Steric Fitting of the Rodlike Micelle Size

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The model developed in a previous paper (P. C. Schulz, *Colloid Polym. Sci.* **269**, 612 (1991)) was applied to rodlike micelles. The dependence of the aggregation number of rodlike micelles on ionic strength, polar head size, temperature, and alkyl chain length predicted by the present model agrees well with the experimental data in the literature. © 1992 Academic Press, Inc.

INTRODUCTION

$$l(nm) = 0.13n_{\rm c} + 0.1704 + 2r_{\rm ph},$$
 [1]

In a previous paper (1), a model was developed which predicts the size of a spherical micelle based on the assumption that (a) the micelle volume must be equal to n (n = aggregation number) times the volume of a micellized surfactant molecule, and (b) the micelle area must be equal to n times the area occupied by a polar head with its ionic atmosphere.

When *n* increases, the spherical micelle grows (1). The fully extended surfactant molecule length, *l*, is the maximum radius for spherical micelles when there is no inner cavity or polar head immersion into the micelle core. This corresponds to a critical aggregation number, $n_{\rm crit}$. When $n > n_{\rm crit}$, spherical micelles deform into prolate ellipsoids (2, 3), and then into rodlike micelles (4, 5). This was first proposed by Debye and Anacker (6). Below a critical length of about 100 *n*m, the rodlike micelles are rigid (7), while above this critical length, they have wormlike flexibility (7–10).

THEORY

Micelle Shape Change

The full surfactant molecule length is given by

¹ To whom correspondence should be addressed at Departamento de Química e Ingeniería Química, Universidad Nacional del Sur, Avda. Alem 1253---(8000) Bahia Blanca, Argentina. where n_c is the number of carbon atoms in the tail, and r_{ph} is the polar head radius (1). When the spherical micelle radius reaches l, the micelle can grow as a rod. This is because the area per micellized polar head is larger in a rodlike micelle than in a disklike one, as can be seen with a simple geometrical derivation. Cetyltrimethylammonium bromide rodlike micelles were directly observed by electron microscopy by several authors (11). The model adopted for rodlike micelles consists of a cylindrical body whose radius is l, capped at each end by hemispheres of radius l(1), as may be seen in Fig. 1.

The change in micelle shape occurs when the micelle core volume is given by

$$V_{\rm m,crit} = n_{\rm crit} (n_{\rm c} V_{\rm CH_2} + (V_{\rm CH_3} - V_{\rm CH_2})$$
$$= \frac{4}{3} \pi (l - 2r_{\rm ph})^3 \quad [2]$$

where V_{CH_3} and V_{CH_2} are the micellized molar volumes of methyl and methylene groups (1). For $n_c = 12$ at 298°K, the critical value of *n* is 57.3. For a compact hard particle model, when $n > n_{\text{crit}}$, first ellipsoidal and then rodlike micelles must appear. However, the upper limit of micellar growth keeping the typical spherical shape behavior seems to be a radius 1.2 times the fully extended chain length (5, 12, 13). There are several explanations for this: Hartley (14) suggests that the Brownian translation of the micelle as a whole and its

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FIG. 1. Model of a rodlike micelle.

Brownian rotation about a variable axis must be accompanied by an amoeba-like movement of its surface, due to the liquid-like state of the micelles (15-17). This may create a small flat area depressed below the mean surface to keep a possible central cavity filled with a terminal methyl group. Hartley (14) also questions the supposition that a central cavity may not occur in the micelle core. Since the creation of such a cavity with the volume of a methyl group could decrease the core density by less than 0.5%, it would be difficult for any existing method to detect this difference. The micelle core density is less than that of liquid hydrocarbons (17). Gruen (18, 19) stated that the free energy cost of forming such a hole is about 1.9kT at room temperature. It is clearly not a prohibitive cost, and it increases the maximum micelle aggregation number by about 50% with a chain length of 12 carbon atoms (18, 19). Aniansson (20) considers the increased aggregation number to be compatible with sphere behavior due to the monomer protrusion from the hydrophobic core. The protruding monomers decrease the volume of the hydrophobic core so that those not protruding are able to reach the innermost space of the micelles when their chains are almost fully extended.

Some authors (21–23) found that SDS micelles are spherical or globular until $n \approx 100$, and then rodlike when n > 100 (24). Missel *et al.* (4) found that when the axial ratio L/l < 2, micelles behave as spherical. This means that micelles behave as spherical until $n \approx 126$, for $n_c = 12$.

In Fig. 2, $\log n$ vs $\log I$ (I = ionic strength) was plotted for data of Hayashi and Ikeda

(24), who employed extremely pure SDS. The slope changes at $I \approx 0.34$ M and $n \approx 105$. Figure 2 also shows data for other surfactants. For dodecyldimethylammonium chloride, the transition occurs at n = 108, and for dodecyltrimethylammonium bromide, at $n \approx 103$, while for dodecyldimethylammonium bromide the transition occurs at $n \approx 95$ (7, 9, 25). However, for $n_c = 14$, $n_{crit} = 84$, a value close to that found for tetradecyltrimethylammonium chloride and bromide (7, 10, 25).

These changes correspond to an axial ratio of 1.73, which in turn corresponds to a spherical micelle whose radius is 1.28l, close to that of 1.2l shown by other surfactants (26, 27).

The Rodlike Micelle Size

Following the concepts of (1), the rodlike micelle volume (V_{Mr}) is

$$V_{\rm Mr} = \pi l^2 (L - 2l) + \frac{4}{3}\pi l^3 = n V_{\rm s}.$$
 [3]

Vs is the volume of a micellized surfactant molecule, given by (1)



FIG. 2. Logarithm of the aggregation number vs logarithm of the ionic strength plot. (a) Dodecyldimethylammonium chloride + NaCl \bullet (25), \bigcirc (38); (b) sodium dodecylsulfate 0.05 M + NaCl (28); (c) sodium dodecylsulfate + NaCl (24); (d) dodecyltrimethylammonium bromide + KBr (37).

$$V_{\rm s} = n_{\rm c}V_{\rm CH_2} + (V_{\rm CH_3} - V_{\rm CH_2})$$

+ $V_{\rm ph} + n_{\rm h}V_{\rm w}$, [4]

where $V_{\rm ph}$ is the volume of the polar head group, $V_{\rm w}$ is the volume of one water molecule, and *n*h is the number of micellized water molecules per micellized surfactant molecule.

The micelle surface area is (1)

$$A_{\rm Mr} = 2\pi L l = n\pi r_{\rm e}^2, \qquad [5]$$

where r_e is the effective radius of the micellized polar head, given by (1)

$$r_{\rm e} = r_{\rm x} + r_{\rm ph} + Z_{\rm ph} \alpha \left[\frac{\epsilon \epsilon_0 kT}{2e^2 I} \right]^{1/2}, \quad [6]$$

where r_x is the hydrated counterion radius, Z_{ph} is the charge of the polar head, and α is an adjustable parameter which holds for specific (nonelectrostatic) interactions between counterions and micelles (1). ϵ is the dielectric constant in the micelle stern layer, ϵ_0 the vacuum permitivity, k the Boltzmann constant, e the elementary charge, T the temperature, and I the ionic strength, computed without the contribution of co-ions (1).

Elimination of L from Eqs. [3] and [5] gives

$$n = \frac{4\pi l^3}{3(\pi l r_e^2 - 2V_s)}$$
[7]

and by introduction of Eqs. [4] and [6]

$$n = 4\pi (0.13n_{\rm c} + 0.1704 + 2r_{\rm ph})^{3} / 3 \left\{ \pi (0.13n_{\rm c} + 0.1704 + 2r_{\rm ph}) \times \left[r_{\rm x} + r_{\rm ph} + Z_{\rm ph} \alpha \left(\frac{\epsilon \epsilon_{\rm g} kT}{2e^{2}I} \right)^{1/2} \right]^{2} - \left[2n_{\rm c} V_{\rm CH_{2}} + (V_{\rm CH_{3}} - V_{\rm CH_{2}}) + V_{\rm ph} + n_{\rm n} V_{\rm w} \right] \right\}$$
[8]

TEST OF THE MODEL

When the chain length is large enough, Eq. [8] may be written as

$$n \approx \frac{0.52\pi n_{\rm c}^2}{0.39\pi r_{\rm e}^2 - 6V_{\rm CH_2}}$$
[9]

which means that *n* is a linear function of n_c^2 . This has been verified in the literature (1).

Keeping n_c as a constant, from equation [8] we obtain

$$\frac{1}{n} = \frac{3r_{\rm e}^2}{4l^2} - \frac{2V_{\rm s}}{4\pi l^3}$$
$$= A(r_{\rm x} + r_{\rm ph} + BZ_{\rm ph}(T/I)^{1/2})^2 - C. [10]$$

This means that 1/n is roughly a quadratic function of rx and rph and a linear function of T and I^{-1} .

Many examples of the varying dependence of log n on log I for spherical and rodlike micelles exist in the literature (see Fig. 2). All show positive slopes, as in the model presented here (25, 28-34).

Figure 3 shows the linear dependence of 1/n on 1/I for various surfactants in the rodlike



FIG. 3. Inverse of the aggregation number vs the inverse of the ionic strength plot. (a) Dodecyldimethylammonium bromide + KBr (33); (b) sodium dodecylsulfate + NaCl (40); (c) dodecylammonium chloride + NaCl (39); (d) sodium dodecylsulfate at 40°C + NaCl (31); (e) sodium dodecylsulfate + NaCl (24); (f) sodium dodecylsulfate at 25° C + NaCl (30); (g) hexadecyltrimethylammonium chloride + KCl (34); (h) octadecyltrimethylammonium bromide + KBr = (41), ∇ (42); (i) hexadecyltrimethylammonium bromide + KBr + (41), \diamond (42).

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domain. It should be noted that when I is large, the Debye-Hückel term becomes small in comparison with rx and rph. This means that 1/n is no longer a linear function of 1/I, as may be seen for very large rodlike micelles (32, 33).

Figure 4 shows the linear dependence of 1/n on T. The linearity is good. According to this model, nonionic micelles grow when T rises, because the polyoxyethylene chain hydration diminishes. Such behavior may be seen in the work of Brown *et al.* (35) and is the inverse of the behavior of ionic micelles.

Figure 5 shows the dependence of 1/n on $r_{\rm ph}$, for nonionic surfactants. According to Van Voorst Vaader (36), the area per surfactant molecule in polyoxyethylene surfactants is proportional to the square root of the number of ethylene oxide units:

$$\pi r_{\rm e}^2 = \pi r_{\rm ph}^2 \alpha(n_{\rm OE})^{1/2}$$
. [11]

This is why in Fig. 5 1/n is plotted vs $(nOE)^{1/2}$. The linearity is good.



FIG. 4. Inverse of the aggregation number vs T plot. (a) Triton X-100 (36); (b) sodium dodecylsulfate + 0.8 M NaCl (22); (c) tetrabutylammonium tetradecylsulfate (43); (d) tetradecyldimethylammonium bromide (45); (e) hexadecyltrimethylammonium bromide + 0.025 M KBr (44); (f) sodium dodecylsulfate (30); (g) sodium dodecylsulfate + 0.5 M NaCl (22).

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FIG. 5. Dependence of the inverse of the aggregation number vs the square root of the number of oxyethylene units in the hydrophilic chain of nonionic surfactants. (a) polyoxyethylene dodecyl ether (47); (b) polyoxyethylene hexadecyl ether (46).

The dependence of 1/n on rx is very difficult to test, because large counterions give spherical micelles (1).

REMARKS ON THE MODEL

The model of steric fitting of micelle size developed in a previous paper (1) has been extended to rodlike micelles. The predictions of this model regarding the dependence of the micelle aggregation number on temperature, ionic strength, hydrocarbon chain length, and polar head size agree with information available in the literature.

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