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Abstract
Hairy wormlike micelles are constituted of surfactant micelles onto which amphiphilic copolymers are adsorbed. The copolymer layer induces a steric repulsion between the micelles, which is evidenced by the emergence of a broad peak in the structure factor for semi-dilute solutions. In this paper, we propose three experimental determinations of the thickness of the copolymer layer, h. We compare the results of the different approaches and show that both the numerical values of h and its variation with the surface density of the copolymer layer are in very good agreement with simple theoretical expectations.

1. Introduction

We have recently reported on a novel type of mixed self-assembled system: hairy wormlike micelles [1, 2]. They consist of long and flexible surfactant cylinders (wormlike micelles) decorated with amphiphilic copolymers. Using small-angle neutron scattering (SANS), we have shown [2] that the addition of amphiphilic copolymer correlates with the emergence of a broad peak in the structure factor at a finite wavevector. This peak originates from an additional intermicellar steric repulsion due to the copolymer layer covering the micelles. The steric interaction is short range, with a typical range of the order of the thickness of the copolymer layer.

In this paper, we propose three experimental determinations of the thickness of the copolymer layer, h. We compare the results of the different approaches and show that both the numerical values of h and the variation of h with the surface density of the copolymer are in very good agreement with simple theoretical expectations. First, we show how the phase diagram of the micellar phase is modified upon copolymer addition and how the variation of the critical surfactant volume fraction, above which a solution of hairy wormlike micelles phase-separates, can be used to estimate the polymeric thickness h. Second, the comparison

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of the osmotic compressibility of semi-dilute solutions of hairy micelles to the theoretical equation of state of isotropic solutions of long flexible cylinders [3] allows another estimation of the steric layer thickness. Finally, using the strong analogy between wormlike micelles and polymer solutions [4], we have constructed a random phase approximation (RPA) model [5] to predict the structure factor of semi-dilute solutions of hairy micelles. From the fit of the experimental variations of the peak position observed in the SANS patterns, a third evaluation of the thickness layer is derived.

2. Experimental system

We use a mixture of cetylpyridinium chloride (CpCl), as surfactant, and sodium salicylate (NaSal), diluted in brine ([NaCl] = 0.5 mol l^{-1}) at a fixed molar ratio [NaSal]/[CpCl] = 0.5. This system is known to form long and flexible micelles even at low concentration [6]. We add to this host phase various amounts of a triblock amphiphilic copolymer, Synperonic F108 (produced by Serva), which consists of two identical polyoxyethylene (POE) blocks of 127 monomers each, symmetrically bonded to a central hydrophobic block of polyoxypropylene (PPO) of 48 monomers. The PPO unit adsorbs onto the micelle, while the PEO units remain swollen in the solvent and decorate the micelles. The radius of gyration of a POE block is $R_G \approx 26$ Å. By means of SANS [2], we have shown that the local cylindrical structure of the micelles is maintained upon copolymer addition, with a constant radius for their hydrophobic core ($r_c \approx 21$ Å).

   We define ϕ, the volume fraction of surfactant, and α, the molar ratio of PEO blocks to surfactant molecules. In our experiments ϕ and α have ranges 0.22–40% and 0–4.2% respectively. All scattering experiments presented here were done in the semi-dilute regime (ϕ larger than the overlap concentration ϕ^*). The crossover between the mushroom and the brush structure [7] is estimated to be at $\alpha^* \approx 1.5\%$ [2] and both regimes are therefore probed in our experiments.

   Temperature is fixed at $T = 30\,°C$. SANS experiments have been performed on the spectrometer PACE at the Laboratoire Léon Brillouin (Saclay, France) and on the D11 beamline at the Institut Laue-Langevin (Grenoble, France).

3. Three determinations of the copolymer layer thickness

3.1. Phase diagram

We recall here the main results of [2]. Without copolymer, the solutions are isotropic for $\phi < \phi_T(0) = 36\%$ and for $36\% < \phi < 38\%$, an isotropic (I) and a nematic (N) phase coexist [6, 8]. Figure 1 shows how the threshold concentration ϕ_T, above which a phase separation occurs, continuously decreases as copolymer is added, from 36% for $\alpha = 0$ down to 17% for $\alpha = 4.2\%$. With copolymer, three phases very often coexist above ϕ_T, one of them being birefringent and revealing an ordering of the micelles, but a I/I biphasic sample is also obtained for $\alpha = 2.1\%$ and $\phi = 22\%$.

   In a coarse-grained approach, the effective volume fraction of hairy micelles, ϕ_{eff}, is larger than their nominal volume fraction, ϕ, due to the copolymer layer of effective thickness h. For infinitely long micelles, $\phi_{eff} = \phi(1 + h/r_0)^2$, where $r_0 \approx 30$ Å is the radius of the naked micelles (r_0 is larger than the hydrophobic core radius r_c since it takes into account the surfactant polar heads). The phase separation observed at ϕ_T may originate from two distinct mechanisms:

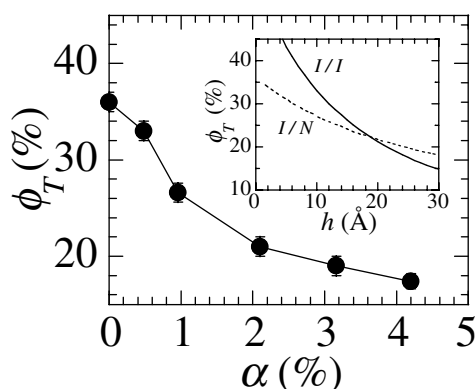 (i) a transition towards order, leading to a I/N phase separation, as observed for naked micelles;

Figure 1. The phase diagram for hairy wormlike micelles: the surfactant volume fraction ϕ_T separates homogeneous isotropic samples ($\phi < \phi_T$) from multiphasic samples ($\phi > \phi_T$). Inset: theoretical variations of $\phi_T^{I/N}$ and $\phi_T^{I/I}$ with the polymer thickness.

 (ii) a close packing of isotropic cylinders, assuming that the compression or interpenetration of polymer layers is less favourable than a phase separation;

this is expected to lead to an I/I phase separation. Simple models predict the h-dependence of the concentrations $\phi_T^{I/N}$ and $\phi_T^{I/I}$ at the I/N and I/I transitions respectively. First, from Onsager theory [9], one derives $\phi_T^{I/N} = \phi_T(0)(1 + h/r_0)^{-1}$. Second, we define $\phi_T^{I/I}$ as the critical effective volume fraction for which an arrangement of cylinders on a cubic lattice becomes compact ($\phi_{compact} = 58.9\%$): $\phi_T^{I/I} = \phi_{compact}(1 + h/r_0)^{-2}$. The two theoretical concentrations, $\phi_T^{I/N}$ and $\phi_T^{I/I}$, are plotted in the inset of figure 1. They do not have the same h-dependence and cross for $h = 19$ Å and $\phi_T = 22\%$, implying that the relevant mechanism at the origin of the phase separation changes with the amount of copolymer: (i) at low α and (ii) at higher α. The values of h derived from the experimental variation of ϕ_T are plotted in figure 2: h increases linearly with α in the mushroom regime ($\alpha < \alpha^*$) and more slowly in the brush regime, and is moreover of the order of R_G at $\alpha = \alpha^* \approx 3\%$. These results, in excellent agreement with theoretical expectations, are compared in the next two subsections with two other novel determinations of the polymer layer.

3.2. Osmotic pressure

We have measured the scattered intensity, $I(q)$, for solutions of hairy micelles in the semi-dilute regime in absolute units (cm^{-1}) by means of SANS and light scattering. In the small-q range, a fit of $I(q)$ to the Ornstein–Zernike [10] relation allows a determination of $I(0)$, the scattered intensity at zero angle. Very generally, for a solution of concentration ϕ, $I(0)$ is proportional to the osmotic compressibility [11]:

$$I(0) = (\Delta\rho)^2 k_B T \phi \left(\frac{\partial \Pi}{\partial \phi}\right)^{-1} \tag{1}$$

where Π is the osmotic pressure and $\Delta\rho$ a contrast factor. For semi-dilute solutions of polymers, scaling theory predicts the des Cloizeaux law [12]: $\Pi \propto \phi^{2.31}$, which leads to $I(0) \propto \phi^{-0.31}$. For naked micelles (data not shown), $I(0)$ follows the expected scaling law, for ϕ in the range 2–15%, but decreases more abruptly for higher ϕ, in agreement with other experiments [13, 14] and with numerical simulations [15]. Radically different behaviour is obtained for hairy
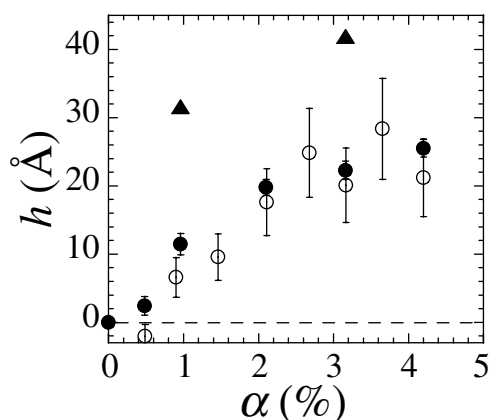
Figure 2. Variation of the effective thickness h of the steric copolymer layer covering the micelles with the copolymer to surfactant molar ratio α; h is determined from the phase diagram (full circles), the osmotic compressibility (empty circles) and a RPA model (triangles). The first empty circle data point does not have any physical meaning ($h < 0$).
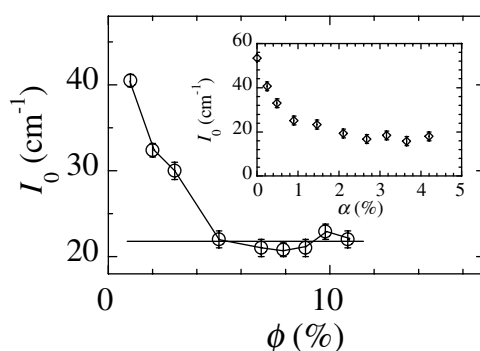

Figure 3. Variation of the scattered intensity at zero angle $I(0)$ with the surfactant concentration ϕ for samples with $\alpha = 3.2\%$. Inset: the α-dependence of $I(0)$. The surfactant concentration is $\phi = 9\%$. All values are in the plateau regime except the first two data points.

micelles. As can be seen in figure 3, $I(0)$ decreases with ϕ at low ϕ until it reaches a plateau. The threshold concentration at which the plateau appears is smaller at higher α and the plateau value $I(0)_{plateau}$ decreases with increasing α. The plateau seems thus to be a specific signature of the copolymer layer covering the micelles. Selinger and Bruisma [3] have calculated the equation of state of an isotropic phase of long flexible *non-entangled* chains, in the presence of excluded-volume interactions. They found

$$\Pi = k_B T \frac{\pi}{4} b \sigma^2 \tag{2}$$

where b is the diameter of the chains (for hairy micelles, $b = 2(r_0 + h)$) and σ is the density of chains per unit area perpendicular to their average orientation; for micelles locally packed on a cubic lattice, σ and ϕ are related through $\sigma = \phi/(3\pi r_0^2/4)$ and (2) implies thus a ϕ-independent variation of $I(0)$, in agreement with our experimental observations. The osmotic pressure should be the sum of two contributions: one is the standard osmotic pressure of semi-dilute polymer solutions (des Cloizeaux law) which decreases with ϕ; the second one is the additional contribution induced by the copolymer layer, and is ϕ-independent. We

find that the latter dominates at large ϕ. Hence, this allows us to directly extract from the data for $I(0)_{plateau}$ versus α (inset of figure 3) an 'osmotic' thickness of the polymer layer: $h = (\Delta\rho)^2\left(\frac{9\pi r_0^4}{16 I(0)_{plateau}}\right) - r_0$. The corresponding values of h are reported in figure 2 (empty circles). In this plot, we have normalized the scattered intensity values by a factor of 5.8 to make the values of h at large α coincide with the ones obtained previously. We note that, apart from the normalization, the two approaches (phase diagram and osmotic pressure) provide very similar variations of the polymer thickness with the amount of copolymer.

3.3. Random phase approximation (RPA)

The RPA [5] is a powerful tool for obtaining the statistical properties of concentrated solutions of polymer in a mean-field approximation. We apply this theory to semi-dilute solutions of hairy micelles. Details of the model will be given in a future publication [16]. The more salient results are presented here. For a wormlike micelle, the statistical unit (or 'monomer') to consider is a portion of surfactant cylinder of length l_K equal to twice the persistence length ($l_K \approx 380$ Å). We write the mean-field interaction potential $U(r)$ between two 'monomers' separated by r as the sum of a classical excluded-volume term potential for polymers in good solvent and a soft short-range potential to account for the specific contribution of the copolymer layer (we choose a Gaussian shape for this potential): $U(r) = v_0 \delta(r) + U_0 \exp(-r^2/2\delta^2)$, where v_0 is the excluded-volume parameter. The range 2δ of the Gaussian potential should be of the order of the effective diameter of the cylinders $b = 2(r_0 + h)$, while its amplitude U_0 is related in a subtle way to the mean elastic modulus of the hairy micelles. Both δ and U_0 are expected to increase with α. The RPA then allows the calculation of the structure factor $S(q)$:

$$V S^{-1}(q) = V S_0^{-1}(q) + v_0 + U_0 (2\pi\delta)^{3/2} \exp\left(-\frac{(q\delta)^2}{2}\right) \tag{3}$$

where $S_0(q) = NV\rho_0 f((qR_G)^2)$ is the structure factor of ideal chains; $f(x) = \frac{2}{x^2}(e^{-x} + x - 1)$ is the Debye function, V the volume of the solution, N the mean number of 'monomers' per micelle, ρ_0 the mean density of 'monomers', and R_G the ideal radius of gyration of the micelles (the last three parameters can easily be expressed as functions of ϕ and l_K). The structure factor exhibits a maximum (correlation peak) above a threshold surfactant concentration, as shown in figure 4(a), its origin being the short-range potential that we have introduced to model the copolymer-induced interactions. The position q^* of this maximum has a simple analytical ϕ-dependence:

$$q^* = \frac{\sqrt{2}}{\delta}\sqrt{\ln\left(\frac{6(2\pi)^{3/2}}{\pi r_0^2 l_K^3}\delta^5 U_0\right) + \ln\phi}. \tag{4}$$

A comparison with experimental data (figure 4(b)) shows that our model captures the essential experimental features. These are the α-dependent threshold concentration above which a peak appears and the ϕ-dependence of the peak position q^*. A good agreement (inset of figure 4(b)) is obtained by fitting the experimental values of q^* with equation (4), with U_0 and δ as unique fitting parameters. Finally, one evaluates the polymer thickness h as the distance at which the Gaussian potential is equal to 1 $k_B T$ (h thus depends solely on U_0 and δ). One finds that h increases with α and has a correct order of magnitude, although the numerical values are slightly larger than the ones derived by the previous methods.
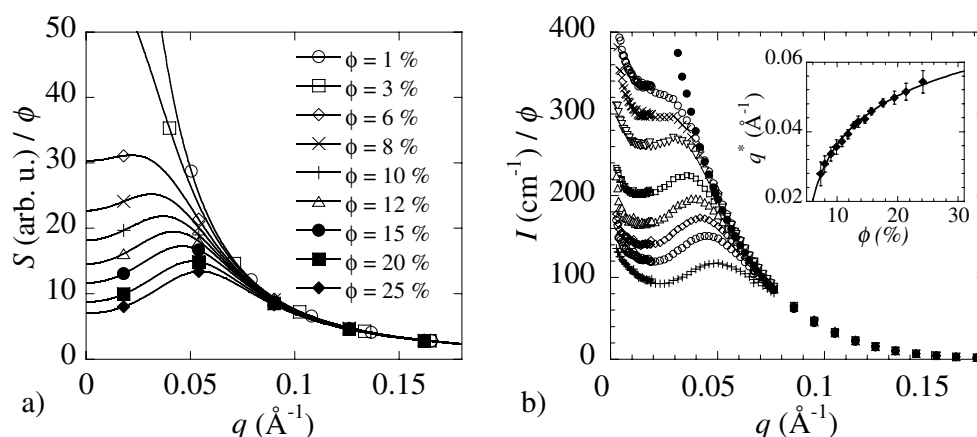
Figure 4. (a) The theoretical structure factor (3) with a Gaussian potential of range $\delta = 34$ Å and magnitude $U_0 = 800\, k_B T$, for various surfactant concentrations ϕ; (b) normalized SANS patterns for various concentrations ϕ (from top to bottom: $\phi = 2.8$, 6.5, 7.3, 8, 9.9, 11.8, 13.5, 15.7, and 19.5%) and $\alpha = 1\%$. Inset: variation of the peak position with ϕ for the same data as in the main plot. Symbols are experimental data and the solid line is a best fit using (4); one finds $\delta = 34$ Å and $U_0 = 793\, k_B T$.

4. Conclusions

Hairy wormlike micelles are a new class of polymer/surfactant systems which may be interesting experimental models for polymer physics, because of the copolymer-induced steric repulsion between the polymer chains. In fact, both the range and the magnitude of these interactions can be monitored independently by varying the amount or the length of the copolymer chains added in the micellar solutions. We have presented in this paper three different physical approaches to quantify the variation of thickness h of the copolymer layer which covers the micelles with the adsorption density of the copolymer. They all lead to similar results, in good agreement with simple theoretical expectations. The more promising and more quantitative approach, RPA, will be developed in a future publication.

Acknowledgments

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