-(*N*-octadecanoylamino)fluorescein (respectively C_{12}, C_{16}, and C_{18} hereafter) and the double-chain (fluorescein DHPE) fluorescent probes were purchased from Molecular Probes. Their molecular weights are 529, 585, 613, and 1183, respectively. All these molecules have the same fluorescent polar head, but different hydrophobic tails. In the case of the linear molecules, we have aliphatic chains with 12, 16, and 18 carbon atoms, respectively, while fluorescein DHPE has a linear section equivalent to six carbon atoms which splits into two chains of 17 carbon atoms.

Experimental Technique. The fringe pattern fluorescence recovery after photobleaching technique (FRAPP) has been described in detail elsewhere.[25] Briefly, a fluorescent probe is homogeneously dissolved in the sample, and an irreversible destruction of the fluorescent groups is induced by a very brief, powerful laser pulse. A less powerful laser beam is used to monitor the fluorescence signal as diffusion of the probes leads to a new homogeneous concentration in the illuminated region of the sample. We use a Spectra Physics argon laser (400 mW at 4880 nm) for the photobleaching pulse; the weaker beam has a 1000 times smaller power. Both the bleaching and the monitoring beams are divided and superposed in the sample to create a fringe geometry. After the bleaching pulse, a piezoelectric crystal makes the monitoring beam sweep the bleached fringes in the sample, which reduces the noise to signal ratio in the recovery exponential signal. The diffusion coefficients are deduced from the characteristic times τ of the recovery curves by the classical relation $D = i^2/4\pi^2\tau$, where the interfrange values i are in the range 10−100 μm and the typical time values are from 0.1 to 10 s. The D values fitted to the above relation are obtained with an error smaller than 5%.

Samples Preparation. The phase diagram of our system is shown in Figure 1. The L_3 phase extends over a large range of surfactant concentrations. In this work, we have measured the self-diffusion coefficient of the fluorescein-modified molecules for L_3 phases with surfactant (plus cosurfactant) concentrations between 5 and 35 wt %. Since the fluorescence signal depends on the pH of the system, we have added a small amount (≈1 mM) of ammonium bicarbonate to keep pH near 8.5 and enhance the fluorescence emission. At this pH, C_{14}DMAO behaves like a nonionic surfactant. We have checked, using X-ray scattering data, that the addition of the buffer does not modify the phase diagram appreciably as compared to that with pure water. Furthermore, the addition of different probe molecules does not modify significantly neither the X-ray scattering spectra nor the phase diagram.

Although the diffusion coefficient of the probe is rather insensitive, within our experimental error, to its concentration, the fluorescent molecule is added in a concentration big enough to have a good signal but small enough to prevent the problems of a strong absorption of light (photomultiplier saturation or convection in the sample due to excessive heating by the absorbed bleaching beam). The optimal dye concentration (about 10^{-4} M) is too small to affect the phase diagram of the system.

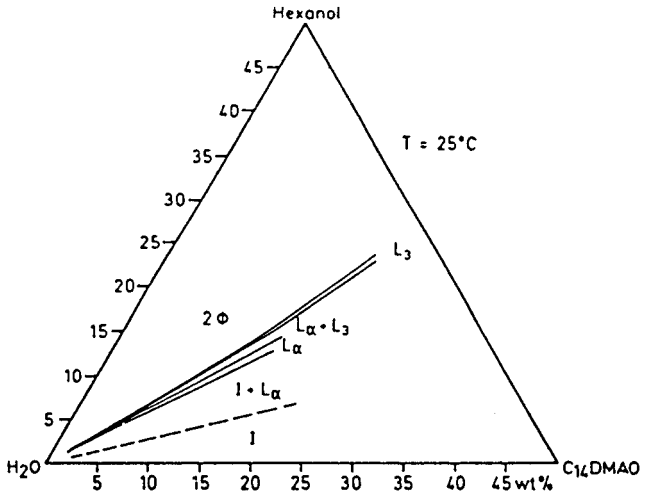

Figure 1. Phase diagram of the system C_{14}DMAO−hexanol−water at 25 °C from ref 13. The FRAPP experiments were performed in the concentration range between 5 and 35% (weight percentage of surfactant plus cosurfactant).

The samples prepared as described were put in Hellma quartz cells of 1 mm path length and kept at constant temperature (23 ± 0.1 °C) during the experiment.

IV. Results and Discussion

We have measured the self-diffusion coefficients of fluorescein-modified molecules in the bilayers of the L_3 phases of the water−C_{14}DMAO−hexanol system for several surfactant concentrations. The amphiphilic probe lies within the bilayers with the fluorescent head at the aqueous interface and the aliphatic tail in the interior of the surfactant region. There is a probability of having dye molecules dissolved in the solvent. If p is the fraction of such water-dissolved molecules, the observed diffusion coefficient is

$$D_{obs} = (1 - p)D_{bil} + pD_{vol} \tag{8}$$

where D_{obs} is the diffusion coefficient measured in the experiment and D_{bil} and D_{vol} are the diffusion coefficients of the dye in the bilayers and in the solvent, respectively. The recovery signals from the C_{12} probe solubilized in water are very poor (of the same order as the background noise), meaning that p is very small. Furthermore, using our experimental data, we have simulated the effect of the solubilized probe on the diffusion coefficient D_{obs}, and we have found that this contribution is negligible, in agreement with previously reported results.[26] The correction represented by eq 8 is therefore not required in our analysis.

In this section we consider two sets of data: the variation of D, the self-diffusion coefficient of the probes, with the surfactant concentration, and for the constant surfactant concentration, the D variation when the shape and the mass of the probe are changed. Figure 2a,b depicts experimental results for the self-diffusion coefficient of two of the fluorescein-modified molecules in the bilayers of a L_3 phase as a function of the bilayer volume fraction ϕ. We have represented only the curves for the shortest linear molecule and for the double-chained DHPE fluorescein since the results are qualitatively the same for all probes. In the dilute regime, a nearly constant diffusion coefficient is in agreement with previous results;[9] however, in the more concentrated regime the diffusion coefficient decreases

TABLE 1: Numerical Parameters Obtained from the Fits with Eq 1 of the Experimental Points for the Four Probes[a]

probe	$\alpha D_0 \times (10^{-7})$	$bD_0 \times (10^{-7})$	b
C_{12}	4.06	−3.95	−0.6468
C_{16}	3.92	−3.26	−0.5546
C_{18}	3.78	−3.55	−0.625
DHPE	3.30	−3.91	−0.7898

[a] The computed b values are close to those of the I−WP family of minimal surfaces reported in ref 16.

as ϕ increases. The experimental points are fitted to eq 1, indicating that the diffusion model for cubic phase is in good agreement with experimental diffusion data in L_3 phase for all bilayer volume fractions. Similar conclusions have been obtained for the AOT−brine system.[29]

The values obtained for αD_0 and bD_0 from our fits are listed in Table 1. The theoretical value of α is exactly $^2/_3$ for a cubic symmetry . To determine this value for our system, self-diffusion experiments must be performed in an oriented lamellar phase which allows the measurement of D_0. We have oriented a lamellar phase using the usual thermal treatment.[27] The sample, placed in a Hellma cell of 200 μm width, was heated above the lamellar-isotropic (L_3) transition and then slowly cooled to room temperature. (The cooling rate was 1 °C/h). All the processes were followed by optical microscopy between crossed polarizers. The thermal cycles were repeated until the lamellar was oriented with bilayes parallel to the cell walls. For the C_{12} fluorescein the D_0 value, measured with the FRAPP technique leads to $\alpha = 0.68 \pm 0.05$, in excellent agreement with theoretical prediction and previous results.[9]

From the b values one can, in principle, infer the minimal surface topology of our L_3 phase. Anderson et al. have calculated b values for only two topological families: P ($b = -0.45$) and I−WP ($b = -0.6$).[16] From our data the mean value of b (−0.654) is close to those of the I−WP family . A unit cell of an approximation to this periodic minimal surface is shown in ref 28; its genus per unit cell is 4, and the acronym I−WP comes from the fact that it is a body centered cubic structure (denoted I in crystallography), while its shape has some resemblance to a wrapped package (WP). However, this is not an unambiguous topology determination since we cannot compare it with more than two theoretical b values.

The free-area model of dye diffusion presented above leads, for dyes with identical projected area, to $D\sqrt{M} =$ constant. (M is the molecular weight of the probe.) To check this relation, we plotted $D\sqrt{M}$ versus the bilayer volume fraction, ϕ, for three different linear fluorescein molecules used in this work which differ in their chain lengths (Figure 3). Obviously, for a given ϕ value, $D\sqrt{M}$ is constant, within experimental error, which is in excellent agreement with theory as expressed in eq 7.

Equation 7 could still be used for the DHPE fluorescein. However, since its cross section is greater than that of the linear molecules, the self-diffusion coefficients measured for this double-chained molecule are smaller than those measured for the other probes by about 20%. Similar results have been found for double-chained lipids.[6] Since the DHPE molecule does not have a homogeneous cylindrical shape, the origin of these differences cannot be completely explained by eq 6.

Finally, eq 7 can be easily modified in order to emphasize the influence of the chain length of the diffusing molecule on self-diffusion coefficient. To do so let us expand eq 7 around given value of the mass M. This value can be the mass of the smallest dye molecule, i.e., the mass of the molecule with 12 carbons, M_{12}. The mass of the other molecules can be written as $M_{12} + \Delta M$, where ΔM is the extra mass as compared with the shortest molecule. If this extra mass is homogeneously distributed along the extra length of the chain ΔL, eq 7 can be

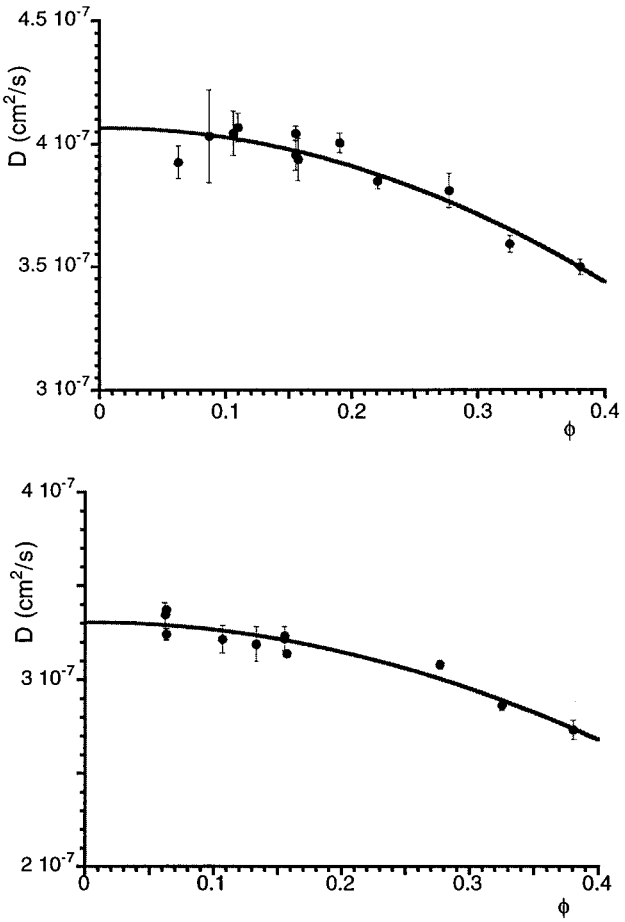

Figure 2. Self-diffusion coefficient D of fluorescein C_{12} (a, top) and DHPE (b, bottom) as a function of the surfactant volume fraction ϕ. The solid line is the prediction of the diffusion model for cubic phases applied to L_3 phases as expressed in eq 1.

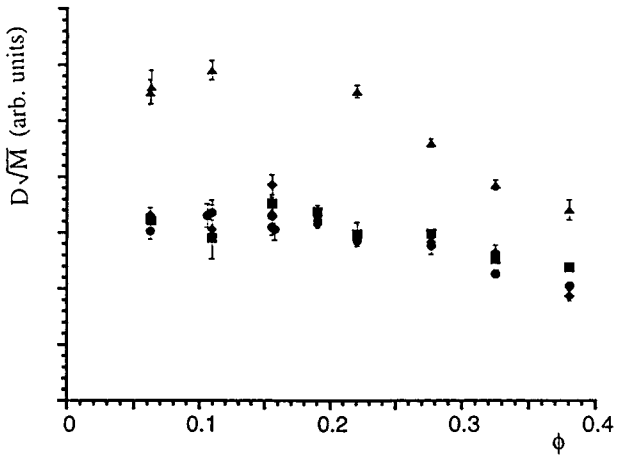

Figure 3. Application of the free-area model for the whole range of surfactant concentrations. For the linear probes (the symbols ●, ■, and ◆ represent the C_{12}, C_{16}, and C_{18} fluoresceins, respectively), the product $D\sqrt{M}$ is nearly constant for every surfactant concentration, as predicted by eq 7. The full triangles represent the DHPE fluorescein.

expanded to give

$$D = D_{12}\left(1 - \frac{a^*\rho}{2M_{12}}\Delta L\right) \tag{9}$$

where the subscripts 12 refer to the shortest fluorescein molecule, a^* is the common cross section of the cylindrical shaped molecules, and ρ is the mass density. The important prediction in this equation is a linear variation of the self-diffusion coefficient with the extra length of the chains. In

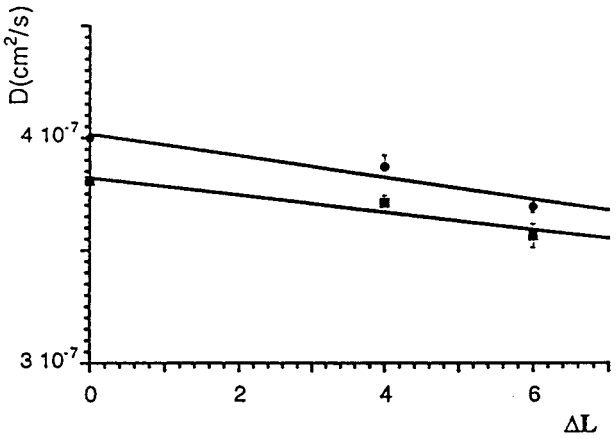

Figure 4. Variation of the self-diffusion coefficient D of the linear probes as a function of their length for a surfactant volume fraction $\phi = 0.19$ (circles) and $\phi = 0.27$ (squares). The straight lines are the best fits from eq 9. The length unit in the x axis is the carbon−carbon distance in the hydrophobic tail of the probes.

Figure 4 the self-diffusion coefficient as a function of ΔL is plotted for two surfactant concentrations, $\phi = 0.19$ and $\phi = 0.27$. (We have chosen the carbon−carbon distance in the hydrophobic tail as the length unit for ΔL. This length is of the order of 1 Å.) The best fits from eq 9 are also shown, confirming the utility of this equation to describe our data. Although no additional physical parameters can be found from these fits, the experimental slopes allow us to test the consistency of the model by estimating, for example, the probe cross section a^*. This parameter varies slightly with surfactant concentration, and its value, 20.85 ± 4.68 Å, is very reasonable for hydrophobic tail cross section of our probes, as compared with the surface per aliphatic chain measured in condensed monolayers. It should be emphasized that we are concerned by the long-time self-diffusion coefficient, and thus the diffusing molecules can be considered as cylinders whose dimension is the time-averaged volume occupied by the fluctuating molecule. This assumption is certainly valid since the typical fluctuation time of the "snaking" molecule hydrophobic tail is of the order of $t_R \approx 5 \times 10^{-10}$ s,[30] whereas the typical diffusion time over one molecular diameter ($d \approx 10$ Å) is $t_D = d^2/D \approx 10^{-7}$ s.

V. Conclusions

We have performed FRAPP experiments in the L_3 phase of the system C_{14}DMAO−hexanol−water. The use of similar probe particles has allowed us to study the effect of their size on their diffusive motion. Our results are in good agreement with the free-area model for the linear probes, in which the diffusion coefficient decreases linearly with the length of the diffusing particle. For the double-chained amphiphilic molecule, significant variations have been found, similar to those described in the literature for double-chained lipids. The fact that the free-area model is in good agreement with our diffusion results indicates that in the L_3 phase, which displays a complex geometry, the dynamics of the bilayers is very similar at the molecular level to that of flat bilayers.

In the dilute regime the self-diffusion coefficients for the amphiphilic molecules agree with those reported in a previous work.[9] In the more concentrated regime we have demonstrated a clear decrease in the diffusion coefficients which, in the framework of the model leading to eq 1, is due to the obstruction effect of the bilayer structure. Another possible explanation to this variation is to allow the D_0 coefficient in eq 1 to be dependent on ϕ, as it was necessary in order to explain the results in the AOT−brine system.[29] However, for our system we assume a ϕ-independent D_0, at least in the range of validity of eq 1; this assumption is reasonable since D_0 must only depend on the local conformation of the lamellar bilayers (thickness, surface area per polar head, etc.) which does not change appreciably in the dilution line studied, as shown by X-ray scattering.[31]

The concentration dependence of the diffusion coefficient is well described by a model elaborated for diffusion in minimal surfaces. From $D(\phi)$ variation one can extract a topological parameter, b, whose value is closely related to the topology of the phase. To best of our knowledge, b values heave been computed for only two different topologies. The b value extracted from our data suggest a I−WP topology for L_3 phase of C_{14}DMAO. However, more theoretical b values would be needed in order to unambiguously assign a topology to our system.

Finally, more accurate theories of diffusion in L_3 phases should take into account dynamic effects such as thermal fluctuations and the tearing of the surfactant bilayers, which certainly affect the motion of the particles along the membranes.

Acknowledgment. We thank M. Waks for the critical reading of the manuscript. A.M. acknowledges a grant from the Consejo Nacional de Ciencia y Tecnología (Conacyt), México.

References and Notes

(1) Porte, G. *J. Phys.: Condens. Matter* **1992**, *4*, 8649.
(2) Gazeau, D.; Bellocq, A. M.; Roux, D.; Zemb, T. *Europhys. Lett.*. **1989**, *9*, 447.
(3) Strey, R.; Winkler, J.; Magid, L. *J. Phys. Chem.* **1991**, *95*, 7502.
(4) Strey, W.; Jahn, W.; Porte, G.; Bassereau, P. *Langmuir* **1990**, *6*, 1635.
(5) Hoffmann, H.; Thunig, C.; Munkert, U. *Langmuir* **1992**, *8*, 2629.
(6) Sackman, E.; Engelhardt, J.; Fricke, K.; Gaub, H. *Colloids Surf.* **1984**, *10*, 321.
(7) Kim, S.; Yu, H. *J. Phys. Chem.* **1992**, *96*, 4034.
(8) Balinov, B.; Olsson, U.; Söderman, O. *J. Phys. Chem.* **1991**, *95*, 5931.
(9) Ott, A.; Urbach, W.; Langevin, D.; Hoffmann, H. *Langmuir* **1992**, *8*, 345.
(10) Vaz, W. L. C.; Criado, M.; Madeira, V. M. C.; Schoellmann, G.; Jovin, T. M. *Biochemistry* **1982**, *21*, 5608.
(11) Radlinska, E.; Zemb, T.; Dalbiez, J.-P.; Ninham, B. *Langmuir* **1993**, *9*, 2844.
(12) Ghosh, O.; Miller, C. A. *J. Phys. Chem.* **1987**, *91*, 4528.
(13) Miller, C. A.; Gradzielski, M.; Hoffmann, H.; Krämer, U.; Thunig, C. *Prog. Colloid Polym. Sci.* **1991**, *84*, 1.
(14) Cates, M. E.; Roux, D.; Andelman, D.; Milner, S. T.; Safran, S. A. *Europhys. Lett.* **1988**, *5*, 733.
(15) Porte, G.; Appell, J.; Bassereau, P.; Marignan, J. *J. Phys. (Paris)* **1989**, *50*, 1335.
(16) Anderson, D. M.; Wennerström, H. *J. Phys. Chem.* **1990**, *94*, 8683.
(17) Goetz, A. *Introduction to Differential Geometry*; Addison-Wesley: Reading, MA, 1970.
(18) Nitsche, J. C. C. *Lectures on Minimal Surfaces*; Cambridge University: Cambridge, MA, 1989, Vol. 1.
(19) Saffman, P. G.; Delbrück, M. *Proc. Natl. Acad. Sci. U.S.A.*. **1975**, *72*, 3111.
(20) Tamm, L. K. *Biochim. Biophys. Acta* **1991**, *1071*, 123.
(21) Peters, R.; Beck, K. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 7183.
(22) Galla, H. J.; Hartmann, W.; Theilen, U.; Sackmann, E. *J. Membr. Biol.* **1979**, *48*, 215.
(23) Cohen, M. H.; Turnbull, D. *J. Chem. Phys.* **1959**, *31*, 1164.
(24) Rörig, H.; Stephan, R. In *Industrial Applications of Surfactants II*; Karsa, D. R., Ed.; Royal Society of Chemistry: London, 1990.
(25) Messager, R.; Ott, A.; Chatenay, D.; Urbach, W; Langevin, D. *Phys. Rev. Lett.* **1988**, *60*, 1410 and references therein.
(26) Lindman, B.; Olsson, U.; Wennerström, H. *Langmuir* **1993**, *9*, 625.
(27) See for example: Zhang, C. Y.; Sprunt, S.; Litster, J. D. *Phys. Rev. E* **1993**, *48*, 2850.
(28) Hyde, S. T. *J. Phys., Colloq.* **1990**, *51*, C7-209.
(29) Olsson, U.; Balinov, B.; Söderman, O. In *The Structure and Conformation of Amphiphilic Membranes;* Lipowski, R., Richter, D., Kremer, K., Eds.; Springer Proceedings in Physics 66; Springer-Verlag: Berlin, 1992.
(30) Pfeiffer, W.; Henkel, Th.; Sackmann, E.; Knoll, W.; Richter, D. *Europhys. Lett.* **1989**, *8*, 201.
(31) Maldonado, A.; Urbach, W.; Ober, R.; Langevin, D. *Phys. Rev. E* **1996**, *54*, 1774.