Surface induced ordering of micelles at the solid-liquid interface

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The surface induced ordering of triblock copolymer micelles in aqueous solution was measured with neutron reflectivity far above the critical micelle concentration. The scattering length density profiles showed a clear indication of ordered layers of micelles perpendicular to a quartz surface. The structure and interactions of the micelles were modeled in detail. The convolution of the center distribution of the micelles, obtained from Monte Carlo simulations of hard spheres at a hard wall, and the projected density of the micelle showed excellent agreement with the experimental profiles. [S1063-651X(98)06712-9]

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Amphiphilic block copolymers composed of two or more blocks with different degrees of hydrophobicity self-assemble in aqueous solution. The hydrophilic blocks repel each other, whereas the hydrophobic blocks strongly attract each other. These opposing interactions make it favorable for the block copolymers to aggregate as, e.g., spherical micelles, rodlike structures, or bilayers. The structure of the aggregate is a delicate balance between the ability to keep the hydrophilic part dissolved and the hydrophobic part shielded from the solvent and packing constraints. Several external parameters, e.g., composition, temperature, and concentration in solution, influence the degree of hydrophobicity of the blocks. Consequently, attention has been given to fundamental studies of the large diversity of bulk phases that occur as a function of these parameters.

The studied triblock copolymer P85 consists of 40 central blocks of propylene oxide (PO) with two symmetrical ends of 25 segments of ethylene oxide (EO). Since ethylene oxide is only weakly hydrophobic at temperatures below approximately 70 °C and propylene oxide is hydrophobic above approximately 15 °C, the copolymer aggregates in aqueous solution, e.g., as spherical micelles, hexagonal rods, or prolate ellipsoids [1–3]. This rich phase diagram makes P85 an ideal model system for investigations of the interactions between the block copolymers and a surface in aqueous solution.

In the surface studies, the experiments [4–11] and simulations [12,13] have mostly been centered around the dilute solutions of block copolymers close to the critical micelle concentrations. In this study we focus our attention on higher concentrations where the aggregation of copolymers is predominant in the bulk.

We present results from neutron reflectivity measurements in the concentration range between 15 and 25 wt % at a temperature of 50 °C P85 in aqueous solution, where P85 forms spherical micelles. In addition we demonstrate that it is possible to model the profile using the results from Monte Carlo (MC) simulations of hard spheres at a hard wall. Insight is thus obtained on the micellar structure and the interactions between micelles.

The neutron reflection measurements were performed at the reflectometer TAS8 situated at the reactor DR3, Risø National Laboratory, Denmark. The setup provides neutrons with wavelength $\lambda = 4.75$ Å with a relative bandwidth of $\Delta\lambda/\lambda = 1\%$. The polymer solution is kept in an approximately 5 ml Teflon enclosure, 1 mm deep and 94 mm long covered with a $100 \times 50 \times 10$ mm^3 lid of single-crystalline quartz. The cell is contained in a thermostated aluminum box, which can be controlled within 0.3 °C. In the experiment the neutrons traverse the crystal after entering the smallest face of the crystal, reflect off the solid-liquid interface, and are detected. The technique benefits from the fact that quartz and aluminum are virtually transparent to neutrons. The specular reflectivity provides information on the scattering length density differences along the surface normal. As a solvent we use heavy water (D$_2$O) due to the contrast with respect to the block copolymers and the low incoherent scattering. Because of the high weight fraction of polymer in solution, the micelles in the bulk solution give rise to considerable small-angle scattering, which is superimposed on the reflectivity signal from the solid-liquid interface. This signal has to be subtracted together with the background. Figure 1 shows reflectivity data for three different concentrations (15, 20, and 25 wt %) at 50 °C. For scattering vectors larger than $Q_{max} = 0.07$ Å^{-1} the interface related signal is indistinguishable from the background limiting the resolution in real space to about $1.5/Q_{max}$, i.e., 25 Å [14].

The reflectivity curves show a broad peak, the position of which varies systematically with concentration. Similar profiles have previously been seen in, e.g., surface ordering of micro-emulsions [6,15]. The reflectivity data were initially analyzed by a free-form method [16]. The scattering length density profile is expressed as a series of cubic b splines the amplitudes of which are found from a constrained nonlinear least-squares fit to the reflectivity curve, calculated from dynamical theory [17] and smeared with the instrumental resolution. All the profiles show oscillations that decay away from the quartz surface as shown in the bottom insert of Fig.

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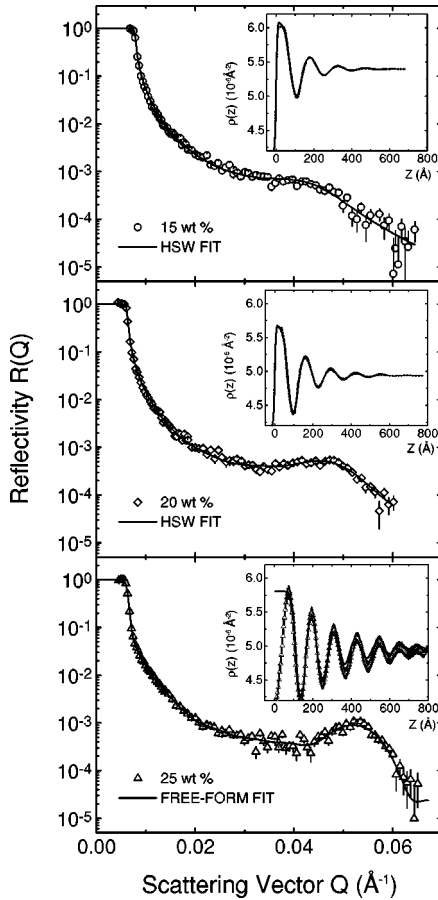
FIG. 1. The background corrected reflectivity profiles for 15, 20, and 25 wt % P85 in aqueous solution at 50 °C. For 15 and 20 wt % the model fit (solid sphere and tethered chains) to the reflectivity curve is shown as the solid line. The corresponding scattering length density profiles are depicted in the insets, where the solid line and the dashed line are the model with and without tethered chains, respectively. The free-form fit to the reflectivity curve is shown as the solid line for 25 wt % and the corresponding scattering length density profile as points in the insert. The solid line in the insert is the real space fit to the free-form profile of the model including tethered chains.

1. Because of the higher scattering length density of the solvent ($\rho_{D_2O} = 6.4 \times 10^{-6}$ Å^{-2}) compared with that of the micelles ($\rho_{P85} \simeq 0.5 \times 10^{-6}$ Å^{-2}), each minimum in the profile represents a micellar layer. Hence, the scattering length density profile can be interpreted as micellar layering with decreasing positional order along the quartz surface normal.

In order to obtain information on the structure and the interactions between the micelles we have performed a detailed modeling of the profiles. From self-consistent field calculations [18] and experimental bulk studies [1,19] it is known that a hard-sphere potential gives a reasonable description of the interactions between micelles. We have therefore performed MC simulations of hard spheres at a hard wall with a hard sphere volume fraction η ranging from 0.049 to 0.46 (See Fig. 2). The density distribution of the centers of the hard spheres in the direction perpendicular to the surface was sampled as a function of the volume fraction η and afterwards parametrized. To include the form of the micelle in the model, the center distribution was convoluted

with the normalized projected radial scattering length density of either a solid sphere [1] or the more realistic solid sphere with tethered Gaussian polymer chains [19].

From bulk measurements [19] it has been shown that the dissolved ethylene oxide chains can be mimicked by Gaussian polymer chains attached at $R + R_g$, where R and R_g are the radius of the solid sphere and the radius of gyration, respectively. The calculated projection of the radial density of 25 ethylene oxide monomers attached at $R = 60$ Å with $R_g = 10.8$ Å [20] was parameterized and properly scaled to take into account the variation in the radius of the sphere. The projection of the solid sphere is straightforward.

It was assumed, that the solid sphere and the chains consist of propylene oxide and ethylene oxide, respectively. Thus, for the weighting of the two parts in the final expression for the normalized projected scattering length density of the micelle as a function of R and the distance from the center of the micelle z we find

$$\rho_{\text{mic}}^{\text{norm}}(z,R)$$

$$= \frac{\rho_t^{\text{norm}}(z,R)\Delta\rho_{\text{EO}}V_{\text{PEO}}^{\text{tot}}(R) + \rho_s^{\text{norm}}(z,R)\Delta\rho_{\text{PO}}V_{\text{PPO}}^{\text{tot}}(R)}{\Delta\rho_{\text{EO}}V_{\text{PEO}}^{\text{tot}}(R) + \Delta\rho_{\text{PO}}V_{\text{PPO}}^{\text{tot}}(R)},$$

where ρ_t^{norm} and ρ_s^{norm} are the normalized scattering length density distribution of the tethered chains and the solid sphere, respectively (see Fig. 2), $V_{\text{PEO,PPO}}^{\text{tot}}$ the volume in the micelle, and $\Delta\rho_{\text{EO,PO}}$ the excess scattering length density with respect to quartz of each of the two constituent parts. As a last step the scattering length density of the solvent has to be taken into account to obtain an expression for the model profiles. Hence, we obtain

$$\rho_m = \Delta\rho_{\text{fluid}} - (\Delta\rho_{\text{fluid}} - 1) \int_{-\infty}^{+\infty} \rho_{\text{mic}}^{\text{norm}}(x,R)$$

$$\times \rho_{\text{HSW}}[(z - z_{\text{onset}}) - x, R, R_{\text{HS}}/R, \eta] dx.$$

Here, ρ_m is in units of the scattering length density of the bulk micellar liquid and the center distribution of micelles, ρ_{HSW}, is appropriately scaled with the hard-sphere interaction radius R_{HS}. Furthermore, z_{onset} marks the onset of the hard-sphere ordering. The convolution integral is depicted in Fig. 2 for the parameters obtained for 20 wt % at 50 °C.

The leading edge of the scattering length density profile was modeled by an error function. The model parameters were optimized by a nonlinear least-squares fit to the reflectivity data calculated from dynamical theory and smeared with the instrumental resolution. The initial conditions were obtained from direct fitting to the free-form scattering length density profiles. The model agreed excellently with the experimental reflectivity curves for 15 and 20 wt % at 50 °C, whereas a fit of the same quality could not be obtained for 25 wt % as seen in the inserts of Fig. 1. The results from the fits of three concentrations 15, 20, and 25 wt % at 50 °C are tabulated in Table I.

Very good agreement is found between the volume fractions η obtained from the model and from bulk measurements [1]. The hard-sphere interaction radii R_{HS} and the radii of the solid sphere R, hence the aggregation numbers $N_{\text{agg}} = \frac{4}{3}\pi R^3 / V_{\text{PPO}}$ where V_{PPO} is the volume of a polypropylene
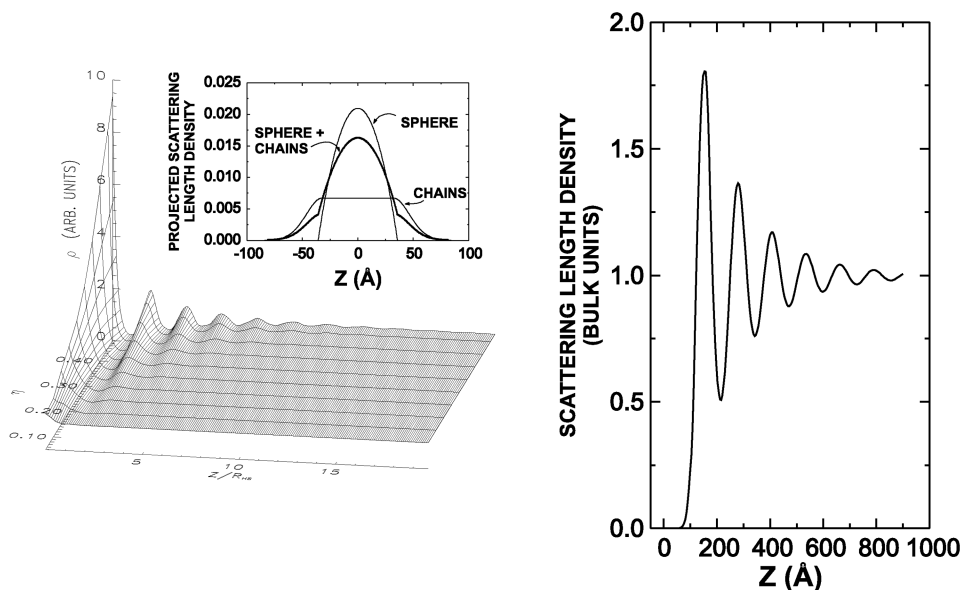
FIG. 2. The different parts in the model calculation. The left-hand side shows the parametrization of density $\rho(z)$ of hard spheres at a hard wall obtained from Monte Carlo simulations as a function of the volume fraction η and distance z from the surface. The inset depicts the normalized scattering length densities of the projection of the sphere, the tethered chains, and the combination. The convolution is depicted on the right-hand side. The 20 wt % values (sphere with chains) were used in the calculation.

oxide block, are slightly smaller than the corresponding bulk values. The interaction radius R_{HS} can be considered equal for the two models, whereas a change is seen in the radius of the solid sphere (core) radius R. The difference is caused by the fact that without the chains the solid sphere also has to mimic the chains and thus becomes larger. The difference between the R_{HS} and R is a measure of the influence of the chains. The tethered chains will contribute with roughly two times the radius of gyration R_g to the hard-sphere interaction radius of the micelle assuming that the PEO chains cannot penetrate the core. The two measures $R+2R_g$ and R_{HS} agree within 10 Å in both cases. However, $R+2R_g$ exceeds R_{HS} in both models suggesting that the tethered chains are more extended than Gaussian chains. The extension may be caused by excluded volume interactions between the chains and inside the chain itself, which effectively extends the polymer chains.

The value obtained for the surface roughness of the solid-liquid interface, 5 ± 2 Å, is below the resolution of the experiment and can thus only be related to the general form of the initial peak and not the true surface roughness.

The close agreement between the models and the experimental profiles confirms that the interaction between the micelles is hard-sphere like. Monte Carlo simulations of hard spheres at a hard wall [21] have shown that the hard spheres are confined in their motion perpendicular to the surface in the near vicinity of the wall. Furthermore, the simulations suggested a pre-crystallization or a solid-liquid coexistence in the innermost layers. The inability of the model to reproduce the amplitudes in the profiles of the 25 wt % solution, which is at the border of the bcc micellar region, might suggest an even stronger precrystallization than the model is able to describe. Another possibility is surface ordering of disordered bcc micellar bulk polycrystallites. From small-angle neutron scattering measurements of P85 in Couette geometry it has been shown that the polycrystallites can be transformed into a single crystal by application of shear [22]. However, shear flow reflectivity measurements [20] in Pouseille geometry [23,8] showed no additional peaks in the reflectivity profile indicative of the formation of a single crystal. Consequently, we see no indication of formation of bulk crystallites for 25 wt % P85 in solution close to the crystallization border.

TABLE I. Results from the model fitting of the reflectivity data from the triblock copolymer P85 at 50 °C. The solid sphere model is compared with values from bulk measurements [1].

	wt %	ρ_{fluid} $(10^{-6}\,\text{Å}^{-2})$	R (Å)	R_{HS} (Å)	η	N_{agg}	$R+2R_g$ (Å)	R^{bulk} (Å)	$R_{\text{HS}}^{\text{bulk}}$ (Å)
Solid spheres	15	6.06	45	71	0.31	97	66	53	81
	20	5.62	41	67	0.35	77	63	52	78
	25	5.80	42	63	0.47	81	64	51	76
Solid spheres	15	6.06	41	72	0.33	73	62		
with tethered	20	5.65	36	68	0.39	50	57		
chains	25	5.80	32	63	0.47	35	53		

The volume fraction of P85, ϕ, at the surface, which is calculated from $\rho_{\text{fluid}} = (1-\phi)\rho_{D_2O} + \phi\rho_{P85}$, is reduced to less than approximately 50% of the bulk solution value. If only EO is present close to the surface, the same result is obtained. This indicates a possible depletion layer close to the surface of the quartz crystal. The formation of a depletion layer has previously been seen in a molecular dynamics study [24] of the aggregation of amphiphilic molecules in a oil-water-surfactant system. The ordering of micelles occurred in the water phase at a distance from the oil-water interface. This depletion layer suggested a short-range repulsion, a solvation force, between the micelles and the monolayer of surfactant at the oil-water interface. With the present resolution of the experiment it is not possible to discern whether PEO adsorbs to the surface as unimers and a depletion layer is formed or EO directly adsorbs from the micelles. The low volume fraction at the surface might signify the competition between the adsorption of water and EO at the hydrophilic quartz surface. A depletion layer has been suggested to be an inherent property of quartz crystals [25,26]. Suggestions [5] concerning the adsorption of hemispherical micelles at the quartz surface is not supported by our measurements.

It has been demonstrated that detailed modeling of block copolymer micelles at a surface is possible and provides extensive information of micellar structure and interactions. Hard-sphere ordering at the solid-liquid interface exists in a system of micelles at concentrations far above the critical micelle concentration. The approach can be extended further to cover e.g. microemulsions. However, microemulsions often have large polydispersity which has to be included in the model.

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