

Viscosity Peak due to Shape Transition from Wormlike to Disklike Micelles: Effect of Dodecanoic Acid

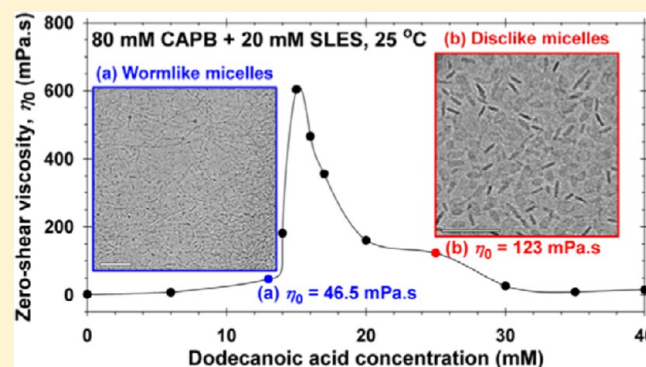
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Supporting Information

ABSTRACT: Here, we have investigated the synergistic growth of long wormlike micelles and their transformation into disklike micelles, which occurs in three-component solutions composed of sodium lauryl ether sulfate (SLES; anionic), cocamidopropyl betaine (CAPB; zwitterionic), and dodecanoic acid (HC12; nonionic). The solution rheology is characterized in terms of zero-shear viscosities and characteristic times for micellar breaking and reptation. Furthermore, the microstructure evolution, leading to the observed rheological behavior, is revealed by cryo-transmission electron microscopy (TEM) micrographs. In all cases, the CAPB-to-SLES ratio is fixed, whereas the fatty acid concentration is varied. At a certain HC12 concentration, the solution viscosity passes through a maximum. The cryo-TEM imaging indicates that wormlike micelles appear before the peak, grow further up to the peak, and finally transform into disklike aggregates (a very rare micellar structure) after the peak. The transformation of worms into disks leads to a drop in viscosity because the length-to-thickness aspect ratio of the disks is significantly lower than that of the worms. In this article, we elucidate the structure–rheology relations in micellar solutions that might be applied for the design of personal-care and household formulations.



1. INTRODUCTION

Amphiphilic molecules (surfactants), when dissolved in water, self-assemble into different structures and mesophases.¹ Just above the critical micelle concentration (CMC), spherical micelles represent the dominant form of self-assembly.¹ At higher surfactant concentrations, above the so-called second CMC,² cylindrical, wormlike or disklike micelles appear in the solution. By increasing the surfactant concentration further, the amphiphilic molecules form liquid-crystalline mesophases, which typically appear in the following order: hexagonal, cubic, lamellar, inverted cubic, and inverted hexagonal.^{1,3}

Because the liquid-crystalline phases, containing infinite aggregates, are prone to phase separation,¹ the isotropic micellar formulations are preferred in many industrial applications. For instance, isotropic worm-forming mixtures are commonly used as thickeners in cosmetics and home-care^{4–6} and even as drug-delivery vehicles in biomedicine.⁵ These worm-forming surfactant solutions have also attracted considerable attention because of their complex phase behavior, as well as the non-monotonic trends in their viscoelastic properties. Rehage and Hoffmann,^{7,8} followed by many others,^{9–34} have shown that the zero-shear viscosity of such worm-forming solutions can pass through one or even two peaks as a function of the concentration of additive.

Mechanistic understanding of the origins of the viscosity peaks was first summarized in ref 29 and then expanded in ref 35. To the left of the viscosity peak, the spherical or elongated micelles transform into cylindrical or even wormlike micelles, thus leading to a rise in viscosity. To the right of the viscosity peak, three nontrivial pathways for viscosity reduction have been found: (1) micellar branching: branches, which are not covalently bonded as in cross-linked polymers, can either form 4-fold ghostlike crossings or slide along the micelle;^{25,36–39} (2) micellar shortening: the micelles decrease in size at higher additive concentrations as observed in catanionic mixtures;^{4,15,29} and (3) phase or shape transition: micellar solutions transform into lyotropic mesophases or worms convert into disks.³⁴ The growth of rodlike micelles^{40,41} and the formation of a transient network of wormlike micelles can be investigated with small-angle neutron scattering and/or dynamic light scattering.⁴² To find the viscosity reduction pathway for a given surfactant mixture, direct imaging by cryo-transmission electron microscopy (TEM) could be applied.

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In a previous paper,²⁵ we investigated the growth of giant wormlike micelles promoted by the addition of octanoic (caprylic) acid (HC8) to mixed solutions, containing sodium lauryl ether sulfate (SLES; anionic) and cocamidopropyl betaine (CAPB; zwitterionic). A high and sharp peak in the zero-shear viscosity vs the HC8 concentration plot was found. By cryogenic TEM, it was established that long threadlike micelles form before the peak and intertwined worms are present at the peak, whereas after the peak, the viscosity decreases due to the formation of multiconnected micelles.²⁵ Such SLES–CAPB–fatty-acid-based systems are very interesting from both fundamental and applied viewpoints^{23–26,34} because they are the main components of many personal-care products and their non-monotonic rheological behavior affects the product consistency and stability. Therefore, if we understand better the physicochemical properties of such shampoo-like solutions, we could devise design rules for preparing formulations with desired texture and microstructure.

In the present article, our main goal is to investigate the structure–rheology relations in three-component solutions that contain CAPB, SLES, and dodecanoic (lauric) acid (HC12) as a nonionic cosurfactant. Concerning the texture, SLES–CAPB-based systems have been recently studied in terms of their viscoelastic properties;^{23–26,34,43–46} however, direct structure-specific information for the underlying microstructure is still lacking (apart from our previous paper, ref 25). For that reason, to reveal the structure–rheology (microstructure–texture) relationships, we employed here both polarized-light optical microscopy and cryogenic TEM. The latter method revealed quite different micelle morphology; instead of multiconnected micelles (as for HC8), at higher HC12 concentrations, we observed disklike micelles, which represent a very rare micellar structure.^{24,34,47}

The article is structured as follows. The theory used for the interpretation of the rheological data is summarized in Section 2. The materials and experimental methods used are described in Section 3. Finally, we present and discuss the experimental results with focus on the cause-and-effect relationship between the microstructure and rheology in Section 4.

2. THEORETICAL BACKGROUND

In the semidilute regime, the rheological properties of wormlike micelles are often described by the model of Maxwell for viscoelastic bodies. According to Maxwell's model, in the regime of oscillatory shear deformations, the storage and loss moduli, G' and G'' , obey the following relationships⁴⁸

$$G' = \frac{\omega^2 \tau_R^2}{1 + \omega^2 \tau_R^2} G_0, \quad G'' = \frac{\omega \tau_R}{1 + \omega^2 \tau_R^2} G_0 \quad (1)$$

where G_0 is the elastic modulus at its high-frequency plateau and ω is the angular frequency of oscillations. In this model, the magnitude of the complex viscosity, $|\eta^*|$, reads⁴⁸

$$|\eta^*| = \frac{G_0 \tau_R}{\sqrt{1 + \omega^2 \tau_R^2}} \quad (2)$$

An important parameter that is determined from the oscillatory deformations is the so-called crossover frequency, ω_c . At $\omega = \omega_c$, the storage and loss moduli become equal, i.e., $G' = G''$. From the last equality and eq 1, we have that $\omega_c \tau_R = 1$. Then, we find that $\tau_R = 1/\omega_c$ and $G_0 = 2G'$ at the crossover point.

Knowing both G_0 and τ_R , we can determine the zero-frequency viscosity, $\eta_{\omega=0}$ ^{7,8,48,49}

$$\eta_{\omega=0} = G_0 \tau_R \quad (3)$$

The above expression for $\eta_{\omega=0}$ follows from eq 2 at $\omega = 0$. In addition, knowing G_0 , the mesh size of the transient micellar network (i.e., the correlation length), ξ , can be estimated from the following expression^{7,8,48,49}

$$\xi \approx \left(\frac{k_B T}{G_0} \right)^{1/3} \quad (4)$$

Furthermore, by algebraic transformations of eq 1, we see that G' and G'' , which are both positive, obey the equation of a semicircle in the plane (G' , G'')

$$(G' - G_{\text{osc}})^2 + G''^2 = G_{\text{osc}}^2 \quad (5)$$

where $G_{\text{osc}} = G_0/2$. Equation 5 is thus often applied to check whether the Maxwell model is valid by plotting G'' vs G' , which is also known as a Cole–Cole plot.^{48,50–52}

To interpret the Cole–Cole plots, we used the Cates' model that describes the modes of stress relaxation in semidilute or concentrated micellar solutions.^{49–55} In Cates' model, the stress relief processes are (i) reptation, i.e., curvilinear diffusion of a worm through the transient micellar network,⁵⁵ and (ii) reversible scission, the micelle ability to break and reform. The said processes are characterized by times for reptation τ_{rep} and for breaking τ_{break} . These characteristic times determine the ratio, $\zeta = \tau_{\text{break}}/\tau_{\text{rep}}$, as well as the overall rheological response. If $\tau_{\text{break}} \ll \tau_{\text{rep}}$, i.e., $\zeta \ll 1$, such worm-forming solutions behave as Maxwellian fluids with a single relaxation time τ_R given by^{49,53}

$$\tau_R \cong (\tau_{\text{break}} \tau_{\text{rep}})^{1/2} \quad (6)$$

Deviations from the pure Maxwellian behavior of wormlike micellar solutions typically occur at high frequencies, resulting in an upturn of G'' .^{50–52} These deviations are typically due to the appearance of “breathing” or Rouse modes. To characterize quantitatively the departure from the ideal Maxwell model, Turner and Cates⁵⁰ defined the following parameter

$$\bar{\zeta} = \frac{\tau_{\text{break}}}{\tau_R} \quad (7)$$

By comparing experimental Cole–Cole plots with numerical calculations, one can determine $\bar{\zeta}$ and then estimate τ_{break} from viscoelastic data only using eq 7.

3. MATERIALS AND METHODS

3.1. Materials. We used cocamidopropyl betaine (CAPB; zwitterionic), $M = 342.52$ g/mol, with commercial name TEGO Betain F50, product of Evonik Nutrition & Care, GmbH Germany; sodium lauryl ether sulfate with one ethylene oxide group (SLES-1EO or briefly SLES; anionic), $M = 332.43$ g/mol, with commercial name STEOL CS-170 UB, product of Stepan Co.; and dodecanoic (lauric) acid (HC12; nonionic), $M = 200.32$ g/mol, product of Sigma-Aldrich, Germany. Here, CAPB and SLES are industrial-grade surfactants, whereas HC12 is of analytical grade. Figure 1 shows the structural formulas of CAPB, SLES, and HC12. As shown in ref 25, we found that 100 mM CAPB solution contains 118 ± 6 mM NaCl as an admixture (see Figure S1 in Appendix A). All chemicals were used as received without further purification. We prepared all aqueous solutions using deionized water from an Elix 3 water purification system (Merck Millipore, Merck KGaA, Germany).

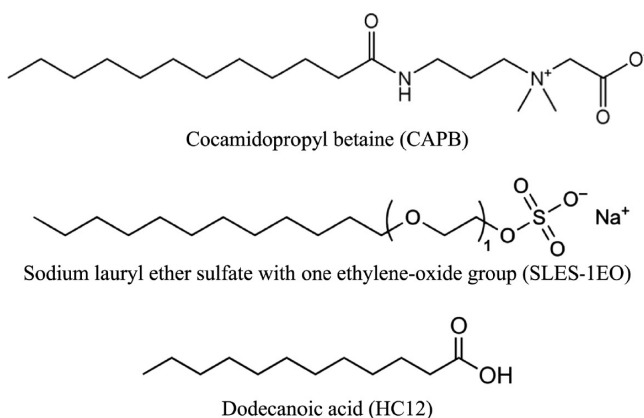


Figure 1. Structural formulas of the amphiphilic molecules used.

3.2. Solution Preparation. At a fixed CAPB/SLES molar ratio equal to 4:1, we studied the effect of fatty acid (HC12) on the micellar growth. First, we prepared the stock (binary) surfactant solution (CAPB/SLES = 4:1) in a reaction bottle, where it was homogenized by stirring at room temperature. Second, the necessary amount of dodecanoic acid (HC12) was dissolved in the mixed micelles by vigorous agitation on a temperature-controlled magnetic stirrer (at 70–75 °C) for at least 1.5 h. To reach chemical equilibrium, we kept the resulting three-component mixture in a thermostat at 25 °C for 24 h. Finally, we used the solutions for rheological and pH measurements, as well as for cryo-TEM imaging and polarized-light microscopy.

3.3. Shear Rheology. A rotational rheometer (Bohlin Gemini, Malvern Instruments, U.K.) was used to characterize the rheological properties of the micellar solutions. The experiments were carried out using a cone-and-plate geometry with plate temperature, $T = 25$ °C, maintained by a Peltier unit. To minimize the change in sample composition by evaporation, a solvent trap was used during each measurement. If $\eta_0 \leq 40$ Pa·s, a 60 mm cone with a cone angle of 2° (the gap distance is 70 μm) was used. If $\eta_0 > 40$ Pa·s, a 40 mm cone with a cone angle of 4° (the gap distance is 150 μm) was used instead. We then performed the rheological experiments in both (i) steady shear and (ii) oscillatory deformation regimes.

In the case of steady shear, we measured the shear stress, σ , dependence on the shear rate, $\dot{\gamma}$, in the range from 0.01 to 10 s^{-1} . Here, the apparent viscosity is defined as $\eta(\dot{\gamma}) = \sigma/\dot{\gamma}$, whereas the zero-shear viscosity, η_0 , represents the limiting value of η at $\dot{\gamma} \rightarrow 0$.

In the case of oscillatory deformation (stress-controlled frequency sweep), we measured how the storage and loss moduli, G' and G'' , depend on the oscillation frequency, $\nu = \omega/(2\pi)$, in the range from 0.01 to 10 Hz. For all studied samples, the viscoelastic response was linear at 2% shear-strain amplitude that was applied.

3.4. Cryo-TEM Imaging. A controlled environment vitrification system (CEVS) was used to prepare the specimens at 25 °C and 100% relative humidity. First, we placed a microliter droplet of the examined solution on a TEM grid covered with a perforated carbon film. Second, we manually blotted off the excess liquid with filter paper. The blotting duration and mode of application were tuned, so that the final film thickness did not exceed 250 nm.⁵⁶ Furthermore, to reduce the shearing effects caused by the blotting procedure, we kept the blotted samples in the CEVS for several seconds.⁵⁶ Third, we plunged the relaxed samples into liquid ethane (−183 °C) to form vitrified specimens, which we then stored in liquid nitrogen (−196 °C) until examination. All specimens were finally examined in a Tecnai T12 G² transmission electron microscope (FEI Co.), which operated at an acceleration voltage of 120 kV using a Gatan cryo-specimen holder that maintained the vitrified specimens below −175 °C. We used the low-dose imaging mode of the microscope to minimize the electron-beam radiation damage: the electron dose (always below 150 e/nm^2) was kept minimal, yet sufficient to record informative micrographs. DigitalMicrograph software was used to record digitally the micrographs taken on a cooled Gatan Ultrascan 1000 camera.

3.5. Light Microscopy. The phase behavior of the three-component mixtures was investigated by polarized-light optical microscopy in transmission mode. We used an optical microscope (Axioplan, Zeiss, Germany), equipped with two crossed polarizers (a polarizer and an analyzer) and a compensator (retarder), to distinguish between micellar (isotropic) and liquid-crystalline (birefringent) media. To improve visibility by introducing vivid interference colors, we placed a compensator (λ -plate or red-I plate) just below the analyzer. As a result, the micellar (isotropic) solutions appeared magenta-red without any distinct structures, whereas the liquid-crystalline (birefringent) specimens looked iridescent with textures determined by the respective mesophase.⁵⁷

4. RESULTS AND DISCUSSION

4.1. Rheology in Steady Shear Regime. In this work, we have used a binary surfactant solution, which consists of CAPB and SLES in 4:1 molar ratio, respectively. The said CAPB-to-SLES ratio was selected because it nearly corresponds to the maximal micelle size of the binary (CAPB/SLES) system.⁵⁸ The solution's pH is ca. 5.7, and the solution viscosity is slightly above 1.7 mPa·s when the total surfactant (CAPB + SLES) concentration, c_{tot} is 100 mM. As explained in refs 25 and 58, the viscosity of the binary (CAPB + SLES) solution is determined by the synergistic growth of rodlike micelles. Here, we will study the effect of a third component, namely, a medium-chain fatty acid (HC12), which in its nonionic form can reduce the intramicellar electrostatic repulsion and thus promote further micellar growth.^{23–26,34}

In Figure 2, we examine the rheological properties of our ternary solutions in the steady shear regime. These experiments were performed at $c_{\text{tot}} = 100$ mM (80 mM CAPB + 20 mM SLES), whereas we varied the HC12 concentration from 0 to 40 mM. In Figure 2a, one can see the respective flow curves, where apparent viscosity η is plotted vs shear rate $\dot{\gamma}$. As seen from these flow curves, almost all solutions behave as quasi-Newtonian fluids: the viscosity stays nearly constant when the shear rate changes from 0.1 to 10 s^{-1} . Only the most viscous solution ($\eta_0 = 603$ mPa·s; with 15 mM HC12 added) is slightly shear-thinning because of the presence of wormlike micelles. These elongated micelles become aligned at high shear rates, and, as a result, the viscosity decreases. It is important to mention here that even in the most viscous solution (with 15 mM HC12) the wormlike aggregates do not seem entangled because the shear stress does not level off and the viscosity is not proportional to $\dot{\gamma}^{-1}$; for a comparison, see ref 25.

Figure 2b presents the non-monotonic trend of the zero-shear viscosity η_0 vs the HC12 concentration. As we add HC12 to the binary solution, η_0 increases and passes through a maximum at 15 mM HC12, where $\eta_0 = 603$ mPa·s (see Figure 2b). The maximal viscosity is 350 times higher than the viscosity (1.7 mPa·s) of the CAPB–SLES solution without lauric acid. Recently, viscosity peaks were also observed in CAPB–SLES mixtures with either octanoic acid²⁵ or lauric acid (HC12).²⁴

As shown in ref 34, the viscous mixtures that contain lauric acid can form either isotropic micellar or liquid-crystalline mesophases. Here, by using polarized-light optical microscopy, we did not detect birefringence (double refraction), meaning that the studied solutions (shown in Figure 2b) are micellar (isotropic) up to 30 mM HC12. For these three-component solutions, the pH decreases from 5.7 (no HC12) to ca. 5.4 (30 mM HC12); see Figure S2a in Appendix A. Above 30 mM HC12, the solutions become opalescent because the fatty acid reaches its solubility limit in the mixed micelles and the excess

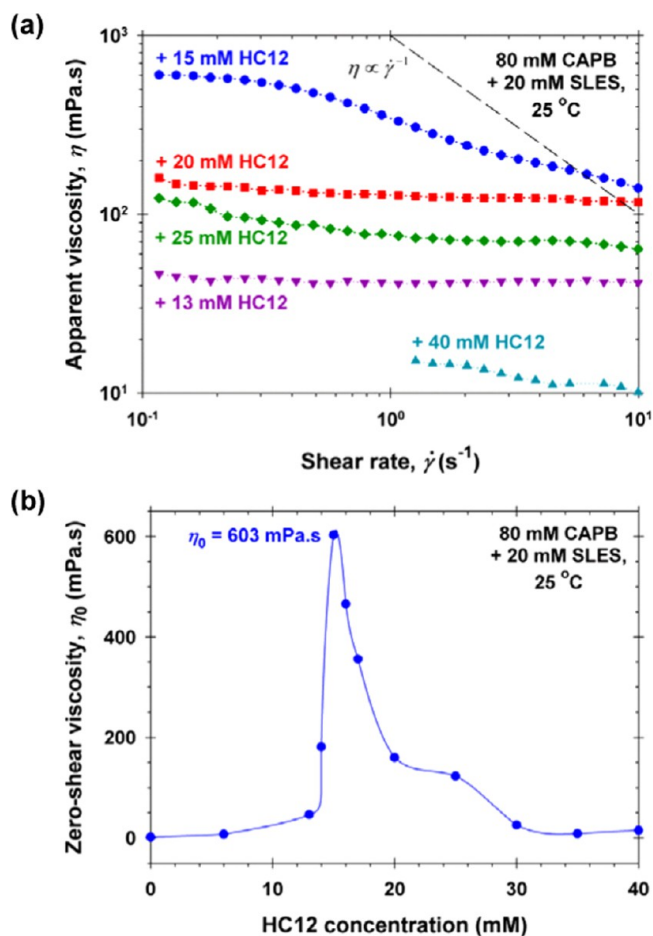


Figure 2. Effect of HC12 on the sample's shear rheology at $c_{\text{tot}} = 100$ mM. Plots of (a) η vs $\dot{\gamma}$ and (b) η_0 vs the HC12 concentration.

HC12 starts to form crystals in the bulk; see Figure S2 in Appendix A and ref 59. The turbid dispersions have nearly constant pH because the HC12 concentration in the bulk is fixed to 0.013 mM, which corresponds to the solubility of dodecanoic acid in water at 25 °C.⁵⁹

Furthermore, to understand better the intricate mechanism of the micellar growth, we investigated how the ionization state of HC12 affects the solution viscosity. First, as demonstrated in Figure S2b (Appendix A), we see that the degree of HC12 ionization in the mixed micelles is less than 1.0%, meaning that the micelles accumulate the nonionic fatty acid (>99%) rather than the anionic carboxylate (<1%). Second, to directly compare the effects of HC12 and sodium laurate (NaC12) on the solution viscosity, we prepared the solutions from Figure 2 using NaC12 instead of HC12. The results, presented in Figure S3 (Appendix A), show unequivocally that NaC12 does not induce micellar growth but instead favors the formation of short rodlike or even spherical micelles. The most probable explanation is the following: NaC12 increases the intramicellar electrostatic repulsion by bringing more charges to the mixed micelles. As a result, the optimal headgroup area increases, which induces micellar shortening. Finally, the appearance of shorter rods with lower (length-to-thickness) aspect ratios leads to a drop in viscosity. In contrast, nonionic HC12 promotes micellar growth by decreasing the intramicellar electrostatic repulsion and by separating the negatively charged SLES headgroups farther apart.

Figure 3a presents our steady shear measurements for the effect of HC12 on η_0 at a fixed surfactant ratio (CAPB/SLES = 4:1) and varying total surfactant (CAPB + SLES) concentration c_{tot} from 100 to 400 mM. As one can see from the figure, the 2-fold increase of c_{tot} leads to a drastic (50 times) increase of η_0 at the peak: from 0.6 Pa·s at $c_{\text{tot}} = 100$ mM to 32 Pa·s at $c_{\text{tot}} = 200$ mM. We should note here that the peak position shifts to the

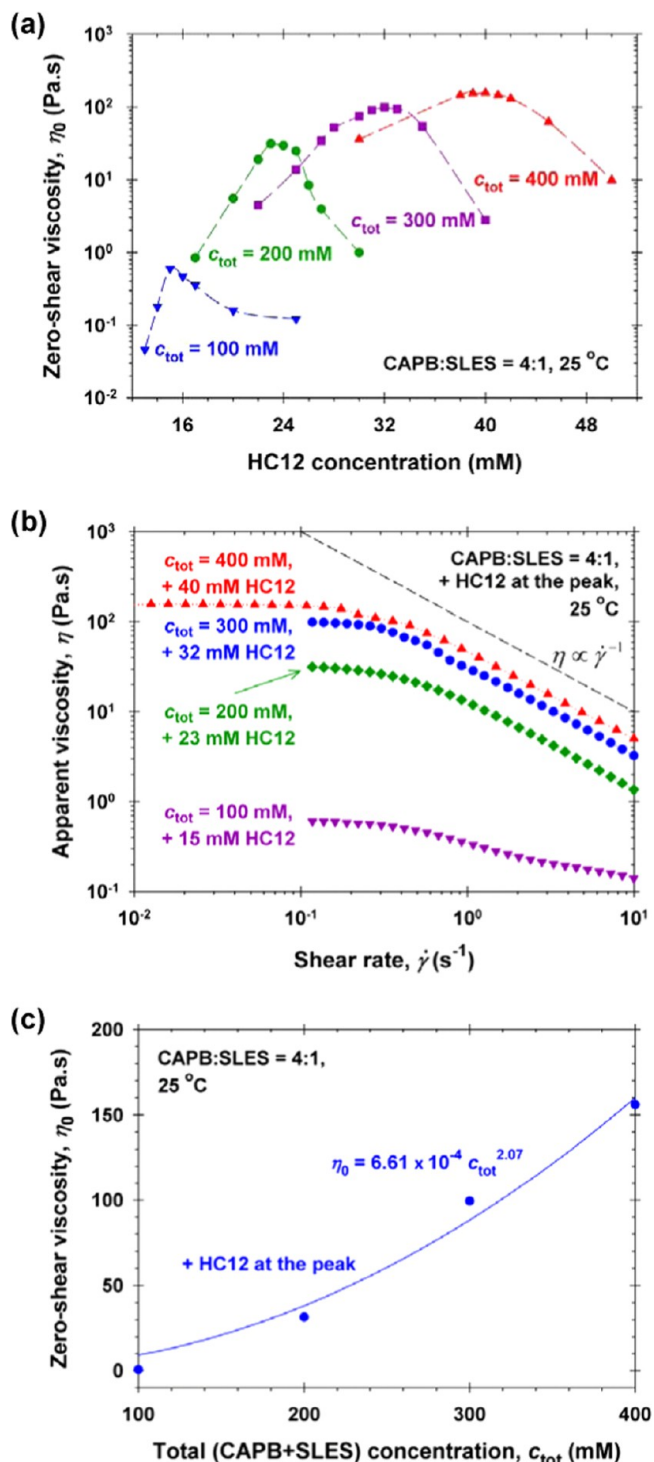


Figure 3. Effects of the HC12 concentration and c_{tot} on the viscosity at a fixed CAPB/SLES ratio equal to 4:1. Plots of (a) η_0 vs the HC12 concentration, (b) η vs $\dot{\gamma}$ at the peaks, and (c) η_0 vs c_{tot} at the peaks. In (c), the solid line depicts a power-law relationship that fits the data.

right as follows: 15 mM HC12 at $c_{\text{tot}} = 100$ mM; 23 mM HC12 at $c_{\text{tot}} = 200$ mM; 32 mM HC12 at $c_{\text{tot}} = 300$ mM; and 40 mM HC12 at $c_{\text{tot}} = 400$ mM. As one can notice, the peak position depends linearly on c_{tot} but with a nonzero intercept. Hereafter, the rheological behavior is examined at a fixed ratio, 4:1 CAPB/SLES, and at fatty acid concentrations corresponding to the viscosity peak at the respective c_{tot} .

In Figure 3b,c, we present how the flow curves, $\eta(\dot{\gamma})$, and the zero-shear viscosity, η_0 , depend on the total (CAPB + SLES) concentration, c_{tot} , where the HC12 concentration corresponds to the peak position. From Figure 3b, one can see that the flow curves for $c_{\text{tot}} \geq 200$ mM have two distinct regions: (i) at low shear rates, $\dot{\gamma} < \dot{\gamma}_N$, $\eta \approx \eta_0$ (plateau value) and (ii) at high shear rates, $\dot{\gamma} > \dot{\gamma}_N$, $\eta \propto \dot{\gamma}^{-1}$ (the shear stress σ becomes nearly constant, known as shear-banding). Such behavior is typically associated with entangled wormlike micelles in solution.^{23,25,28} In Figure S4 in Appendix A, one can find additional data for the shear stress vs shear rate, which illustrate a typical shear-banding behavior.

In Figure 3c, we continue with the effect of c_{tot} on η_0 , where the HC12 concentration corresponds to the peak position. As expected, η_0 rises with c_{tot} , e.g., at $c_{\text{tot}} = 100$ mM, $\eta_0 = 0.6$ Pa·s, whereas at $c_{\text{tot}} = 400$ mM, $\eta_0 = 160$ Pa·s. The data follow a power-law relationship, $\eta_0 \propto c_{\text{tot}}^{2.1}$. The power-law index of 2.1 is closer to the values 1–2 measured for multiconnected micelles³⁷ than to the values 3.5–3.7 for one-component wormlike micelles.^{49,52}

4.2. Rheology in Oscillatory Regime. Here, we will discuss the rheological properties of the ternary solutions obtained in the oscillatory regime. As before, the molar CAPB/SLES ratio is equal to 4:1 and the HC12 concentration corresponds to the peak position for a given total surfactant concentration c_{tot} . We should mention here that for $c_{\text{tot}} = 100$ mM the obtained rheological data are very noisy because of the sensitivity of our rheometer; hence, these results are deemed unreliable and are not presented below.

In Figure 4a (for $c_{\text{tot}} = 200$ and 400 mM) and Figure S5a (for $c_{\text{tot}} = 300$ mM), we see how the storage and loss moduli, G' and G'' , depend on the angular frequency, ω , at 2% shear-strain amplitude, for which the viscoelastic response of the samples is still linear. As one can see from these plots, the studied three-component mixtures are viscoelastic: they are fluidlike ($G'' > G'$) at low frequencies and solidlike ($G' > G''$) at high frequencies. From each plot, we can determine the crossover frequency, ω_c , where $G' = G''$. Knowing ω_c , the relaxation time can be estimated from the following relationship: $\tau_R = 1/\omega_c$; see Section 2.

The relaxation time, τ_R , as well as the plateau modulus, G_0 , can be determined in a more reliable way (using more experimental data, not just the crossing point) by simultaneously fitting $G'(\omega)$ and $G''(\omega)$ up to the crossing point with the Maxwell model described by eq 1. In such a way, τ_R and G_0 are determined as adjustable parameters from the fit and the solid lines in Figures 4a and S5a (Appendix A) are calculated. In Table 1, in the second and third columns, one can find the estimated values for G_0 and τ_R . From these results, we see that G_0 increases monotonically from 15 to 150 Pa as a function of c_{tot} following a power-law dependence with an exponent of 2.8 ± 0.4 . The latter is slightly higher but still in good agreement with the value of 2.3 ± 0.2 expected from refs 49 and 52, as well as with the value of 2.25 determined in ref 60. In contrast to G_0 , τ_R decreases monotonically from 1.7 to 0.89 s with c_{tot} also

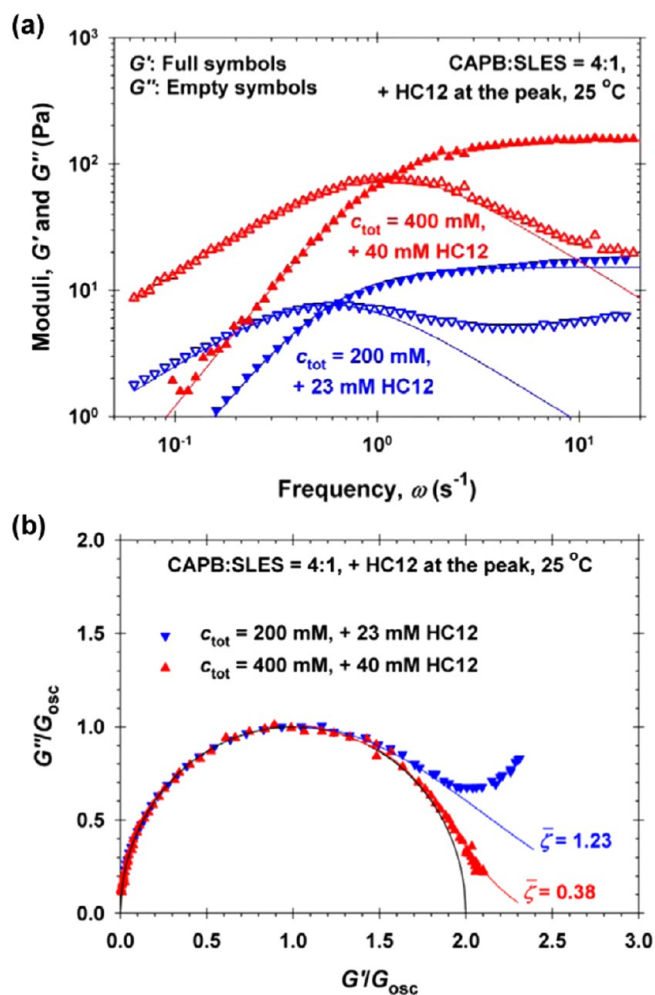


Figure 4. Effect of c_{tot} on the rheology in the oscillatory regime. Here, $c_{\text{tot}} = 200$ and 400 mM, whereas the HC12 concentration corresponds to the respective viscosity peak position. (a) G' and G'' are plotted vs ω ; the solid lines are the best fits with the Maxwell model. (b) Cole–Cole plots of G''/G_{osc} vs G'/G_{osc} , where $G_{\text{osc}} = G_0/2$ and the solid lines are fits of numerical data from refs 50 and 52, whereas the semicircle shows pure Maxwellian behavior.

following a power-law dependence with an exponent of -0.8 ± 0.2 .

Knowing the values of G_0 (see Table 1) and using eq 4, the mesh size of the transient micellar network, ξ , can be calculated. As one can see from the fourth column in Table 1, ξ decreases nearly 2 times, from about 65 to 30 nm, as c_{tot} increases, that is, the characteristic distances between the worms diminish with the micelle volume fraction. Given G_0 and τ_R , we can substitute them in eq 3 and estimate the zero-frequency viscosity, $\eta_{\omega=0}$. For the sake of comparison, the values of $\eta_{\omega=0}$ and η_0 are presented in the fifth and sixth columns of Table 1, respectively. Here, we remind that η_0 is determined from the steady shear experiments at low $\dot{\gamma}$, whereas $\eta_{\omega=0}$ is obtained independently from the oscillatory experiments. As we notice from Table 1, $\eta_{\omega=0}$ and η_0 coincide within 20%, which is to be expected in the linear viscoelastic regime and also follows from the limiting case of the Cox–Merz rule.^{48,61}

Next, we studied the mechanisms for micelle stress relaxation: breaking (or reversible scission) and reptation. These mechanisms are often characterized by parameter $\bar{\zeta}$, introduced by Turner and Cates.⁵⁰ $\bar{\zeta}$ is then related to ζ , as well

Table 1. Rheological Properties of the Studied Micellar Solutions, Where the Total (CAPB + SLES) Concentration, c_{tot} , Varies from 200 to 400 mM and the Dodecanoic Acid (HC12) Concentration Corresponds to the Respective Viscosity Peak Position

c_{tot} (mM)	G_0 (Pa)	τ_R (s)	ξ (nm)	$\eta_{\omega=0}$ (Pa·s)	η_0 (Pa·s)	$\bar{\zeta}$	ζ	τ_{break} (s)	τ_{rep} (s)
200	15	1.7	65	26	32	1.23	0.30	2.1	6.9
300	72	1.3	39	96	99	0.70	0.10	0.94	9.4
400	150	0.89	30	140	160	0.38	0.03	0.34	11

as to the characteristic times for micelle breaking τ_{break} and for micelle reptation τ_{rep} ; see Section 2. The procedure to obtain $\bar{\zeta}$ is as follows:

- (1) The experimental data from the oscillatory regime are depicted as a Cole–Cole plot (G''/G_{osc} vs G'/G_{osc}). In the case of ideal Maxwell body (see eq 5), the experimental data should collapse on a semicircle of radius $G_{\text{osc}} = G_0/2$. At high frequencies (high G'), deviations from the semicircle may occur, which are described by $\bar{\zeta}$.
- (2) To find $\bar{\zeta}$, one should compare the experimental vs the theoretical Cole–Cole plots (for $\bar{\zeta} = 0.13, 0.38, 0.70, 1.23, 2.38, 4.61, \text{ and } 10.2$); see refs 50 and 52.
- (3) As a result, $\bar{\zeta}$ can be estimated. Then, ζ is found from the values listed in refs 50 and 52 and the characteristic times are calculated: $\tau_{\text{break}} = \bar{\zeta}\tau_R$ (see eq 7) and $\tau_{\text{rep}} = \tau_{\text{break}}/\zeta$ ($\zeta = \tau_{\text{break}}/\tau_{\text{rep}}$; Section 2).

In Figure 4b (for $c_{\text{tot}} = 200$ and 400 mM) and Figure S5b (for $c_{\text{tot}} = 300$ mM), we have constructed the respective Cole–Cole plots, where the symbols represent our rheological measurements and the solid lines correspond to numerical calculations from refs 50 and 52. As a result of the above comparison, $\bar{\zeta}$ and ζ are now known and are given in Table 1 (in the seventh and eighth columns, respectively). Having obtained $\bar{\zeta}$ and ζ , we estimated the characteristic times for reversible scission, τ_{break} , and for reptation, τ_{rep} . We should stress here that τ_{break} was estimated solely from rheology using Cates' theory.⁵⁰ For the characteristic times, Cates' theory⁴⁹ predicts that $\tau_{\text{break}} \propto \bar{L}^{-1}$ and $\tau_{\text{rep}} \propto \bar{L}^3$, where \bar{L} is the average micellar length. For rodlike and wormlike micelles, we also have that $\bar{L} \propto (c_{\text{tot}})^{1/2}$; see, e.g., refs 1 and 24. Therefore, τ_{break} should decrease with c_{tot} , whereas τ_{rep} is expected to increase with c_{tot} . Both qualitative predictions are in concurrence with the tendencies of our results (last two columns) in Table 1.

4.3. Cryo-TEM Imaging. We employed cryogenic TEM to acquire direct structure-specific information for the microstructure evolution occurring at $c_{\text{tot}} = 100$ mM, while we vary the HC12 concentration. At c_{tot} higher than 200 mM (~ 6.8 wt %), the cryo-TEM imaging becomes complicated because (i) the preparation of thin vitrified specimens is very challenging and (ii) the two-dimensional cryo-TEM micrographs become crowded due to overlapping micelles. The cryo-TEM images shown below were taken at 0 and 13 mM HC12, before the peak, as well as at 20, 25, and 40 mM HC12, after the peak; see Figure 2b. (The preparation of a vitrified sample exactly at the viscosity peak turned out to be a considerable challenge.)

Figure 5a (at 0 mM HC12) and Figure 5b (at 13 mM HC12) show typical cryo-TEM micrographs taken to the left of the peak. In Figure 5a ($\eta_0 = 1.7$ mPa·s), spherical, ca. 6 nm in diameter, and short wormlike, up to 200 nm in length, micelles coexist. This is in accord with the theoretical predictions^{1,24} and with the previous experimental work of Christov et al.⁵⁸ It should be noted that almost all elongated micelles in Figure 5a appear to have a dumbbell-like shape, worms with swollen

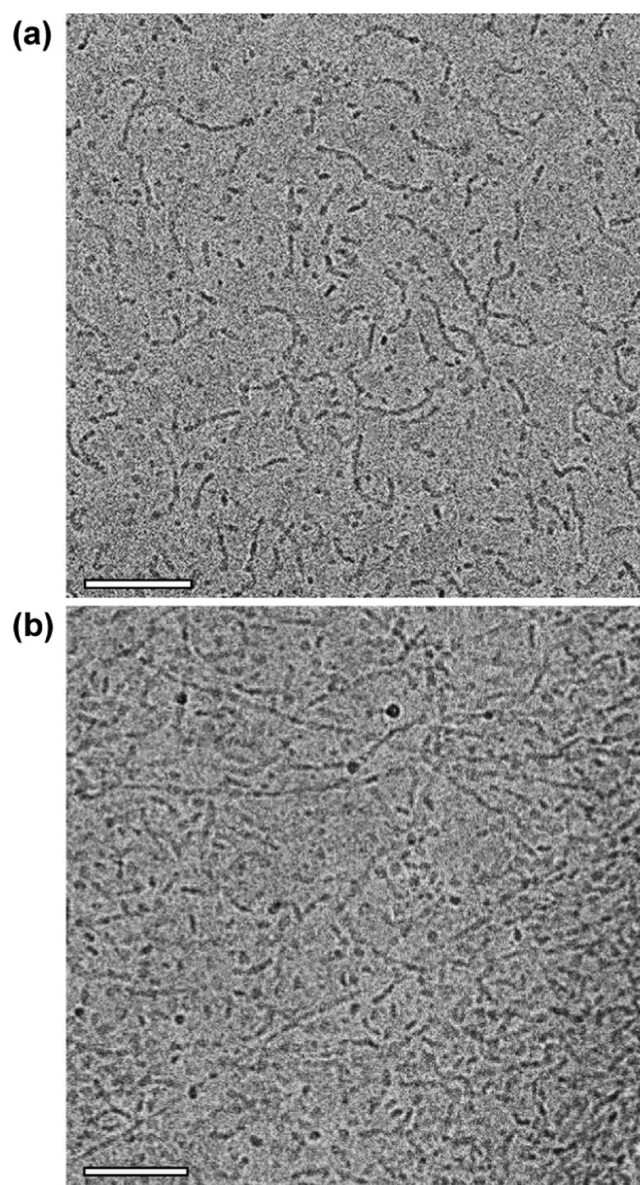


Figure 5. Cryo-TEM micrographs before the viscosity peak; 80 mM CAPB; 20 mM SLES; 100 nm scale bars. (a) No added HC12; $\eta_0 = 1.7$ mPa·s; rodlike and short wormlike micelles coexist with spherical micelles. (b) 13 mM added HC12; $\eta_0 = 46$ mPa·s; several long worms, reaching up to 0.5 μm in length, are in equilibrium with many short rods.

endcaps. Similar self-assembly structures with swollen endcaps have been also observed by cryo-TEM imaging in refs 29, 35, 56, 62, and 63.

Figure 5b ($\eta_0 = 46$ mPa·s) shows that the micellar growth is promoted by the addition of lauric acid (HC12), which serves as a nonionic spacer between the negatively charged headgroups of SLES. In the presence of 13 mM HC12, the aggregates transform from short rods to long wormlike

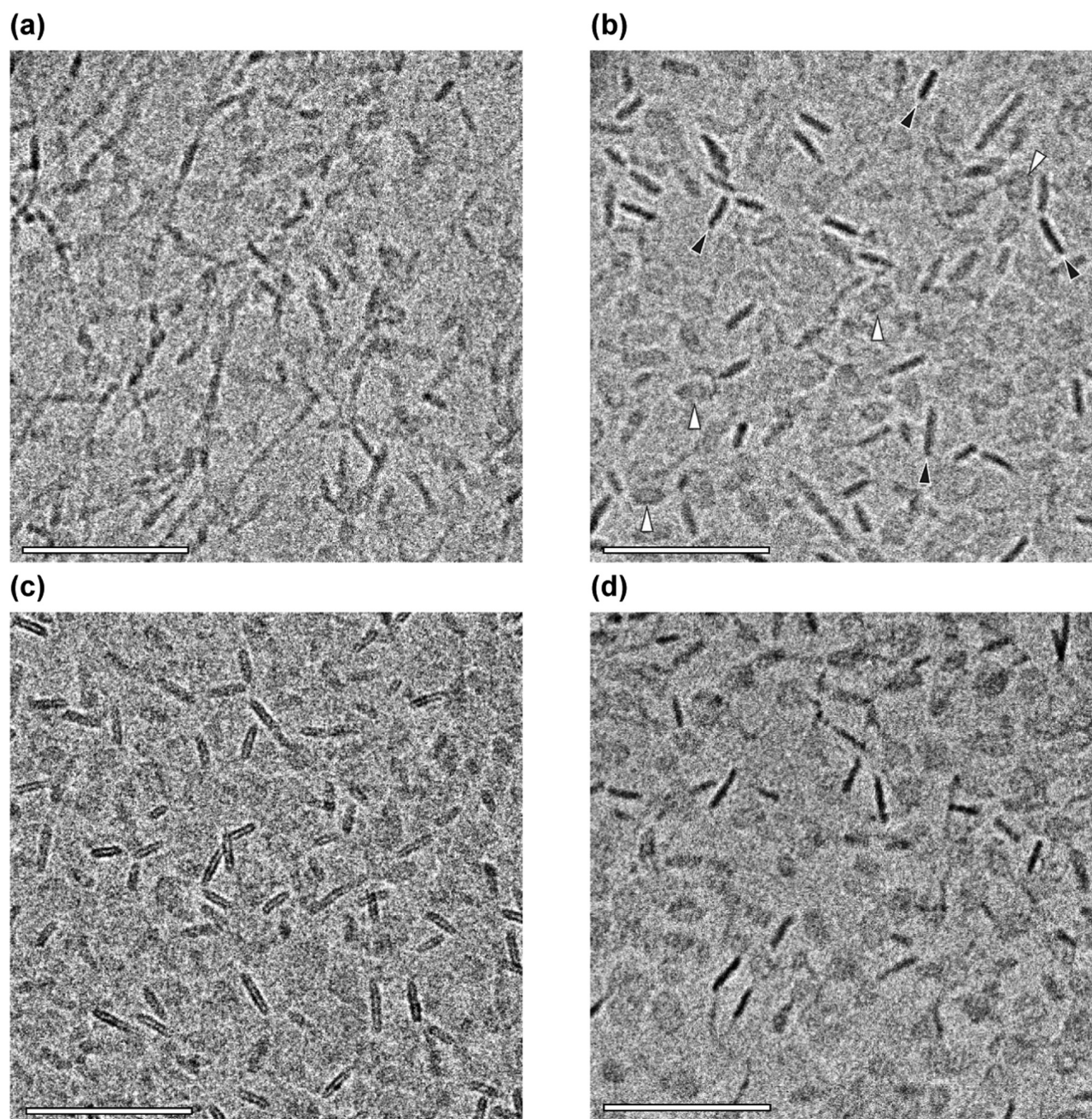


Figure 6. Cryo-TEM micrographs after the viscosity peak; 80 mM CAPB; 20 mM SLES; 100 nm scale bars. (a) 20 mM HC12 added; $\eta_0 = 160$ mPa·s; ribbonlike micelles with undulating thickness. (b, c) 25 mM HC12 added; $\eta_0 = 120$ mPa·s; disklike micelles with parallel (black arrowheads) and perpendicular (white arrowheads) orientations with respect to the electron beam. In (c), we see the boundary (thin white line) between the two surfactant layers in a given disk. (d) 40 mM HC12 added; $\eta_0 = 15$ mPa·s; disklike micelles with different orientations with respect to the electron beam.

micelles, reaching up to $0.5 \mu\text{m}$ in length; see Figure 5b. These observations prove that in the vicinity of the viscosity peak the length-to-thickness aspect ratio of the micelles increases abruptly from less than 35 to nearly 85. As a consequence, the effective volume fraction of the micelles, depending on the micelle aspect ratio and on the flow conditions, increases and so does the zero-shear viscosity, η_0 .

Next, we will discuss the structures that form to the right of the peak; see Figure 6. In Figure 6a (at 20 mM HC12; $\eta_0 = 160$ mPa·s), we see flat ribbonlike structures as in ref 63. The formation of ribbons could be driven by the segregation of the different components along the micelle and/or by the addition

of HC12 that imparts flatness to the micelles. Moreover, these ribbons seem to represent an intermediate state from worms to disks.

Indeed, as shown in Figure 6b,c (both at 25 mM HC12; $\eta_0 = 120$ mPa·s), the micelles transform from worms (at the peak) to disks. This transformation leads to a drop in viscosity because the diameter-to-thickness aspect ratio of the disks (<10) is much lower than the aspect ratio of the worms (>85). Figure 6b distinctively shows disks in different orientations: parallel (black arrowheads) and perpendicular (white arrowheads) with respect to the electron beam. In Figure 6c, we can

even distinguish the two surfactant monolayers (separated by a thin white line) that form the discoidal micelles.

Analogously, in Figure 6d (at 40 mM HC12; $\eta_0 = 15$ mPa·s), the dominant form of self-assembly is still discoidal aggregates. Because the HC12 concentration exceeds its solubility limit in the micelles, the samples are turbid and the disks coexist with fatty acid crystals.

In summary, the changes in the microstructure of the micellar solutions that contain 80 mM CAPB, 20 mM SLES, and varying concentration of fatty acid (HC12) are presented in Figure 7. To the left of the viscosity peak (see Figure 2b), we

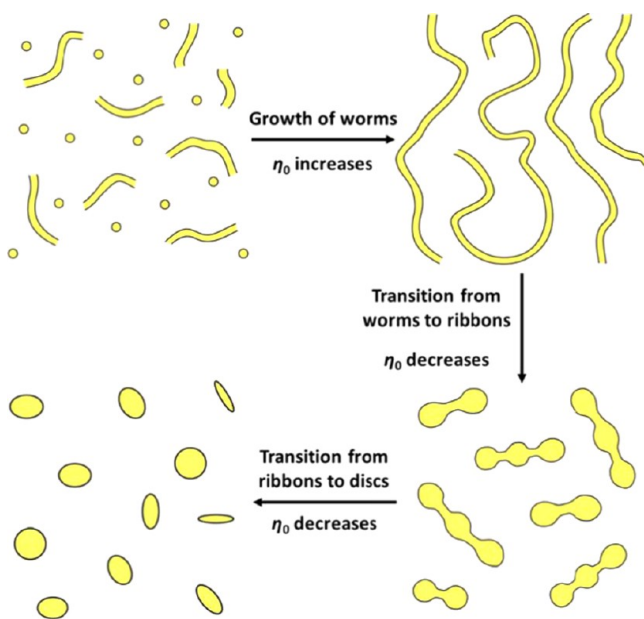


Figure 7. Schematic illustration of the microstructure evolution that occurs in the micellar solutions, containing 80 mM CAPB, 20 mM SLES, and varying concentration of HC12.

first have spherical and short wormlike micelles that transform into longer worms (Figures 5b and 7). Here, the synergistic micellar growth is induced by the addition of fatty acid. At some point, to the right of the viscosity peak, long flat ribbons are formed (Figures 6a and 7), which then break into disks (Figures 6b,c,d and 7). Such ribbonlike micelles have been directly observed via cryo-TEM.⁶³ Finally, at high enough concentrations of HC12, the discoidal micelles (Figures 6b,c,d and 7) become the dominant form of surfactant self-assembly.

The uniformity of the disks evidences for the existence of a minimum in the free energy of the system at a certain value of the disk radius. Qualitatively, the optimal disk radius is determined by the balance of two opposing effects. The incorporation of more surfactant molecules in the energetically favorable disk (lamellar) zone promotes micellar growth, but the growth is limited by the rising positive peripheral energy of the micelle.²⁴

Here, we should stress that the microstructure evolution in the presence of a medium-chain fatty acid (such as HC12) differs from the structural changes in the presence of a short-chain fatty acid (e.g., octanoic acid or HC8); see ref 25. At high fatty acid concentrations, to the right of the respective viscosity peak, HC8 favors the formation of branched or multiconnected micelles, whereas HC12 promotes the formation of flatter ribbonlike or even disklike aggregates. Given that both fatty

acids have a similar headgroup cross-sectional area, one might expect that the longer one (HC12) has a nearly cylindrical packing shape, whereas the shorter one (HC8) more closely resembles a truncated cone; see Table 20.3 in ref 1. Then, from ref 1, we know that cylindrically shaped molecules pack into bilayers or disks, whereas molecules that resemble truncated cones assemble into rodlike (or wormlike) micelles.

5. CONCLUSIONS

Here, we studied the rapid micellar growth in three-component surfactant solutions, containing zwitterionic (CAPB), anionic (SLES), and nonionic (HC12) surfactants. We investigated the effect of fatty acid (HC12) on the solution rheology and microstructure at a fixed 4:1 CAPB/SLES molar ratio. As in other surfactant-based mixtures,^{7–34} the zero-shear viscosity, η_0 , of our ternary mixtures follows a non-monotonic trend as a function of the fatty acid concentration. At 100 mM total (CAPB + SLES) concentration, we found a high viscosity peak: $\eta_0 \approx 603$ mPa·s at 15 mM HC12 (see Figure 2b). This viscosity is 350 times higher than the viscosity of the CAPB–SLES solution without fatty acid (HC12) and increases further with the total surfactant concentration (Figure 3).

Using polarized-light microscopy, we proved that all three-component mixtures up to 30 mM HC12 are micellar (isotropic), rather than liquid-crystalline (birefringent). In the concentration range from 30 to 40 mM HC12, the surfactant micelles coexist with fatty acid crystals because HC12 exceeds its solubility limit in the micelles. Comparing our ternary system to a similar one studied in ref 34 (see Appendix A, Figures S6 and S7), we found that the origin of our viscosity peak is not due to a transition from an isotropic micellar to a liquid-crystalline mesophase but rather due to shortening of the micelles (worms transform into disks). A similar mechanism of micelle shortening, where worms transform into spherical micelles, was directly observed in catanionic mixtures by Ziserman et al.²⁹

Employing oscillatory and steady-shear rheological measurements, we demonstrated that all studied surfactant mixtures are viscoelastic and follow the Maxwell viscoelastic model in a wide range of frequencies. For total (CAPB + SLES) concentrations $c_{\text{tot}} \geq 200$ mM, the shear stress levels off (shear-banding) and $\eta \propto \dot{\gamma}^{-1}$ at high shear rates, which is typically associated with intertwined wormlike micelles.^{23,25,28,64} However, Maxwellian behavior and shear-banding response have also been detected with mixtures containing disklike structures.³⁴ Therefore, cryogenic TEM imaging was applied to acquire structure-specific information and to relate the microstructure evolution to the non-monotonic rheological trends in viscosity.

Indeed, the cryo-TEM imaging uncovered the structural transformations causing the non-monotonic rheological trends. Before the viscosity peak, we first have spherical and short wormlike micelles that transform into longer worms. At some point, after the viscosity peak, flat ribbonlike structures form as an intermediate state from worms to disks. Finally, at high enough concentrations of fatty acid (HC12), the discoidal micelles become the dominant form of surfactant self-assembly. The formation of disks leads to a drop in viscosity because their length-to-thickness aspect ratio (or effective volume fraction) is significantly lower than that of wormlike micelles. We should also stress here that the discoidal micelles represent a very rare self-assembly structure and there are few papers^{35,63,65–70} showing cryo-TEM micrographs of such aggregates.

To the best of our knowledge, this is the second article that studies SLES–CAPB–fatty-acid mixtures thoroughly by both cryo-TEM imaging and rheological measurements, despite the wide applications of such mixtures in many industrial products such as shampoos, body washes, etc. (The first article is also a paper of ours,²⁵ where SLES–CAPB–octanoic-acid mixtures were studied.) Furthermore, the current results elucidate the structure–rheology relationships in multicomponent surfactant formulations forming various microstructures. Moreover, we established that by varying the micelle composition and/or the cosurfactant charge (HC12 vs NaC12) one can alter both the intramolecular interactions and the molecular packing within the micelle, thus causing drastic changes in both solution's rheology and microstructure. Such observations could serve as guiding principles for the design of low-surfactant formulations with applications in household and personal-care detergency.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.langmuir.8b00421](https://doi.org/10.1021/acs.langmuir.8b00421).

Additional experimental and numerical results; electrolytic conductivity measurements; NMR measurements, spectra; polarized-light microscopy images, and interpretation (PDF)

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Author Contributions

P.A.K. and S.E.A. devised and defined the study. G.S.G. performed all rheological, pH, and conductivity measurements. S.E.A. interpreted the rheological, pH, and conductivity data. L.A. prepared the vitrified specimens and carried out the cryo-TEM imaging. D.D. and S.E.A. analyzed the cryo-TEM micrographs. S.E.A. and P.A.K. wrote the manuscript.

Notes

The authors declare no competing financial interest.

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