

Bunchy Micelles

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This paper presents a theoretical study of the micellization of macrosurfactants, tailored by attaching a soluble long polymer chain to an insoluble solid bead. I show that the porous structure of the micelle core leads to a new micellization scenario and provides simple geometric rules for determining the aggregate properties. The results are discussed within the context of the micellization of diblock copolymers in a selective solvent.

I. Introduction

Diblock copolymers in a selective solvent have often been studied as an archetype for micellization of macromolecular surfactants.^{1–5} These molecules include also, but not exclusively, linear triblock copolymers,⁶ random copolymers,⁷ chains with end⁸ or middle functional groups,⁹ polysoaps,¹⁰ and in general any macromolecular object with amphiphilic-like activity. In the case of diblock copolymers, an isolated chain in the solution has a tadpole configuration, with a short collapsed head-block connected to a swollen tail. Each head is commonly assumed to be a liquid molten globule that merges with other heads in order to minimize exposure to the poor solvent. The resulting micellar aggregate can be pictured as a molten spherical core surrounded by the swollen tails (see Figure 1). The liquid nature of the core determines the structure of the micelles not only because it allows for mixing the chains in the core but also because it enables the assembly to reach a *thermodynamic equilibrium* state where the balance between core–solvent interfacial tension and stretching of the chains can be achieved. Under these equilibrium conditions the micelle aggregation number p has been theoretically predicted^{4,5} to vary almost linearly with the polymerization index N_A of the collapsed block: $p \sim N_A^{4/5}$. This prediction has been quantitatively tested¹¹ for polystyrene–poly(ethylene oxide) block copolymers in water, and a reasonable agreement has been found between theory and experiments. However, results for polystyrene–poly(4-vinylpyridine) in butanone and in

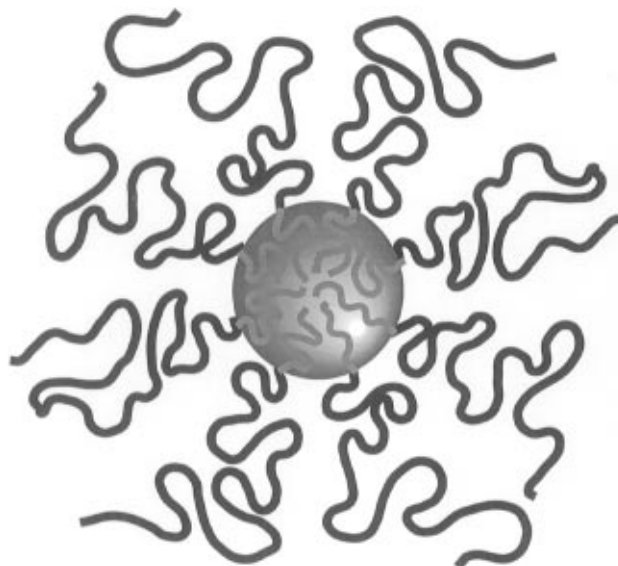


Figure 1. Sketch for the structure of a diblock copolymer micelle with a molten liquid core. The core is free of solvent or tail monomers.

THF present¹² a rather different power law dependence, the measured exponent being closer to 2 than to the predicted value of $4/5$. Such results that do not comply with the classical picture strongly suggest that the hypothesized liquid nature of the core does not generally hold. If the core is not a molten globule but is instead in a glassy-like state, two possible core structures can be considered, depending on the preparation method. When micelles are prepared in an equilibrium solution (usually at high temperature) and then quenched, the molten core will undergo a glass transition leading to a final structure that carries the signature of the micellization temperature and of the quenching process. The central glassy region is then likely to have a uniform monomer density of entangled glassy chains. The initial aggregation number being determined under equilibrium conditions, this preparation method should lead, at least for fast quenching rates, to micelles which bear no differences with the equilibrium ones, as far as the static properties (like the N_A dependence of the aggregation number) are concerned. The second possible geometry will arise if the micellization proceeds by aggregation of copolymer chains which already have a glassy head. Although little is known about the structure of individual glassy chains in solution, the characteristic relaxation time of the chain is likely to

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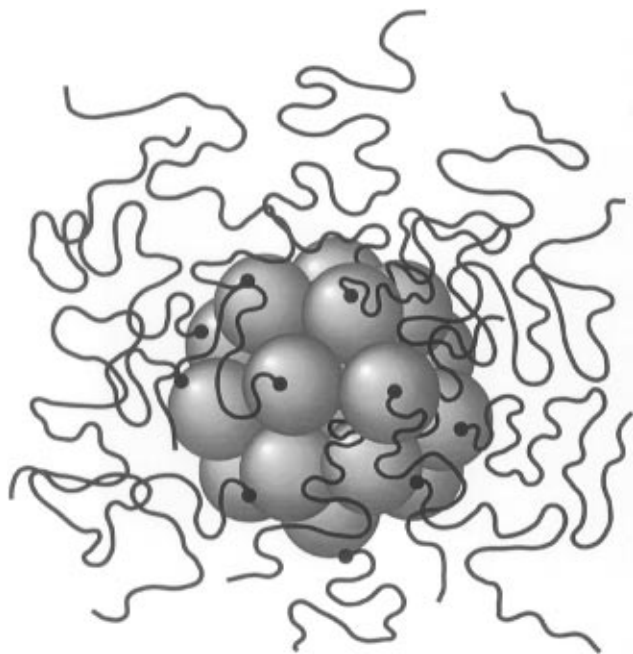


Figure 2. Core structure of a bunchy micelle, which allows for a significant penetration of solvent and tails in the core region. The tails are assumed to be repelled by the beads and therefore to protrude toward the solvent in order to escape confinement.

depend on the amount of solvent actually present in the collapsed globule. We consider here the extreme case of zero solvent content (zero plasticizing effect) and infinite relaxation time. In this case the core will have a porous structure (see Figure 2), the pores being filled with solvent and copolymer tails. As we will see below, this picture leads to a different micellization scenario and to new predictions for the properties of the micelles.

In this paper I investigate the micellar aggregation of tadpole-like molecules, where the tadpole head is a solid particle and the tadpole tail a swollen polymer. I will refer to the resulting aggregates as bunchy micelles. Diblock copolymer chains with a glassy block might be, as discussed above, examples of such molecules, but any system where a long polymer chain is grafted to a solid bead (for instance a complex of biotinylated DNA strands tethered to streptavidin-covered particles¹³ or gold-end-labeled macromolecules¹⁴) also provides an actual realization of these macrosurfactants.

In order to stress the differences between the classical scenario for micellization of large surfactants and the scenario proposed here for large surfactants with solid heads, I present first, in the next section, a summary of the classic theory for micellization of diblock copolymers and will discuss in section III the geometry and aggregation of the bunchy micelles. The conclusions are devoted to the discussion of the experimental relevance and the limitations of this model.

II. Micelles with a Liquid Core

I review in the following paragraphs the structure and aggregation of asymmetric diblock copolymers with a molten head much smaller than the swollen tail. The polymerization indices of the collapsed and swollen blocks are respectively N_A and N_B . I consider only in the following the asymmetry range $N_A \ll N_B^{15/11}$, where, as we will see below, the outer corona of the micelles is much larger

than the core. The representation of the structure of the micelle in Figure 1 shows the central, solvent-free core, surrounded by a corona of well swollen tails. The number p of chains in the micelle determines the radius of the core: $R_A = (3pN_A/(4\pi))^{1/3}b$, where b is the size of one monomer. For simplicity I choose in the following unit lengths where $b = 1$ and assume that monomers A and B have equal sizes. The outer corona forms a starlike polymer object, first described by Daoud and Cotton¹⁵ as a semidilute polymer solution with a local, position-dependent correlation length. Pictorially one associates a blob with the correlation length and describes the external shell as a succession of blobs of increasing size. At a given distance r from the center of the micelle (with $r > R_A$) there are p blobs occupying a surface $4\pi r^2$. This gives a blob size which varies as

$$\xi(r) \approx rp^{-1/2} \quad (1)$$

The external radius of the micelle R_B is then obtained by the conservation constraint $pN_A = 4\pi \int_{R_A}^{R_B} c(r)r^2 dr$, where the monomer concentration in the corona decays as $c(r) \approx \xi(r)^{-4/3} = p^{2/3}r^{-4/3}$. This gives $R_B = N_B^{3/5}p^{1/5}$, in the limit where $R_B \gg R_A$. The chains in the corona are thus extended by a factor $p^{1/5}$ with respect to their free radius in the solution. The free energy associated with these stretched configurations can be calculated by integrating the local free-energy density of an equivalent semidilute solution

$$F_e = 4\pi k_B T \int_{R_A}^{R_B} \phi^{9/4} r^2 dr \approx k_B T p^{3/2} \log[R_B/R_A] \quad (2)$$

Approximating the logarithmic contribution by a constant A , the free energy of a micelle of p chains is written as

$$F_p = Ap^{3/2} + 4\pi\gamma R_A^2 \quad (3)$$

in units where $k_B T = 1$. The second contribution to the free energy of the micelle is due to the core-solvent interfacial tension γ . The aggregation scenario that results from the structure of such free energy can be described by recognizing that for large macromolecules aggregation sets in at low concentrations, which allows us to write the total free energy density of the solution as

$$F = \sum_{p=1}^{\infty} c_p [\log(c_p/e) + F_p] \quad (4)$$

where c_p is the concentration (number per unit volume) of micelles with p molecules. Minimizing the free energy density (eq 4) with respect to c_p , under the constraint of conservation of the total chain density ϕ , one finds $c_p = \exp\{-F_p + \mu p\}$ with μ a chemical potential associated with the conservation requirement. When μ is large enough, the grand potential $\Omega_p = F_p - \mu p$ associated with the free energy (eq 3) has a minimum at a finite value \bar{p} . This corresponds to a peak in the micelle size distribution and allows for calculating the conservation of total chain number by a steepest descent method. Considering monomers and \bar{p} -mers, one gets for their respective concentrations c_1 and $c_{\bar{p}}$, and for the chemical potential μ the following values:

$$\phi \ll \phi_{\text{cmc}} \quad c_1 \approx \phi; \quad c_{\bar{p}} \approx 0; \quad \mu \approx F_1 + \log \phi$$

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$$\phi \gg \phi_{\text{cmc}} \quad c_1 \approx \phi_{\text{cmc}}; \quad c_p \Delta \approx \frac{\phi - \phi_{\text{cmc}}}{\bar{p}}; \quad \mu \approx F_1 + \log \phi_{\text{cmc}} \quad (5)$$

The critical micellar concentration is defined by $\phi_{\text{cmc}} \approx (\bar{p}\Delta)^{-1/p} \exp\{-(F_1 - F_p/\bar{p})\}$ with $\Delta^2 = 2\pi/(\partial^2 F_p/\partial p^2|_{p=\bar{p}})$, the width of the micelle size distribution. Below the cmc unimers are the dominant species, but above the cmc most of the chains aggregate into micelles, leading to almost constant, concentration-independent values of the chemical potential and aggregation number \bar{p} . This implies that, to a good approximation, the aggregation number and the critical micellar concentration can be determined from the two conditions $d\Omega/dp = \Omega = 0$, which lead to

$$\bar{p} = N_A^{4/5} \gamma^{6/5} \frac{4\pi}{3} \left(\frac{3}{\pi A^2} \right)^{3/5} \quad \phi_{\text{cmc}} \approx \exp\{-\gamma N_A^{2/3}\} \quad (6)$$

The size of the core scales thus as $R_A \sim N_A^{3/5}$, and the size of the corona as $R_B \sim N_B^{3/5} N_A^{4/25}$. The corona is much larger than the core in the asymmetry range $N_A \ll N_B^{5/11}$.

III. Bunchy Micelles

When the unimers have a solid-like insoluble head, a different structure for the core of the micelle needs to be considered (see Figure 2). The most important feature of the aggregate is that the core is no longer a region containing only A monomers, but it can accommodate also solvent and tails. I assume in the following that the solid, spherical heads behave like impenetrable, repulsive walls with respect to the B tails. The amount of space filled by the solvent and by the tails will depend on the exact packing geometry of the solid heads and on how deformable the solid is. For an infinitely rigid head the porosity may vary from a minimum of 26%, when spherical heads close pack in a crystal hcp or fcc structure, to the most likely case, corresponding to an amorphous structure of $\sim 45\%$ porosity. Each bead being connected to a tail and the tails escaping from the core in order to avoid confinement, the actual concentration of B monomers in the interstitial spaces actually increases from the center. In order to calculate this concentration I assume, as in the Daoud-Cotton model, that the chains in the gaps follow the statistics of a semidilute polymer solution and can then be characterized by a position-dependent correlation length $\xi(r)$. The number of beads inside a sphere of radius r being $p(r) \approx (r/r_0)^3$, with r_0 the radius of the bead, there are $p(r)$ tails crossing the spherical surface at r . There are thus $p(r)$ blobs occupying a surface $4\pi r^2$, which gives a blob size variation of the form

$$\xi(r) \approx r_0 \left[\frac{r_0}{r} \right]^{1/2} \quad (7)$$

Because the solution is locally semidilute, this translates into a concentration variation of the form

$$\phi(r) = Cte \left[\frac{b}{r_0} \right]^{4/3} \left[\frac{r}{r_0} \right]^{2/3} \quad (8)$$

where we reintroduced dimensional lengths and the monomer size b . Cte is an unknown constant of order unity. It is clear from the radial dependence of the concentration (or of the blob size) that there is a maximum number of chains that can be accommodated into the micelle before the outer interstitial region is saturated

with tail monomers. Setting the concentration ϕ to unity, one gets a maximum aggregation number p_{max} and the maximum core size r_{max}

$$p_{\text{max}} = \frac{\alpha}{Cte^{9/2}} \left[\frac{r_0}{b} \right]^6; \quad r_{\text{max}} = Cte^{-3/2} \left[\frac{r_0}{b} \right]^3 b \quad (9)$$

where α is a filling fraction that depends on the packing geometry. Note that in the case of diblock copolymers the radius of the tadpole head scales as $N_A^{1/3}$, which leads to an aggregation number dependence of the form $p \approx N_A^2$, rather close to the experimental results of Antonietti *et al.*¹² Interestingly, assuming a complete saturation of the profile and a reasonable value for α (say $\alpha = 2/3$), one can also extract from ref 12 the value of the unknown constant. One gets $Cte = 1.9$. The possibility of reaching a saturation value for the profile depends on several factors that will be discussed below.

A first geometric factor is the polymerization index of the tails. The preceding arguments do not apply if the tails are too small. A tail attached to a bead at a given position r' will spend $n(r')$ monomers before it escapes the core:

$$n(r') = 4\pi \int_{r'}^{R_A} \frac{\phi(r)}{p(r)} \frac{r^2 dr}{b^3} \approx \frac{r_0}{b^{5/3}} (R_A^{2/3} - r'^{2/3}) \quad (10)$$

The minimum value of N_B that allows all the chains to escape the core can be calculated by considering the tail attached to the bead at the geometric center of the core, for which the escape conditions are the most stringent. Setting $r' = 0$ and $R_A = r_{\text{max}}$, in eq 10 we get $N_B \gg (r_0/b)^3$ in general and $N_B \gg N_A$ for the particular case of diblock copolymers. Note that this condition, which requests the displaced volume of the tail to be much larger than that of the insoluble head, is more stringent than the condition for solubilization:¹⁶ $N_B \gg (r_0/b)^2$ or $N_B \gg N_A^{2/3}$ for diblocks.

The second factor which controls saturation is the sticking energy of the different heads. For large sticking energies we expect the aggregation behavior to be dominated by the geometric saturation effects described previously herein. However, for smaller sticking energies a thermodynamic equilibrium state may be attained, in which the interfacial tension and the stretching energies balance. The interfacial tension of the core is given by the work necessary to move a bead from the middle of the core to the surface. I estimate its value here by noting that a bead at the core surface has on average 6 neighbors, instead of 12 average neighbors everywhere else in the core. With a bead-bead sticking energy δ , the surface tension is therefore given by $F_s = p^{2/3} 6\delta$. There are two osmotic contributions to the free energy, from the chains in the core and from the (same) chains in the corona. The latter has the structure of the Daoud-Cotton contribution (eq 2), with a slight different logarithmic prefactor. The former can be calculated from a similar argument:

$$F_0 = 4\pi \int_0^{R_A} \phi^{9/4} r^2 dr \approx p^{3/2} \quad (11)$$

This contribution has, up to the logarithm factor, the same power-law dependence as the contribution (eq 2) from the outer corona, which allows us to write the grand potential as

$$\Omega = Bp^{3/2} + p^{2/3} 6\delta - \mu p \quad (12)$$

and gives an equilibrium aggregation number $p_0 = (4\delta/$

$B)^{6/5}$. Another important contribution from the chains in the core is the energy associated with the depletion of the tails from the assumed impenetrable hard spheres. This can easily be checked to give a term scaling as $p^{4/3}$ and thus to be irrelevant for our analysis.

If the aggregation number p_0 is larger than the saturation number p_{\max} , the micelle can reach its saturation structure with an aggregation number p_{\max} . In the opposite case the aggregation number is given by p_0 . The actual value of the parameter δ depends in general on the microscopic details of the contact between two spheres, but a possible estimation can be obtained from the adhesive contact energy for rigid or for deformable spheres. In the limit where the diblock head is infinitely rigid, the area of contact between two spheres is the area from which molecules of size b are excluded. This gives $\delta = \gamma\pi r_0 b$, where γ is the bead-solvent interfacial tension. In diblock copolymers this leads to the scaling form $p \sim N_A^{2/5}$, but the actual numerical coefficients are important, because they may bring the aggregation number into the saturation range. For the more realistic case where the tadpole heads have a finite elastic constant K , the relevant results for the contact energy are provided by the JKR theory for the adhesive contact of elastic spheres.¹⁷ In this theory the adhesion energy balances the elastic deformation of the spherical surfaces, leading to an actual area of contact $\pi^{5/3} (3\gamma/K)^{2/3} r_0^{4/3}$ and a contact energy of the form $\delta = \frac{2}{5} (3\pi\gamma)^{5/3} r_0^{4/3} K^{-2/3}$. For diblock copolymers this gives $p \sim N_A^{8/15}$, but there is as before a possibility of saturation.

IV. Discussion

I have theoretically studied the micellization of macrosurfactants with a soluble long polymer chain attached to an insoluble solid spherical particle. These tadpole molecules are likely to describe micellization in a diblock copolymer solution, where one of the blocks is in a glassy state, but they can also be prepared for instance by tethering biotinylated DNA strands to streptavidin-covered particles. The micellar architecture resulting from the aggregation of such molecules is rather different from the conventional structure of polymeric micelles. Here, the core of the micelle has a porous structure which allows for penetration of the chains in the core. This bunchy aspect leads to a new distribution of monomers in the micelles and provides simple geometric rules determining the micellar aggregation number.

The configuration of the polymers in the micelle has been studied within the framework of the Daoud-Cotton model for star polymers. This model assumes that all the chain ends lie at the outer surface of the corona, therefore overlooking the possibility of a chain-end distribution. Although this approximation, also known in the context

of grafted polymer layers as the Alexander-de Gennes model,¹⁸ does not correctly predict the concentration profile, it does lead to the correct scaling forms for all the relevant quantities in the problem.¹⁹ More insight into this question could also be obtained from numerical simulation methods similar to those performed for the polymer dendritic structures.²⁰

I also showed that the calculated scaling form for the aggregation number in diblock copolymers with a glassy head is in close agreement with results by Antonietti *et al.*¹² This suggests that bunchy micelles are good candidates for modeling micellization in that system. However care should be exerted when extracting information from a single set of data, because alternative explanations could be invoked. For instance, even in liquid cores, if one considers the unlikely but formal limit of very large interfacial tensions, which lead to large chain deformation in the core, one has the natural maximum value for chain extension $R_A \sim N_A$, which corresponds also to an aggregation number of the form $p \sim N_A^2$.

The construction of a bunchy micellar core can be thought as a process by which individual beads are added until saturation or some equilibrium aggregation number is reached (this clearly involves a smaller activation energy than merging two different micelles of a finite size^{21,22}). A particular feature in these micelles is that the exchange of a bead from the central core region to the bulk is practically forbidden. At a given moment only the surface beads may be easily exchanged. This contrasts with the classical micelles where all the micelle chains are "surface chains" and may then be directly exchanged with the bulk. The implications of such new features on the kinetics are currently under investigation.

The possibility of reaching a porous but compact configuration in the core will in practice depend on the characteristics of the adhesive contact between beads. The geometry described above assumes that local rearrangements are possible, allowing for a maximum number of bead-bead adhesive contacts and therefore for a compact structure. In the opposite case of an infinitely strong, nonsliding, nonrolling type of contact, the resulting core will have instead a fractal structure, with a fractal dimension which is likely to be smaller than the dimension of D.L.A. aggregates.²³

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