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Extension of the ladder model of self-assembly from cylindrical to disclike surfactant micelles

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ABSTRACT

The ladder model of growth of cylindrical micelles gives expressions for the micellar size distribution and for the mean aggregation number, which are in good agreement with the experiment. Here, we consider this model and its extension to the case of disclike micelles. In analogy with the modeling of elongated micelles as spherocylinders, the disclike micelles can be modeled as toro-discs. Upon micelle growth, the hemispherical caps of a cylindrical aggregate remain unchanged, whereas the semitoroidal periphery of a disclike micelle expands. This effect can be taken into account in the expression for the size distribution of the disclike micelles, which predicts the dependence of the micelle mean aggregation number on the surfactant concentration. It turns out that disclike micelles could form in a limited range of surfactant concentrations, and that their mean aggregation number cannot exceed a certain maximal value. Large disclike micelles can exist only near the border with the domain of cylindrical micelles. Then, small variations in the experimental conditions could induce a transformation of the disclike micelles into cylindrical ones.

1. Introduction

The disclike surfactant micelles can be considered as predecessors of the lamellar phase in the same way as the cylindrical micelles are predecessors of the formation of hexagonal phase. Then, a question arises: Why do the disclike micelles represent a rare form of self-assembly [1,2], despite the fact that lamellar phases are often observed? In the present article, we will try to answer this question on the basis of a recently developed model of the growth of disclike micelles [3], which upgrades the ladder model for cylindrical micelles [4].

Although disclike micelles are not so frequently observed, there is a considerable amount of accumulated experimental material from the investigations of such self-assemblies, termed also nanodiscs or bicelles. Single component disclike micelles have been detected in solutions of anionic [5]; nonionic [6] and fluorinated surfactants [7–10]. Nanodiscs have been observed and investigated in various binary mixtures of cationic and anionic (catanionic) surfactant solutions [1,11–15]. Discoidal micelles and nematic phase from such micelles have been detected in ternary mixtures of lauric acid with anionic and zwitterionic surfactants [16]. Disc-shaped aggregates are formed also in solutions of diblock and triblock copolymers [17–22]. Such aggregates are formed also by phospholipids dispersed in water [23,24] and in aqueous surfactant/lipid systems [25]. The self-assembly of discoidal micelles has been found to be a transitional kinetic stage in the processes of formation and decomposition of liposomes [26,27]. Disc-shaped aggregates have been discovered also in solutions of bile salts [28–30] and their mixtures with phospholipids [31].

Shape polydispersity and shape fluctuations in ionic surfactant micelles have been analyzed and transitions from spherical micelles to prolate and oblate spheroids have been predicted in the frame of a theoretical model [32] as well as by computer simulations [33]. Branching instabilities in growing cylindrical and disclike micelles have been also investigated [34]. The formation of such micelles and their transformation into liquid crystalline phases was theoretically described in terms of the Helfrich's curvature moduli [35,36] and lattice Hamiltonian models [37]. The phase transitions between isotropic and columnar phases (for rodlike micelles), as well as between isotropic and lamellar phases (for disclike micelles) have been theoretically studied [38]. It was established that the size of the cylindrical aggregates increases continuously with concentration, while the size of the discs could jump from small to infinite [37,39]. For cylindrical micelles, there are molecular–thermodynamic models, coupled with geometrical-constraint considerations, which quantitatively predict the micelle growth with the rise of surfactant concentration [4,40,41]. A molecular–thermodynamic model of disclike micelles was recently developed [3], which quantitatively describes the variation in the micelle size with the increase of surfactant concentration in agreement with the experiment.

To answer the question formulated in the beginning, here we first compare expressions for the mean aggregation number and area per surfactant-molecule headgroup for different micellar geometries:

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spherical, cylindrical, discoidal and toroidal (Section 2). Next, the ladder model for cylindrical micelles is considered (Section 3) in view of its subsequent generalization to disclike micelles (Section 4). Special attention is paid to the size distribution of the disclike micelles; to its application for predicting the micelle mean aggregation number and to the limitations on the growth of such micelles.

2. Geometrical relations for spherical, cylindrical and disclike micelles

2.1. Aggregation number and area per molecule

Because of the different surface curvature of spherical, cylindrical and disclike micelles, the surface area per headgroup is the largest for the spherical micelles and the smallest for the disclike ones. For the needs of the ladder model extension, here we summarize the basic equations that quantify this effect. For simplicity, we will consider single-component micelles. If the composition of mixed micelles is independent of their size (negligible segregation effects due to the greater peripheral curvature), the expressions for single-component micelles can be applied to multi-component ones in terms of average values [3].

For a *spherical micelle*, we have the following estimates [40,41]:

$$n_{\mathrm{s}} = \frac{\frac{4}{3}\pi R^3}{v}, \qquad a_{\mathrm{s}} = \frac{4\pi R^2}{n_{\mathrm{s}}} = \frac{3v}{R} \tag{2.1}$$

n_{s} is the aggregation number of the spherical micelle; R is the radius of its hydrophobic core; a_{s} is the area per molecule relative to the surface of the hydrophobic core; v is the volume per hydrocarbon chain in the micelle.

Assuming that a *cylindrical micelle* consists of a cylinder of length L and two hemispherical caps of radius R equal to the cylinder's radius (Fig. 1), we obtain:

$$n_{\mathrm{c}} = \frac{\pi R^2 L}{v}, \qquad a_{\mathrm{c}} = \frac{2\pi R L}{n_{\mathrm{c}}} = \frac{2v}{R} \tag{2.2}$$

n_{c} is the aggregation number of the cylindrical part of the micelle; a_{c} is the area per molecule relative to the cylindrical part of the surface of the hydrophobic core.

In analogy with the cylindrical micelles, which are modeled as "sphero-cylinders", the disclike micelles can be modeled as "toro-discs", consisting of a disc of diameter L and thickness $2R$, and of a periphery that represents a semitorus of radius R (Fig. 1). The volume and the surface area of the disclike micelle can be expressed in the form:

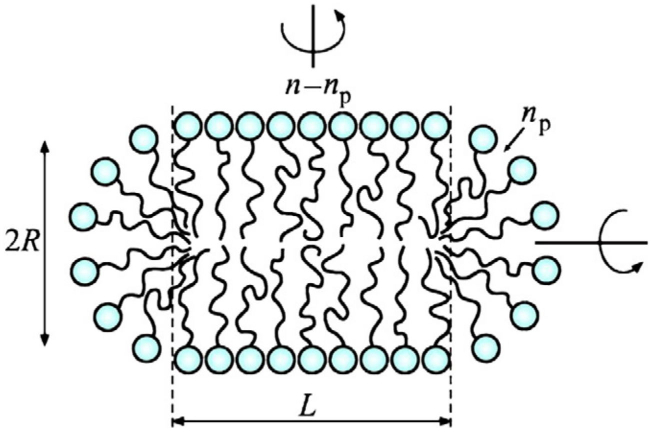

Fig. 1. Sketch of a micelle of aggregation number n, which includes n_{p} molecules belonging to the micellar periphery. A rotation around the *horizontal* axis yields a sphero-cylindrical micelle of cylinder length L and radius R, which equals the radius of the two hemispherical caps. A rotation around the *vertical* axis yields a toro-disc shaped micelle with disc diameter L and thickness $2R$, where R is also the radius of the micelle semitoroidal periphery.

$$V = V_{\mathrm{d}} + V_{\mathrm{t}}, \qquad A = A_{\mathrm{d}} + A_{\mathrm{t}} \tag{2.3}$$

where the indices 'd' and 't' refer to the discoidal and toroidal parts of the micelle, respectively. The volume and the surface area of the discoidal part are:

$$V_{\mathrm{d}} = \frac{\pi}{2} R L^2, \qquad A_{\mathrm{d}} = \frac{\pi}{2} L^2 \tag{2.4}$$

Likewise, the volume and surface area of the toroidal periphery of the micelle are [3]:

$$V_{\mathrm{t}} = \frac{\pi^2}{2} R^2 L + \frac{4}{3}\pi R^3, \qquad A_{\mathrm{t}} = \pi^2 R L + 4\pi R^2. \tag{2.5}$$

The number of surfactant molecules n_{d} and the area a_{d} in the *discoidal part* of the micelle are as follows:

$$n_{\mathrm{d}} = \frac{V_{\mathrm{d}}}{v} = \frac{\pi R L^2}{2v}, \qquad a_{\mathrm{d}} = \frac{\pi L^2}{2 n_{\mathrm{d}}} = \frac{v}{R} \tag{2.6}$$

where Eq. (2.4) was used. Summarizing Eqs. (2.1), (2.2) and (2.6), we obtain:

$$a_{\mathrm{d}} = \frac{v}{R}, \qquad a_{\mathrm{c}} = \frac{2v}{R}, \qquad a_{\mathrm{s}} = \frac{3v}{R}. \tag{2.7}$$

In other words, the area per molecule is the smallest for the discoidal part of a micelle and the largest for a spherical micelle.

For the *toroidal periphery* of the disclike micelle, in analogy with Eq. (2.6), using Eq. (2.5) we obtain:

$$n_{\mathrm{t}} = \frac{V_{\mathrm{t}}}{v} = \frac{1}{v}\left(\frac{\pi^2}{2} R^2 L + \frac{4}{3}\pi R^3\right), \tag{2.8}$$

$$a_{\mathrm{t}} = \frac{A_{\mathrm{t}}}{n_{\mathrm{t}}} = \frac{\pi L + 4R}{\pi L + \frac{8}{3}R}\,\frac{2v}{R} \tag{2.9}$$

where n_{t} and a_{t} are, respectively, the total number of surfactant molecules and the area per molecule in the toroidal part of the disclike micelle. Eq. (2.8) shows how the number of surfactant molecules in the toroidal part of the micelle increases with the micelle diameter L. In the limit $L = 0$, the "toro-disc" becomes a sphere, and Eq. (2.8) yields $n_{\mathrm{t}} = n_{\mathrm{s}}$; see Eq. (2.1).

The comparison of Eqs. (2.1), (2.2) and (2.9) leads to the following inequalities:

$$\frac{2v}{R} = a_{\mathrm{c}} \le a_{\mathrm{t}} \le a_{\mathrm{s}} = \frac{3v}{R}. \tag{2.10}$$

Thus, the area per molecule in the toroidal part of the micelle is greater than that for a cylindrical micelle, but smaller than that for a spherical micelle. For large disclike micelles ($L \to \infty$), Eq. (2.9) yields $a_{\mathrm{t}} \to a_{\mathrm{c}}$, whereas for small disclike micelles ($L \to 0$), Eq. (2.9) yields $a_{\mathrm{t}} \to a_{\mathrm{s}}$.

The expression $a_{\mathrm{d}} = v/R$ was obtained only on the basis of considerations about the radius and volume of the micelle *hydrophobic core*; see Eq. (2.6). This is possible only if the surfactant headgroups are relatively small and do not impose any geometrical constraints. For the *headgroups*, we can define a_{h} as the average excluded area per headgroup at close packing, projected on the surface of the micelle