

# Micelle to Vesicle Transition Induced by Cosurfactant: Rheological Study and Direct Observations

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We report a micelle–vesicle transition induced by the addition of a neutral cosurfactant, hexanol, into a wormlike micellar solution of gemini cationic surfactant. This transition was investigated with rheology measurements as well as direct imaging techniques. It was observed by cryo transmission electron microscopy that micelles first become elongated with an increase of hexanol, which increases the viscosity. As the hexanol concentration is increased, another more fluid phase appears, where micelles are highly branched and coexist with small vesicles. One can describe this transition as a decrease of the spontaneous curvature caused by the cosurfactant molecule, which induces the elongation, and then the branching of micelles as well as the formation of small unilamellar vesicles. With a further increase of hexanol, these vesicles grow in size, which allows their observation by optical microscopy with differential interferential contrast. Some of these vesicles show long tubule-like shape, typically a few micrometers thick and up to several hundred micrometers long.

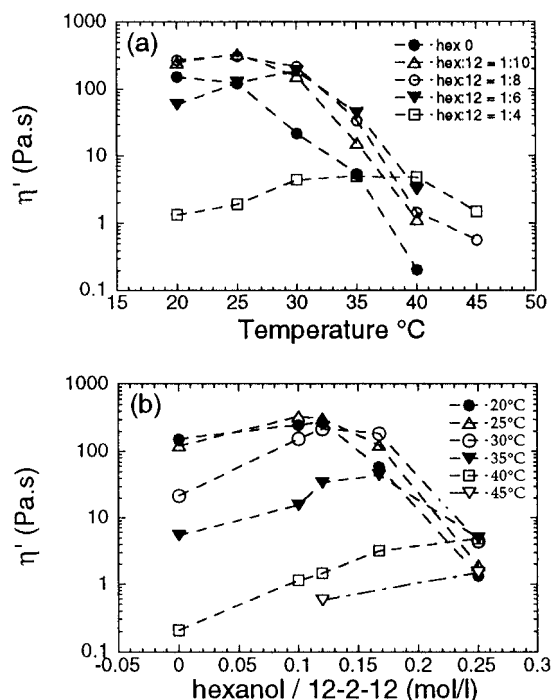
## Introduction

Recently, the effect of cosurfactants and counterions on the micelle–vesicle transition that is associated with the variation of the curvature of the amphiphilic film has been of particular interest and has been investigated experimentally<sup>1–4</sup> as well as theoretically.<sup>5</sup> Addition of alcohols with certain hydrophobic chain length was shown to decrease the curvature of surfactant film: wormlike micelles were observed to grow<sup>6</sup> and show transitions to vesicles.<sup>4,7</sup> Hassan et al. have, on the other hand, investigated<sup>2</sup> the thermally reversible transition between vesicles (room temperature) and micelles (high temperature) of CTAHNC,<sup>8</sup> and they have shown that this transition was caused by an increase in the ionization degree of HNC<sup>−</sup> counterions.

In the present study, we report on a micelle–vesicle transition induced by a neutral cosurfactant,<sup>4,7</sup> hexanol, in the solution of gemini cationic surfactant 12-2-12.<sup>9</sup> Several experimental studies have shown<sup>9,10</sup> that aqueous solutions of the gemini surfactant form giant wormlike micelles at low concentration without addition of salt. We have observed, by both rheological and direct observation techniques, that the solution shows a transition to a vesicle phase when a roughly equimolar concentration of hexanol is added. These vesicles show a tubule-like structure. The rheological behavior suggests that an increase of temperature triggers a vesicles–micelles transition, which can be explained by the variation of the solubility of hexanol.

## Materials and Methods

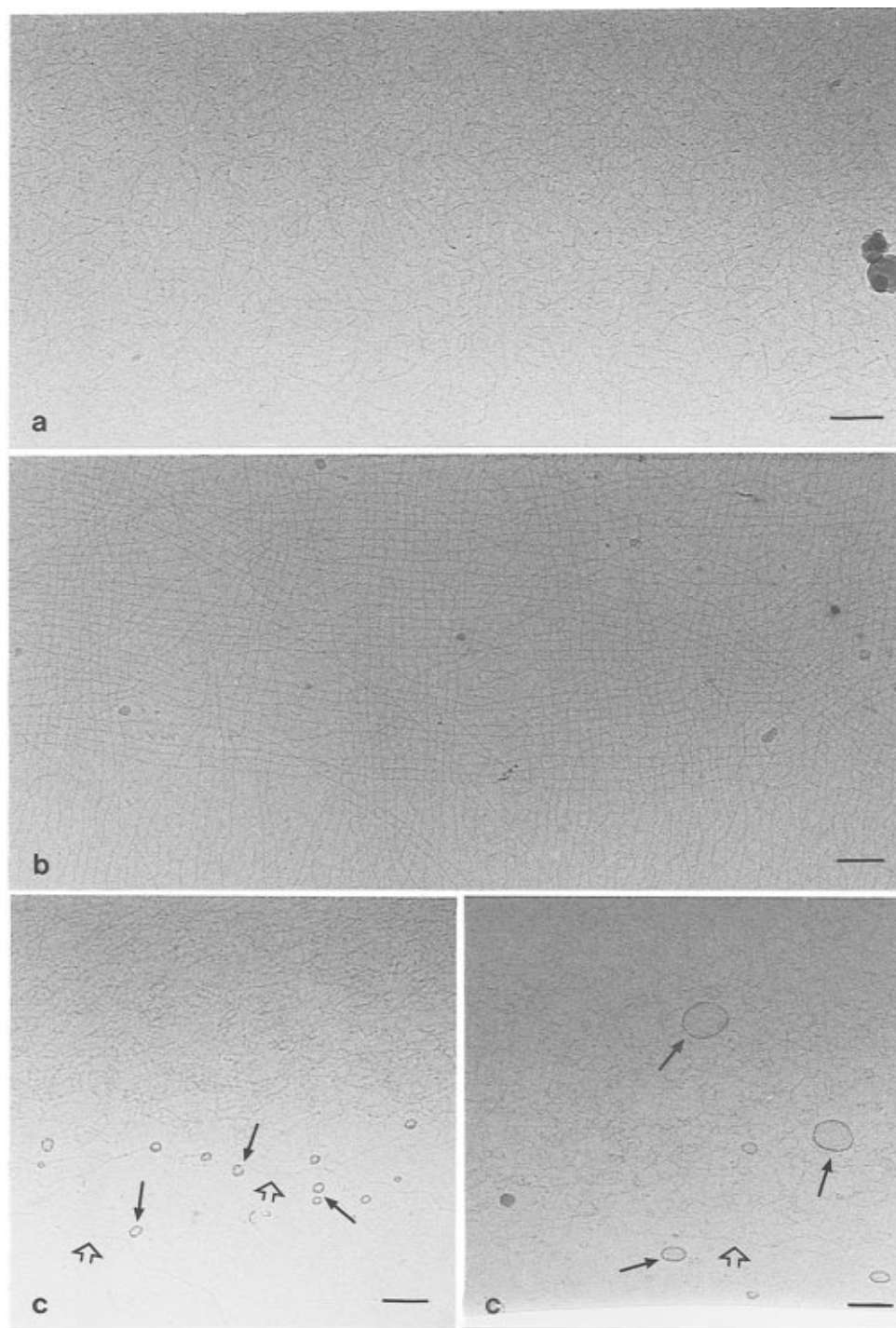
The surfactant molecule, 12-2-12 consists of two amphiphilic moieties ( $\text{C}_{12}\text{H}_{25}(\text{CH}_3)_2\text{N}^+\text{Br}^-$ ) with a polymethylene spacer ( $\text{CH}_2$ )<sub>2</sub> that connects the two polar heads, i.e. the ammonium ions. The surfactant was synthesized in our laboratory, and the purity was verified by <sup>1</sup>H NMR. Hexanol was purchased from Fluka Chem. Co. and was used without further purification.



**Figure 1.** Viscosity as a function of (a) temperature for various hexanol to 12-2-12 molar ratios and (b) hexanol to 12-2-12 molar ratio for various temperatures.

The rheological measurements were performed on a Rheometrics RFS II strain-imposed Fluid Spectrometer using a parallel geometry that consists of a titanium upper plate and an aluminum-coated lower plate, both of 50 mm diameter. A device to avoid evaporation was installed. The frequency range investigated was from 0.1 to 100 rad/s except for a few samples with which it was necessary to investigate the frequency down to 0.01 rad/s since the plateau of the viscosity at low frequency existed only at frequencies lower than 0.1 rad/s. However, we had to try, whenever possible, to avoid decreasing the frequency

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**Figure 2.** Cryo-TEM images of the 12-2-12 1.5% w/w solutions with (a) no hexanol, (b) hex:12 1:8, (c) hex:12 1:3. Bars = 0.1  $\mu\text{m}$ . (a) Wormlike micelles: the micelles are polydisperse in length, and their diameters are about 40 Å. (b) The micelles are much longer than the ones in (a), and their lengths are up to several micrometers with a diameter of  $\sim 40$  Å. Only a few micelles are short. (c) In this figure three kinds of structures are visible. Vesicles (size between  $\sim 180$  and  $\sim 1000$  Å) (small arrows), long micelles (open arrows), and branched micelles. The latter are the most important population in this preparation. They appear as tangled structures.

to under 0.1 rad/s since this increases the experimental time, which causes unavoidable evaporation even with the device mentioned above (experiments with frequency range 0.01–100 rad/s last eight times longer than those with 0.1–100 rad/s). The investigated temperature range was between 20 and 45 °C.

The optical microscopy observation was made on a Zeiss Axiovert 135 Microscope using a 100 $\times$  objective (Numerical aperture 1.3) and video-enhanced differential interference contrast (DIC). The images were processed using a Hamamatsu CCD camera (C2400-77) and an Argus20 real time image processor. The images were taken at room temperature ( $\sim 23$  °C).

Cryo transmission electron microscopy (cryo-TEM) provides high-resolution images of microstructured fluid systems<sup>11</sup> that can be probed only indirectly with other experiments. We have obtained direct images of micelles as well as vesicles in the frozen-hydrated state. The detailed description of the technique is shown elsewhere.<sup>12</sup>

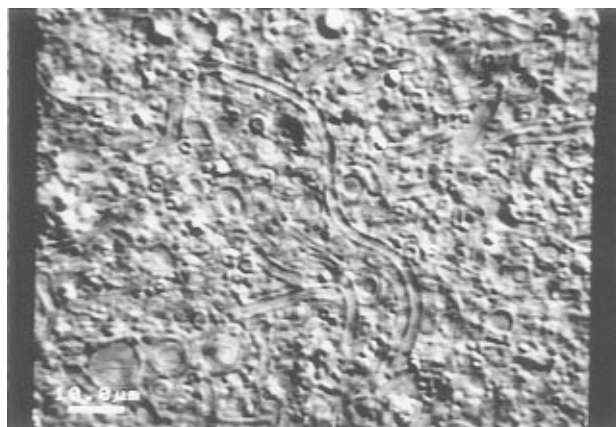
These two imaging techniques were used to give complementary images for a different range of hexanol concentrations. Cryo-TEM allowed us to observe wormlike micelles as well as small vesicles up to several hundred angstroms in diameter. However, for higher hexanol concentrations, the tubule-like vesicles have a radius of the order of micrometers, and therefore

it is not possible to observe them by EM. On the other hand, objects of such size can be observed under the light microscope.

## Results and Discussions

**Rheology.** Five percent w/w 12-2-12 solutions were prepared with various hexanol concentrations that correspond to the molar ratio of hexanol to 12-2-12 (referred to as hex:12) of 1:10, 1:8, 1:6, and 1:4, as well as a sample with no added hexanol. After being mixed at 55 °C for 1 h, the samples were stored in an oven at 30 °C for 2 days to reach equilibrium. The sample with no added hexanol<sup>8</sup> behaves as a typical semidilute solution of wormlike micelles,<sup>13,14</sup> the rheological behavior is quasi-Maxwellian at low frequency where the mechanism is dominated by the reversible scission processes, and a deviation occurs at a frequency of the order of the inverse of the breaking time of the micelles. However, for the samples with hexanol, the Maxwellian behavior was observed only at temperatures higher than a certain temperature that depends on concentration, with significant deviation appearing at lower temperature. In Figure 1a,b, the viscosity at low frequency (plateau value) is shown for various temperatures, as well as various hex:12 ratios. For the sample with no added hexanol, the viscosity shows a simple decrease as the temperature is increased (Figure 1a), which is the classic behavior of micelles,<sup>15</sup> while as the hexanol content is increased, the viscosity shows a maximum at a certain temperature. The temperature at the maximum viscosity increases with the hexanol ratio. This suggests that for the samples with hexanol at low temperature, vesicles and micelles coexist. As the temperature is increased, the solubility of hexanol in water increases, and the vesicles are transformed into micelles. This behavior is in agreement with what was reported in ref 2, where the vesicle–micelle transition induced by the increase of temperature was explained to be due to the increased dissociation of the counterions. Another aspect is shown in Figure 1b, where the viscosity as a function of hex:12 ratio is plotted for various temperatures. The system exhibits a maximum viscosity at a certain hex:12 ratio and then shows a decrease with further increase of hexanol. Beyond a certain hex:12 ratio (about 1:1.5 for 20 °C), solutions become turbid.

**Direct Imagings.** Since it is very difficult to get plausible images with the cryo TEM technique for solutions with surfactant concentrations as high as 5% w/w, the concentration at which the rheology measurements were performed, the cryo TEM observations were performed for the solutions with 1.5% 12-2-12 concentration. On the other hand, we could not perform the rheology measurements at 1.5% solutions because of the nonlinearity of the solutions at this concentration, which show shear thickening behavior.<sup>10</sup> However, it had been shown<sup>9</sup> that without hexanol, samples consist of wormlike micelles for both 1.5% and 5% 12-2-12 concentrations, and the optical observations confirmed that the observed vesicles are very similar in nature for two sets of surfactant concentrations except for their density. Finally the size of the vesicles becomes of the order of micrometers (observable on the optical microscope) at a hex:12 ratio of around 1:1.5 for both surfactant concentrations at room temperature. In Figure 2a–c cryo TEM images are shown for 1.5% solutions of 12-2-12 with various hex:12 ratio. For a solution without hexanol (Figure 2a), micelles are quite polydisperse in length and are slightly entangled. The diameter of the micelles is  $\sim 40$  Å. Figure 2b shows a sample of hex:12 ratio 1:8. The micelles are much longer, up to several micrometers (diameter 40 Å). This concentration corresponds to where the viscosity starts to increase. A new type of phase appears with a further increase of hexanol ratio (Figure 2c), hex:12 molar ratio 1:3. At this concentration, we observe a



**Figure 3.** Optical micrograph of 12-2-12 1.5% w/w solutions with hex:12 1.5:1. Very long tubular-like vesicles are observed. Bar = 10  $\mu$ m.

coexistence of vesicles and micelles. These vesicles are unilamellar vesicles (diameter ranging from 180 up to 1000 Å;<sup>16,17</sup> as for the micelles, they are much shorter than the ones in Figure 2a,b and seem to be highly branched. Only a few micelles are long. The sample becomes turbid for a hex:12 ratio higher than 1:1.5, and for these samples we have performed the optical microscope observations with DIC optics. For the hex:12 ratios 1:1.5 and 1:1, we observed spherical vesicles about a few micrometers in diameter. For the hex:12 ratio higher than 1.5:1, we systematically observed a mixture of spherical vesicles and very long tubule-like vesicles (Figure 3).

These observations suggest that the addition of hexanol to micellar solutions decreases the spontaneous curvature of the film.<sup>18,19</sup> This can be understood as the increase in packing parameter<sup>20,21</sup> by mixing alcohol molecules that have small hydrophilic head groups (OH group) to the 12-2-12 surfactant molecules. As the packing parameter increases, the cap energy<sup>21,22</sup> (the energy needed to form two ends from a cylinder) also increases; thus, micelles become elongated<sup>23,24</sup> until they reach their maximum length. The viscosity increases as a function of the hexanol ratio with surfactant concentration. At a certain hexanol ratio, the spontaneous curvature becomes close to zero and vesicles start to form. At this concentration, coexisting micelles seem to be branched, which is also a consequence of the decrease of the spontaneous curvature, and viscosity shows a strong decrease, primarily because of the formation of vesicles and secondarily probably because of the lower viscosity of the branched micelles.<sup>25</sup>

The size of the vesicles increases with the hexanol to 12-2-12 ratio to up to as much as a few micrometers. The tubule-like shape of these vesicles is probably due to the asymmetric shape of the surfactant molecule.

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