

Confined Diffusion in a Sponge Phase

Amir Maldonado,^{*,†} Claude Nicot,[‡] Marcel Waks,[‡] Raymond Ober,[§] Wladimir Urbach,[†] and Dominique Langevin^{†,#}

Laboratoire de Physique Statistique, URA 1302 CNRS, Ecole Normale Supérieure, 24, rue Lhomond, 75231 Paris CEDEX, France, Laboratoire d'Imagerie Paramétrique, UMR 7623 CNRS, Université Pierre et Marie Curie, 15, rue de l'Ecole de Médecine, 75006 Paris CEDEX, France, and Laboratoire de Physique de la Matière Condensée, URA 792 CNRS, Collège de France, 11, Place Marcelin Berthelot, 75231 Paris CEDEX, France

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Three water-soluble probes with different hydrodynamic radii have been studied by self-diffusion experiments in the sponge (L_3) phases of a zwitterionic surfactant system. In all cases, the self-diffusion coefficient varies linearly with the bilayer volume fraction. The available theories for rigid porous media cannot completely explain our results. Deviations from theoretical predictions appear for bilayer volume fractions greater than 0.2. The L_3 phase cannot be therefore pictured as a disordered network of rigid surfaces at least for transport behavior.

1. Introduction

In recent years there has been a growing interest in the physics of surfactant systems mixed with polymers¹ and colloidal particles.^{2,3} The modification of the phase diagram of surfactant solutions after addition of polymers or colloidal particles has been studied both theoretically and experimentally^{4–6}. Furthermore, transport properties in these complex systems have also been the object of several studies. For example, the variation of the diffusion coefficient of magnetic particles has been determined as a function of the confining distance between the bilayers of a lamellar phase.⁷

On the other hand, theoretical and experimental work has been devoted to the investigation of confined diffusion in disordered media. Porous materials have provided a useful experimental tool to understand the Brownian motion of large and small particles in a complex confining geometry.⁸ For instance, Coffman et al. have reported diffusion results for several proteins in chromatographic media.⁹ In a related problem, the diffusion of Brownian particles has also been studied in bicontinuous surfactant systems, such as cubic or sponge phases.¹⁰

In this paper, we report experimental measurements of self-diffusion coefficients of a polar molecule (fluorescein) as well as of two water-soluble proteins in the aqueous space between the bilayers of a sponge surfactant phase. Our aim is to understand the confining effects of the walls defined by the bilayers on the diffusive motion of the particles. The paper is divided as follows. In section 2 we briefly recall some theoretical results concerning polymer–surfactant systems and self-diffusion in a confined geometry. In section 3 we describe the experimental techniques used and the methods used for prepar-

ing the samples. Finally, in section 4 we present and discuss our experimental results and in section 5 we draw some conclusions.

2. Theoretical Section

2.1. Surfactant Phases Swollen with Polymers or Colloidal Particles. Sponge or L_3 phases are formed by a continuous, randomly connected isotropic network of surfactant bilayers.¹¹ Their structure has been well characterized by freeze-fracture electron microscopy and by small-angle X-ray or neutron scattering. Because these phases lack long-range order, only a wide Bragg peak, related to a characteristic distance d in the system, appears in the scattering spectra. The peak position, $q_{\max} = 2\pi/d$, allows one to follow the swelling of the sponge phase, that is, the variation of d as a function of the bilayer volume fraction.

Engblom and Hyde have used the minimal surface model to analyze the swelling behavior of L_3 phases.¹² Their model predicts two different swelling modes: In the first one, the bilayer thickness remains unchanged during the swelling, and one finds the classical linear law¹³ $q_{\max} = \alpha\phi/\delta$, where ϕ is the surfactant volume fraction, δ is the bilayer thickness, and α is a constant on the order of 1.5. In the second mode, the bilayer thickness varies in order to preserve the position of the neutral surface, that is, of the surface where the area per amphiphilic molecule is constant.¹⁴ In this case, the swelling law is modified by a cubic term $\phi = aq_{\max} + bq_{\max}^3$, where the constants a and b are related to the topology of the phase; their values allow one to determine the position of the neutral surface, if this topology is known.¹²

In the literature one can find several experimental results on the swelling of lamellar phases with polymer or colloidal solutions. For instance, Ligoure et al.¹⁵ have investigated an electrostatically stabilized lamellar phase diluted with a charged (nonadsorbing) polymer solution. These authors show that regardless of the charge content, the polymer molecules are confined between the bilayers. Singh et al.¹⁶ have studied a similar system and found that the phase diagram is not

* Author to whom correspondence should be addressed. Present address: Departamento de Física, Universidad de Sonora, Apdo Postal 1626, 83000 Hermosillo, Sonora, Mexico. E-mail: maldona@fisica.uson.mx.

[†] Ecole Normale Supérieure.

[‡] Université Pierre et Marie Curie.

[§] Collège de France.

[#] Present address: Laboratoire de Physique des Solides, UMR 8502, Université Paris-Sud, Bât. 510, 91405 Orsay Cedex, France.

fundamentally modified by the addition of polymer, which gives a decrease of the interlamellar spacing in the more dilute samples. Ficheux et al.¹⁷ have been able to solubilize up to 50% of a water-soluble neutral polymer in an ionic lamellar phase. On the other hand, Radlinska et al.¹⁸ have studied a nonionic lamellar phase swollen by a highly hydrophobic polymer and showed that the polymer molecules induce both local deformation and softening of the bilayers.

A different but related system has been systematically studied by Quilliet et al.;² in these studies, a lamellar phase is swollen with a suspension of colloidal magnetic particles, creating a ferrosmectic phase. In particular, they performed dynamic light-scattering experiments in order to measure the diffusion coefficient of the magnetic particles D between the bilayers of the oriented lamellar phase.⁹ These authors found that D is highly anisotropic; its value is zero within experimental error in the direction perpendicular to the bilayers and is smaller than the free-diffusion coefficient in the direction parallel to the bilayers. The observed decrease of D as a function of the interbilayer distance d is less steep than that predicted by the Faxen theory, described briefly afterward (section 2.2).

From a theoretical point of view, Brooks and Cates⁴ have computed the phase diagram of a (nonadsorbing) polymer-surfactant system, showing that unbound lamellar phases, that is, those stabilized by Helfrich interactions, expel the polymer if the bilayers are flexible enough. Because the lamellar and sponge phases are made of identical bilayers, although organized in a different way, it seems reasonable to conceive that the same qualitative behavior can be found in both systems, for the swelling by polymers.

2.2. Confined Diffusion. Several theoretical models have been developed in order to understand diffusion in confined geometries. Faxen¹⁹ has studied the motion of a spherical particle of radius r between two rigid walls separated by a distance d . He computed the diffusion coefficient from the hydrodynamic drag on the particle and found a linear law:

$$D = D_0 \left(1 - 2.01 \frac{r}{d} + O\left(\frac{r}{d}\right)^3 \right) \quad (1)$$

where D_0 is the free-diffusion coefficient. When applied to the ferrosmectic phase, this model gives a significantly steeper decrease than what is observed.⁹

In the case of an L_3 phase one can use the two-rigid-walls model as a first approximation, but a more detailed model should take into account the obstruction effect brought about by the disordered bilayer structure. Along these lines the hydrodynamical models developed for porous materials can give useful insights. Such models assume that the particle of radius r diffuses in a cylindrical pore of diameter d . In this case, the diffusion coefficient follows a nonlinear law known as the Renkin equation:²⁰

$$D = D_0(1 - \lambda)(1 - 2.104\lambda + 2.089\lambda^3 - 0.948\lambda^5) \quad (2)$$

which is valid for $\lambda \equiv 2r/d < 0.3$.

Frequently, in eq 2 D_0 is divided by a factor κ introduced to take into account the tortuosity of the media. For an isotropic porous material the κ value is expected to be 2.^{8,9} Brenner and Gaydos also derived asymptotic expressions for the diffusion coefficient in porous media for both small and large values of λ .²¹

Another interesting approach, suitable for L_3 phases, has been proposed by Anderson and Wennerström.¹⁰ They also modeled the L_3 bilayer structure with a mathematical minimal surface,

which allows one to write and numerically solve the bulk diffusion equation for different symmetries and topologies of the system. Their main result for the diffusion of point particles in the solvent of an L_3 phase can be summarized by the following equation:

$$D = D_0(a_v - b_v\phi) \quad (3)$$

where ϕ is the bilayer volume fraction, $a_v \sim 0.6$ (roughly independent of the topology), and b_v is a constant which depends on topology and increases with increasing coordination number. To express the equation in terms of $\lambda = 2r/d$, one can use the swelling laws computed for an L_3 phase together with $q_{\max} = 2\pi/d$. Equation 3 has been successfully used to account for water diffusion in the L_3 phase of the AOT-water-NaCl system.²⁶

3. Experimental Section

The sponge or L_3 phases are prepared in the ternary system formed by a zwitterionic surfactant (tetradecyldimethylaminoxide or C₁₄DMAO), a short-chain alcohol (hexanol) as cosurfactant, and water as solvent. The phase diagram has been extensively studied by Hoffmann and co-workers²² and displays a large range of surfactant volume fractions where the L_3 phase is stable. The characteristic distance d can be varied from values as small as 80 Å to values on the order of 1000 Å.

The swelling behavior of the L_3 phase has been studied by small-angle X-ray scattering (SAXS).²³ We used a Rigaku rotating anode source producing the CuK α lines (1.54 Å) with a fine focus (1 mm \times 0.1 mm). The output was collimated by a gold-plated quartz mirror. The linear detector, with 512 channels, was placed at a distance of 81 cm from the sample position. The resolution of the direct beam was measured to be $\Delta q = 0.0017 \text{ \AA}^{-1}$ full width at half-maximum. The collimation corrections were negligible.

The self-diffusion coefficient was measured by the fluorescence recovery after photobleaching (FRAPP) technique as described in a previous paper.²⁴ Three fluorescent probes were used: fluorescein and two proteins. The proteins have large hydrodynamic radii; human erythrocyte carbonic anhydrase (CA, Sigma C4396) is almost spherical and human serum albumin (HSA, Sigma A3782) displays a prolate form. These proteins are well-defined particles, both in size and shape, which makes them useful for probing diffusion.

To measure the diffusion coefficient of the proteins by the FRAPP technique, we have covalently attached a fluorescent probe to their surfaces. Their overall hydrodynamic properties are not appreciably modified by the labeling procedure. Briefly, proteins were dissolved in a 0.1 M borate solution (pH = 9.2). The fluorescent label, fluorescein isothiocyanate (FITC, Sigma), was dissolved in dimethylformamide (Merck). For carbonic anhydrase, 0.7 μM of FITC (in 20 μL of dimethylformamide) was added in increments of 5 μL to 0.15 μM of protein solubilized in 1 mL of the borate solution. For human serum albumin, 0.9 μM of FITC (in 60 μL of dimethylformamide) was added in increments of 10 μL to 0.47 μM of the protein solubilized in 3 mL of the borate solution. The mixtures were vigorously stirred at 0 °C for 20 min and left overnight at 4 °C with slow mixing. To separate the labeled protein from unbound dye, the solution was filtered through a Sephadex G15 (Pharmacia) column (13 \times 1.5 cm) equilibrated with a 1% ammonium bicarbonate solution. Pure labeled protein solutions were then lyophilized twice.

To determine the molar ratio of bound dye per protein molecule, the absorption spectra of protein solutions were

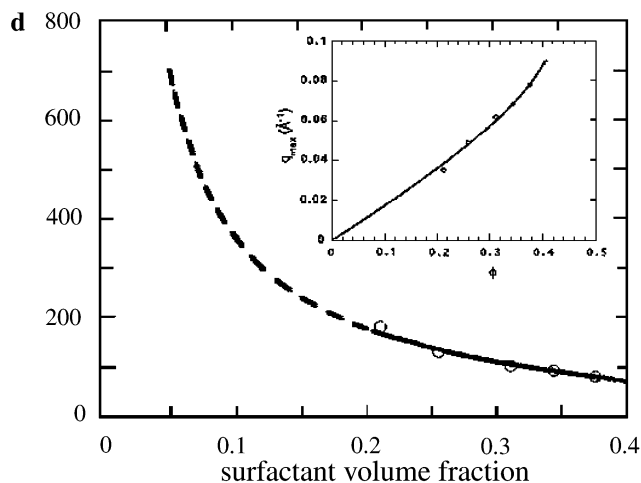


Figure 1. Swelling behavior of the L_3 phase from SAXS experiments.²³ The solid line is the best fit to the data, measured in the $\phi = 0.2$ – 0.4 range; the broken line is an extrapolation of the fit. The inset shows the corresponding q_{\max} data with the fit to the theoretical model of ref 12.

measured on a Cary model 118 spectrophotometer. The molar extinction coefficients used were $3.5 \times 10^{-4} \text{ cm}^{-1}$ at 280 nm for human serum albumin and $4.5 \times 10^{-4} \text{ cm}^{-1}$ at 280 nm for carbonic anhydrase. For the bound dye, the molar extinction coefficient was $7.2 \times 10^{-4} \text{ cm}^{-1}$ at 496 nm, and its contribution at 280 nm was $3.0 \times 10^{-4} \text{ cm}^{-1}$. At the end of the above procedure, 0.7 dye molecules were bound per CA molecule and 1.2 dye molecules were bound per HSA molecule.

In addition, we have also measured the diffusion coefficient of a smaller probe, fluorescein (purchased from Molecular Probes); its hydrodynamic radius is 5 Å in pure water. To all the samples a small amount (20 mM) of NaOH was added, to obtain an optimal pH value for the fluorescence emission (pH > 8). The fluorescence emission spectra of the probes were tested after solubilization in the L_3 phases with a three-dimensional (3D) spectrofluorimeter (Jobin-Yvon). The ion mobility in the L_3 phases (using a 60 mM solution of NaBr as solvent) was tested by conductivity measurements in a Melström apparatus.

4. Results and Discussion

The study of the swelling behavior of our L_3 phases has been reported in a previous paper.²³ The X-ray scattering spectra display a maximum which is related to the L_3 phase characteristic distance d . The variation of q_{\max} with the bilayer volume fraction ϕ can only be explained with the cubic swelling mode of the Engblom and Hyde theory.¹² The characteristic distance can be calculated from experimental points, with $d = 2\pi/q_{\max}$, or from an extrapolation using the theoretical fit. In Figure 1 we show the variation of d with ϕ in the L_3 phases. We use this curve to define the confining distance for the diffusing probes at smaller surfactant concentrations, where the peak can no longer be seen with our X-ray experiment.

The sponge and lamellar regions of the phase diagram of our system are not appreciably modified after addition of either the proteins or of fluorescein. The protein and probe concentrations were large enough to yield a good fluorescence recovery signal and small enough to avoid a strong absorption of light which can produce signal distortion and also heat convection in the samples. The concentration of all three fluorescent probes studied (fluorescein, CA, and HSA) was on the order of 10^{-5} M. The signal-to-noise ratio in the fluorescence recovery was similar for the different probes.

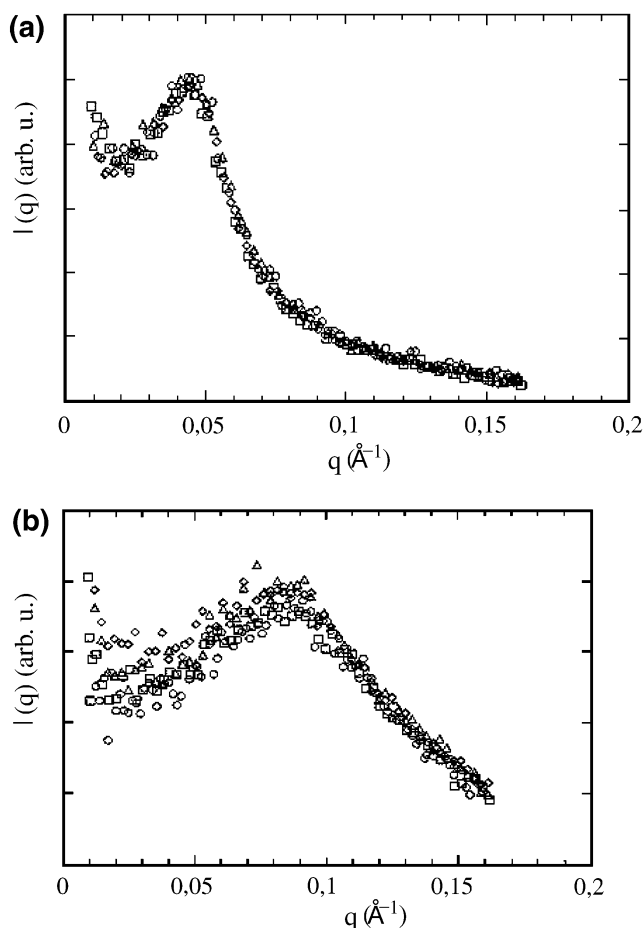


Figure 2. Scattering spectra for sponge phases with (a) $\phi = 0.2$ and (b) $\phi = 0.37$. In both cases the carbonic anhydrase concentrations are as follows: 0 M (circles), 0.1×10^{-5} M (squares), 0.5×10^{-5} M (triangles), and 1×10^{-5} M (diamonds). The Bragg peak position and the interbilayer distance do not change when the proteins are solubilized.

TABLE 1: Hydrodynamic Radii of Carbonic Anhydrase and Human Serum Albumin as Determined by the FRAPP Technique in an Aqueous Solution and in a Saturated Solution of C_{14} DMAO and Hexanol (See Text)

solvent	R_{AC} (Å)	R_{HSA} (Å)
aqueous solution	23 ± 1.1	41 ± 2
saturated solution	24.3 ± 0.4	43.5 ± 1.6

The scattering spectra of the sponge phases were not modified when the optimal amount of protein was added (about 10^{-5} M). In parts a and b of Figure 2 we show two sets of spectra for $\phi = 0.2$ and $\phi = 0.37$, respectively, where the concentration of CA is varied. The main features, particularly the Bragg peak position of the curves, are identical. This means that the interbilayer distances measured in the swelling of the protein-free phases²³ can be used for the analysis of the protein-containing phases.

Because we are investigating the effect of confinement on the diffusion of the proteins, their form or size should not change substantially when dissolved into the L_3 phase solvent which contains surfactant monomers. To verify that the proteins are not substantially modified in our system, we measured their free-diffusion coefficient in water and in a saturated solution of C_{14} -DMAO (around the critical micelle concentration (cmc)) and hexanol. This experiment allows one to determine their hydrodynamical radii, which were found to be unchanged within experimental error (see Table 1). These results indicate that the

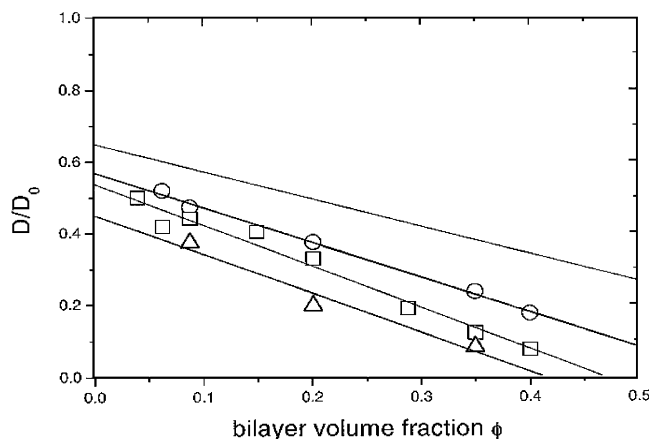


Figure 3. Self-diffusion coefficient of the three fluorescent probes, as a function of the bilayer volume fraction. Circles represent fluorescein, squares represent the carbonic anhydrase, and triangles represent the human serum albumin. The error bars are smaller than the size of the symbols. Obviously, for the same interbilayer distance (same ϕ) the obstruction effects are more important for the molecules larger than the fluorescein molecule. The straight lines are linear fits to experimental data. The upper line represents water diffusion in the AOT–brine system.²⁶

overall size of the proteins is not appreciably modified by the presence of surfactant.

To study the effect of the confining bilayers, we have measured the self-diffusion coefficient D of our probes in L_3 phases of surfactant volume fractions ranging from 0.05 to 0.4. In Figure 3 we plot D/D_0 for the three probes as a function of the bilayer volume fraction. D_0 is the diffusion coefficient of each probe in bulk water. In all cases we observe a smooth decrease in D/D_0 when the confining distance decreases (when ϕ increases). Such a behavior can be approximated by a linear law, similar to that predicted by the Anderson–Wennerström model for point particles (see section 2). It would be interesting to compare our results with NMR data for water diffusion (with the FRAPP technique we cannot follow water diffusion). Unfortunately, no NMR study of our systems is available. We have chosen to add in Figure 3 a line indicating the variation of the water self-diffusion coefficient in the AOT–brine L_3 phase.^{10,26} This system should behave in a way similar to that of our nonionic system since the electrostatic interactions are screened by brine. The slopes measured with our probes are steeper than those for water self-diffusion. We attribute this difference to the effect of walls on the Brownian motion of our probes, which is more important for larger ϕ values, thus smaller confining distances, as expected. The observed linear behavior also indicates that the probes do not adsorb to the bilayers of the system. If adsorption were an important effect, the diffusion coefficient would remain essentially constant for surfactant volume fractions up to 0.2, as observed for amphiphilic probes diffusing along the bilayers and not between them.²⁵

To clarify the influence of the interbilayer distance d on the diffusion of the particles, we plot D/D_0 as a function of $\lambda = 2r/d$ for the two proteins (Figure 4) where r is the radius of the diffusing particle. Again, we find a remarkably linear behavior, qualitatively similar to that observed in the ferrosmectic phase.⁷ The linear decrease observed is qualitatively similar to the behavior of proteins in chromatographic columns made of methacrylate and porous silica which are rigid porous materials.⁹ However, the slope is about 25% steeper in the L_3 phase, probably because of the flexibility of the surfactant bilayers. In fact, this flexibility gives rise to spatial fluctuations (undulations) which effectively reduce the interbilayer distance and thus can

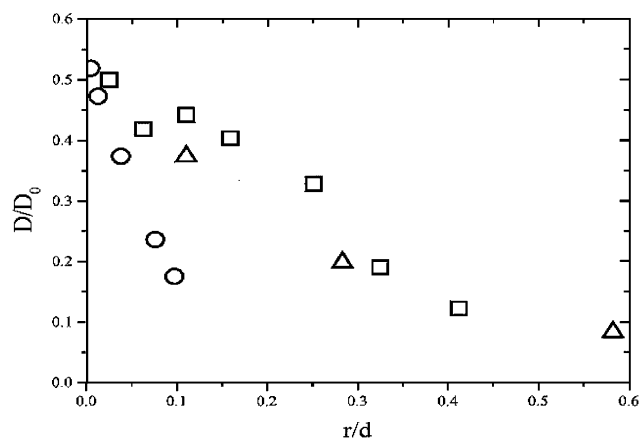


Figure 4. Reduced diffusion coefficient vs r/d , where r is the radius of the diffusing particles and d is the characteristic dimension of the L_3 phase. Symbols are the same as those in Figure 3.

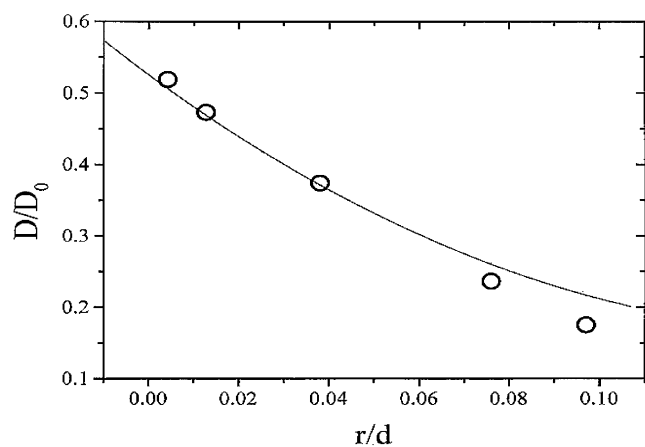


Figure 5. Reduced diffusion coefficient vs r/d for the fluorescein molecule. The solid line represents the theoretical fit to the Renkin equation.

increase resistance. These fluctuations are important in swollen lamellar phases, where they can be of the same order as the interbilayer distance and play a crucial role in phase behavior.²⁷ In L_3 phases fluctuations exist, but their evaluation is a very difficult issue.²⁷ For the fluorescein molecule, a theoretical fit to the Renkin equation for rigid-walls porous media yields a tortuosity factor $\kappa = 1.9$, very close to that predicted for isotropic porous media.⁸ The fit agrees adequately with the experimental data for bilayer volume fractions between 0 and 0.2. Beyond this value, deviations are observed (Figure 5).

To gain more information about the tortuosity of the system, we measured the electrical conductivity σ in order to determine the mobility of small ions in the L_3 phase. For this purpose we have prepared our phases with a 60 mM NaBr brine solution instead of pure water. If we rescale the conductivity results by a factor $1/(\sigma_0(1 - \phi))$, a linear variation should be obtained.¹³ In addition, the value obtained for $\phi \rightarrow 0$ should be 0.66 for L_3 phases formed by hole-free bilayers. In Figure 6 we have plotted the rescaled conductivity as a function of the surfactant volume fraction. We have obtained, as in the FRAPP experiments, a linear variation in agreement with similar measurements found in the literature.¹³ As the ions are small compared to the interbilayer distance, the variation in conductivity can be understood only from the obstruction effect of the sponge structure. This effect produces a linear decrease, very close to that observed in the self-diffusion experiments. As the value found for $\phi \rightarrow 0$ is slightly larger than 0.66 (0.72 ± 0.02), our

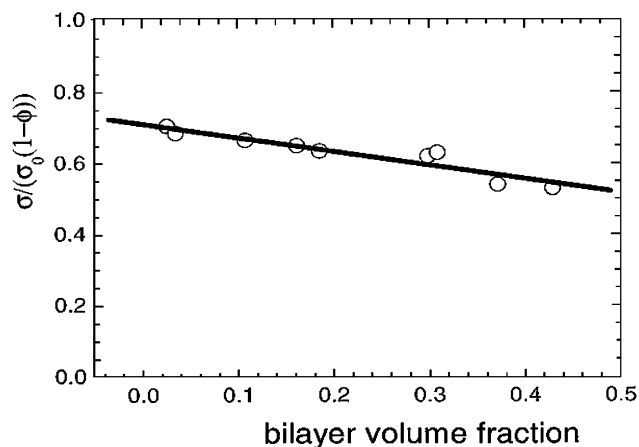


Figure 6. Rescaled electrical conductivity of the L_3 phase, as a function of the surfactant volume fraction. The straight line is a linear fit to experimental data.

experiments suggest that the bilayers of the system might contain a few surface defects or holes. However, the defect density must be very small since previous results are well described within the framework of hole-free minimal surfaces.²³ Note that, competing with the obstruction effect just described, hydrodynamic screening effects, similar to those observed in porous media and in sedimenting colloidal suspensions,²⁸ could enhance diffusion. However, the results found in the literature of colloidal systems suggest that hydrodynamic screening is much more pronounced when Coulombic interactions are strong.²⁸ This is not the case in our system because the surfactant is nonionic, and hydrodynamic screening can be neglected.

5. Conclusions

We have measured the self-diffusion coefficient D of three fluorescent probes of different hydrodynamic radii as a function of the confining distance d in an L_3 surfactant phase. All the probes display a linear dependence between D and d . This behavior can be qualitatively explained by the Anderson–Wennerström model for self-diffusion in networks of minimal surfaces. However, because it has been developed in order to describe the diffusive motion of point particles, the deviations from theory can be interpreted as originating from the finite size of the probe, that is, from wall effects. On the other hand, the available theories for rigid porous media cannot completely

explain our results. Deviations from theoretical predictions appear for bilayer volume fractions greater than 0.2. This means that, at least for transport behavior, the L_3 phase cannot be pictured as a disordered network of rigid surfaces.

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