

Sphere-to-Cylinder Transition in Aqueous Micellar Solution of a Dimeric (Gemini) Surfactant

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The dimeric (gemini) surfactant 12-2-12 (dimethylene-1,2-bis(dodecyl dimethylammonium bromide)) has been known to form threadlike micelles at relatively low concentrations. We investigated the micellar growth of this surfactant in aqueous solutions by the much-improved cryo-TEM technique (transmission electron microscopy at cryogenic temperature) in the concentration range between 0.26 and 1.5 wt %. The digitally acquired electron micrographs of solutions, with concentrations up to about 1 wt %, show the coexistence of spheroidal micelles and long, threadlike micelles, the number and length of the latter increasing with concentration at the expense of the former. The micrographs show very few elongated micelles of intermediate sizes. Also, the endcaps of the elongated micelles can be seen to be of a larger diameter than the cylindrical body of those micelles. These results lend support to the theories, developed by various workers, that predicted these features. Some branching is observed at a surfactant concentration of 0.62 wt %. Above 1 wt %, the elongated micelles show frequent branching. The electron micrographs of the 1.5 wt % solution have the appearance of the saturated network postulated by theory.

Introduction

At concentrations above the cmc (critical micelle concentration), surfactants tend to self-associate in water to form micelles. The micelles are generally spherical or spheroidal at concentrations slightly above the cmc.¹ For most surfactants, micelles tend to grow and, in this process, change shape when an appropriate parameter is modified. Thus, an increase in concentration or temperature² brings about micellar growth. In most instances, this process results in the formation of elongated (locally cylindrical) micelles that can become extremely long. Such micelles have been referred to as “giant”,³ “rodlike”,⁴ “wormlike”,⁵ “threadlike”,⁶ and “polymer-like”.⁷ Each of these adjectives represents an attempt to capture the shape or some of the properties of these micelles. The growth of spherical micelles into elongated ones is a heavily investigated aspect of the solution behavior of surfactants, from both experimental and theoretical viewpoints. Indeed, it is of the utmost importance for the understanding of the rheology of surfactant solutions, as well as a number of other properties.⁸

Many studies report that the transformation of spherical micelles into elongated ones occurs above a certain value of the surfactant concentration, often referred to as “second cmc”.^{9–12} For instance, Reiss—Husson and Luzzatti,⁹ in a low-angle X-ray scattering study, concluded that cetyltrimethylammonium bromide micelles begin growing at concentrations above 0.15 M. Using light scattering and viscosity, Ikeda et al.¹⁰ showed that the molecular weight of the micelles of many surfactants increased sharply above a certain surfactant concentration or ionic strength. Using viscosimetry and magnetic birefringence, Porte et al.¹¹ showed the existence of a second cmc in hexadecylpyridinium bromide solutions. The existence

of a second cmc was also inferred through thermodynamics¹² and electrical conductivity.¹³ The giant micelles present in solutions of many surfactants have been directly visualized by means of cryo-transmission electron microscopy (cryo-TEM).^{5,6,14–17} It has been observed that they are generally flexible, thereby justifying the expressions “wormlike” and “threadlike”.

The growth of spherical micelles into elongated ones has been investigated extensively from the theoretical viewpoint as well. In the lowest approximation, the theory assumes that elongated micelles are of spherocylindrical shape, that is, cylinders terminated by hemispherical endcaps of the same diameter as the cylinder.¹ It is also assumed that the surfactant has a standard chemical potential that is lower in the cylindrical body (μ^0_C) than in the endcaps (μ^0_S).¹ Those two assumptions are sufficient to explain the micellar growth upon modification of a relevant parameter and to account for most of the available experimental data. However, as discussed by Porte et al.,¹¹ this simple model does not predict the existence of the second cmc. In addition, the simple spherocylindrical micelle model has been shown by Eriksson and Ljunggren¹⁸ to be incorrect on the basis of a detailed analysis of the mechanical equilibrium state of the micelle. These authors showed that the cylindrical part must have a slightly smaller diameter than that of the endcaps. Therefore, the endcaps contain a larger number of surfactant molecules than does one hemisphere of the minimum spherical micelle formed by the surfactant, which can be calculated from its alkyl chain carbon number using Tanford's relationships.¹⁹ The theories based on the generalized spherocylindrical micelle model, i.e., with swollen endcaps, involve the standard chemical potential of the surfactant molecules that are at the junction between the cylindrical body and the endcaps, μ^0_J .^{1,11} This chemical potential is larger than either μ^0_C or μ^0_S . In addition to accounting correctly for the existence of a second cmc, this more elaborate model predicts that the micelle size distribution

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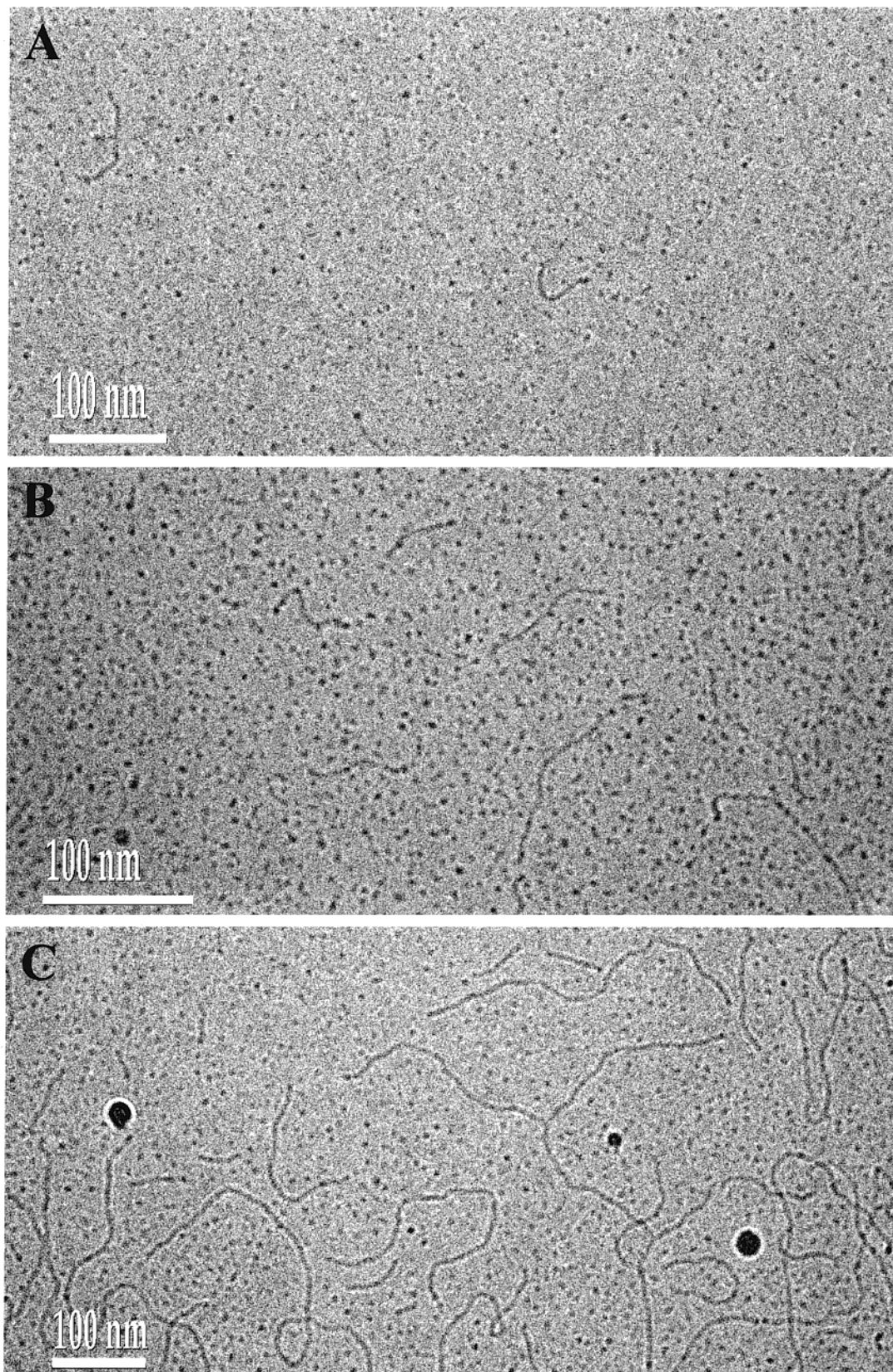
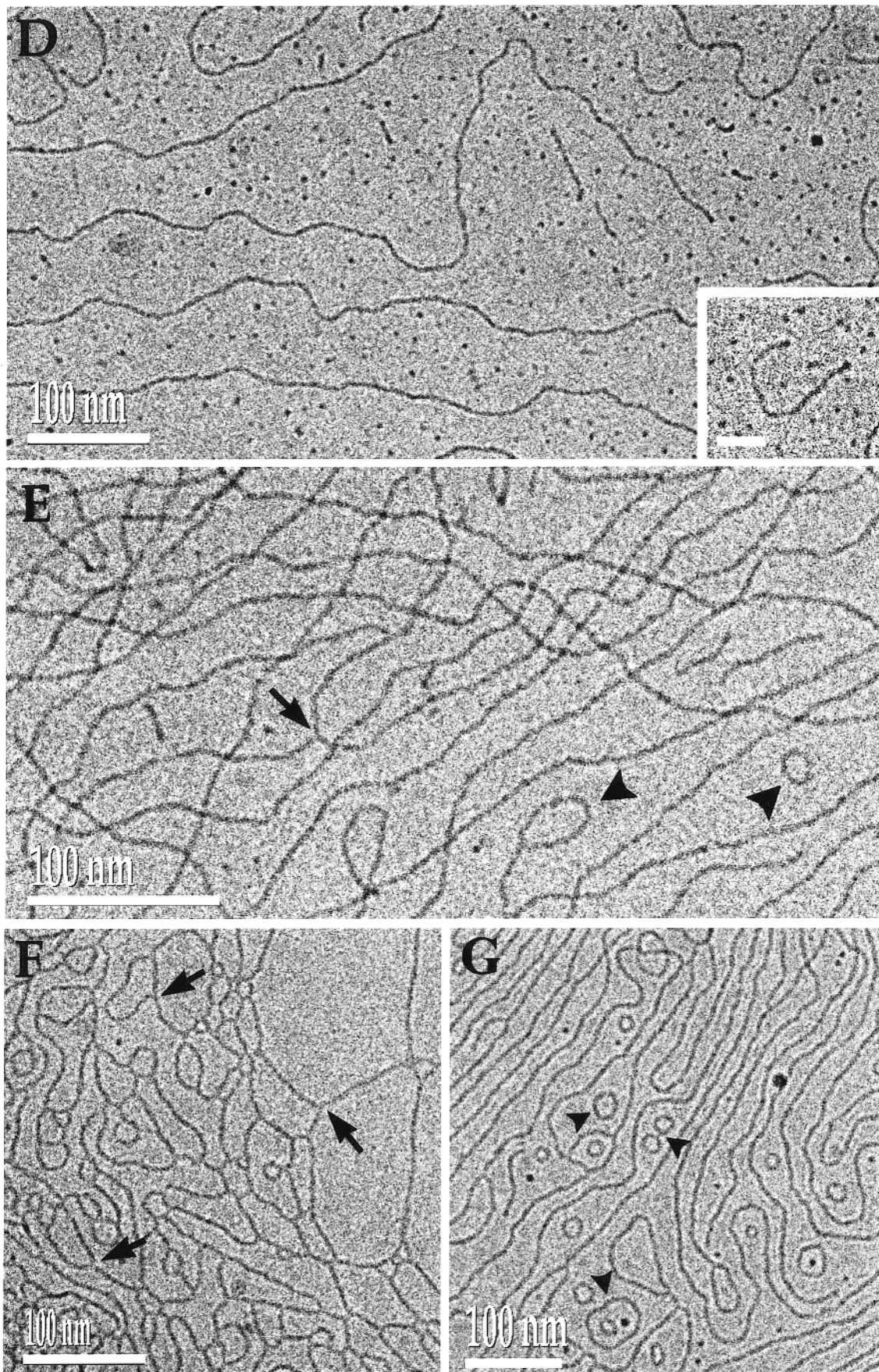


Figure 1. Cryo-TEM images of 12-2-12 solutions at 25 °C: (A) at 0.26 wt % 12-2-12, many spheroidal micelles (seen as dark dots) and a few cylindrical micelles are observed; (B) at 0.50 wt %, the cylindrical micelles are longer in comparison to (A), and their number is larger; (C) at 0.62 wt %, 12-2-12 and (D) at 0.74 wt % 12-2-12, the density of spheroidal micelles has significantly decreased, and the length of the elongated micelles has significantly increased (the inset in (D) shows that the endcap diameter is larger than the cylindrical-body diameter; bar = 25 nm); (E) at 1 wt % 12-2-12, there are very few spheroidal micelles and endcaps but many extremely elongated micelles (notice the existence of branching points (arrows) and rings (arrowheads)); (F) at 1.5 wt %, a saturated network of branched (arrows) cylindrical micelles is observed; and (G) at the same surfactant concentration, many closed rings (arrowheads) in addition to “normal” branching points are detected.



function must present a *gap* between spherical micelles and elongated ones.¹¹ The width of this gap is determined by the value of the standard chemical potential difference $\mu^0_C - \mu^0_I$.

This difference, as well as the value of $\mu^0_C - \mu^0_S$ (which affects the rate of micelle growth), depends on the nature of the surfactant. Note that Ikeda²⁰ presented a model, based on the

“mass-action law”, that also predicted the second cmc and the gap in the micelle size distribution function. In that model, however, the elongated micelles are assumed to be monodisperse.

As discussed above, the need for the general spherocylindrical micelle model arose from the inability of the simple spherocylindrical model to account for a variety of experimental results.^{11,21} The previous cryo-TEM studies of systems of elongated micelles generally focused on showing that the micelles present in the investigated systems were indeed elongated.^{5,6,14–17} However, cryo-TEM was not sufficiently advanced at that time to permit a study, however rough, of the distribution of micelle lengths. Such studies were also hampered by the fact that the surfactants used formed elongated micelles only at fairly high concentrations. Large amounts of material present often resulted in superposition of structures that prevented detailed microstructural study. Even further removed from the mind of the experimentalist was a visualization of the elongated micelle endcaps because of the limited resolution. This situation has recently improved on both fronts. Thus, digital recording of the images in cryo-TEM has resulted in an enormous improvement in the quality of the micrographs. This is due to our ability to select appropriate areas of the specimen by imaging at extremely low electron exposures, and then recording images at much higher magnification than that which was possible by imaging on photographic film. The immediate feedback to the microscopist (as there is no need to wait for the negatives to be developed) is another advantage that improves the efficiency and quality of data collection. Also, new surfactants, which form elongated micelles at relatively low concentration, the so-called dimeric (gemini) surfactants, have been introduced.^{16,17}

The purpose of this letter is to present results obtained by cryo-TEM with a dimeric surfactant, the dimethylene-1,2-bis-(dodecyltrimethylammonium bromide), referred to as 12-2-12. This surfactant, and its homologues with longer polymethylene spacers, have been heavily investigated.²² The 12-2-12 surfactant was selected for the present study because we had previously shown, by cryo-TEM, that it forms elongated micelles at a concentration of 1.5 wt %, in the absence of salt.¹⁶ That preliminary study has been greatly extended now by using our much improved cryo-TEM techniques in the concentration range from 0.26 to 1.5 wt %. The results presented below clearly show the gap in the micelle distribution size between spheroidal and elongated micelles, and the elongated micelle endcaps have a larger diameter than the cylindrical body of the micelles.

Experimental Section

The sample of 12-2-12 used in this study was prepared and purified as described elsewhere.²³ The 12-2-12 solutions were prepared by solubilizing the surfactant between 40–50 °C. No evolution of the solution (i.e., precipitation) was visually observed when the solution was left for weeks at room temperature. This is expected because the Krafft temperature of 12-2-12 is 14.4 °C.²⁴

The preparation of vitrified specimens for cryo-TEM was performed in a controlled environment vitrification chamber.²⁵ All of the solutions were quenched at 25 °C and 100% relative humidity.

The specimens were examined in a Philips CM120 microscope, operated at 120 kV, using an Oxford CT-3500 cryo-holder system. All of the specimens were observed in the microscope below –178 °C. The images were recorded digitally by a Gatan 791 MultiScan CCD camera with the DigitalMi-

crograph software package. The images were prepared for publication using the Adobe Photoshop package.

Results and Discussion

Figure 1 shows micrographs for 12-2-12 solutions of increasing concentration: 0.26; 0.50; 0.62; 0.74; 1.0; and 1.5 wt %, at 25 °C. The micrographs for the 0.26 and 0.50 wt % solutions (Figures 1A,1B) are very similar. They show many spheroidal micelles (seen as dark dots, Figures 1A,1B) and a few very elongated micelles. The most striking feature of these micrographs is probably the near complete absence of short elongated micelles, which would correspond to aggregation numbers equal to two or three times that of the spheroidal micelles. Some short micelles are observed, but their numbers are small, and the amount of surfactant in such micelles is negligible. A rough examination of micrographs of solution in that concentration range shows that the length of the elongated micelles is at least 10 times larger than the diameter of the spheroidal micelles.

The micrograph of the 0.62 and 0.74 wt % solutions (Figures 1C,1D) are somewhat similar to those of the more dilute solutions. However, the density of spheroidal micelles (taken as the number of black dots per unit area of the micrographs) is much decreased, and the length of the elongated micelles has much increased (several hundreds of nm). The occasional branching is also observed. Thus, micellar growth appears to occur via the newly added surfactant and also at the expense of the spheroidal micelles. Again, very few short elongated micelles are seen.

In the four micrographs discussed above (Figures 1A–1D), the chain ends (or endcaps) of several elongated micelles are clearly visible. It is remarkable that these chain ends (“endcaps”) are of larger diameter than the body of the elongated micelles. This feature is clearly seen at the higher magnification of the inset in Figure 1D. It should be pointed out that the 12-2-12 system is the second surfactant system for which we have shown that the endcap diameter is larger than the cylindrical part diameter. This has recently been shown in the commercial surfactant Habon G.²⁶ It has also been shown recently for diblock copolymer micelles in water.²⁷ This feature conforms to that which the mechanical micellar model of Eriksson and Ljunggren¹⁸ predicts. In the study of Porte et al.,¹¹ this difference of diameter is simply assumed, rather than coming as a result of the calculations, and it is used to justify the introduction of the different chemical potential of the surfactants at the endcap/cylinder junction (see above).

The micrograph of the 1 wt % solution (Figure 1E) shows very few spheroidal micelles and many extremely elongated micelles. Only a few endcaps are seen. This micrograph is qualitatively similar to the one originally reported¹⁶ for 12-2-12, but also shows branching points (arrows) and rings (arrowheads). It is of much better resolution and quality. The comparison of the two micrographs gives a good idea of the technological progress since 1992.

Figures 1F and 1G display micrographs of the 1.5 wt % solution. Figure 1F is of much interest in the sense that it resembles, quite nicely, the model of a saturated network^{28,29} reported for multiconnected (or branched, see arrows) threadlike micelles at high salt or surfactant concentration. Figure 1G shows many closed rings (arrowheads) in addition to “normal” branching points. Such isolated (or individual) toroidal or ringlike micelles were also observed by cryo-TEM in solutions of a cationic surfactant tetramer.³⁰ The spheroidal micelles have almost completely disappeared; very few endcaps can be seen.

At first sight, the disappearance of the spheroidal micelles at high surfactant concentration is not in agreement with the

concept of a second cmc. Indeed, the concentration of spheroidal micelles should remain constant at any surfactant concentration, C , above the second cmc. Recall, however, that in solutions of spheroidal ionic micelles, the concentration of free surfactant, C_{free} , that should remain constant and equal to the cmc at concentrations $C > \text{cmc}$, has been shown to decrease as C increases above the cmc.³¹ This decrease is apparently not in agreement with the concept of cmc. However, it was predicted a long time ago by Mysels for ionic micellar solutions.³² It arises because the micelles are partially ionized, and thus, the concentration of free counterion always increases with C . The application of the law of mass action to the micellar equilibrium then directly shows that the concentration of free surfactant, C_{free} , decreases as C is increased above the cmc. The situation is quite similar to that of a system of spheroidal and elongated ionic micelles and of free counterions in equilibrium. The concentration of free counterion increases monotonically with C . Because spheroidal micelles are more ionized than the elongated ones,¹² the concentration of the former will decrease upon increasing C . This arises from the application of the law of mass action to the equilibrium between spheroidal and elongated micelles and counterions. In fact, the concentration of spheroidal micelles goes through a maximum as the total surfactant concentration is increased, just like the concentration of free surfactant ions. These two decreases have the same origin, the monotonic increase of the concentration of free counterion with the total surfactant concentration. This aspect was not considered in the work of Porte et al.¹¹

Conclusions

The present study has permitted us to show that micelle growth in solutions of the dimeric surfactant 12-2-12 conforms to the models of Eriksson and Ljunggren¹⁸ and Porte et al.¹¹ At very low concentration, the micelles are mainly spheroidal. As the concentration is increased, elongated micelles appear and grow both in length and number, at the expense of the spheroidal micelles. The electron micrographs show that the diameter of the endcaps of the elongated micelles is larger than that of the cylindrical body, again in agreement with the above models.^{11,18} A very similar behavior has been observed in the nonionic surfactant C₁₂E₅ (pentaoxyethyleneglycol monododecyl ether),³³ in which micellar growth was induced by increasing the temperature or concentration. Thus, the features of micellar growth into elongated micelles discussed in this paper may be of fairly general character. More work is being carried out to extend the above results.

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