Wormlike micelles formed by mixed cationic and anionic gemini surfactants in aqueous solution

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ABSTRACT

The formation and the properties of wormlike micelles in aqueous solutions of mixed cationic and anionic gemini surfactants, 2-hydroxyl-propanediyl-α,ω-bis(dimethyldodecylammonium bromide) (12-3(OH)-12) and O,0′-bis(sodium 2-dodecylcarboxylate)-p-benzenediol (C12φC12), have been studied by steady-state and dynamic rheological measurements at 25°C. With the addition of a small amount of C12φC12 into the solution of 12-3(OH)-12, the total surfactant concentration of which was always kept at 80 mmol L⁻¹, the solution viscosity was strongly enhanced and its maximum was much larger than that of the mixed system of propanediyl-α,ω-bis(dimethyldodecylammonium bromide) (12-3-12) and C12φC12. The results of dynamic rheology measurements showed that 12-3(OH)-12/C12φC12 formed longer wormlike micelles in comparison with 12-3-12/C12φC12. This was attributed to the effect of hydrogen bonding occurring between 12-3(OH)-12 molecules, which was an effective driving force promoting micellar growth. As few C12φC12 participated in the micelles, the electrostatic attraction between the oppositely charged head groups of 12-3(OH)-12 and C12φC12 made the molecules in the aggregates pack more tightly. This reinforced the hydrogen-bonding interactions and greatly promoted the micellar growth.

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1. Introduction

Mixed cationic and anionic surfactants can produce strong electrostatic attraction between the oppositely charged head groups besides the hydrophobic interaction between the alkyl tails, which leads to synergism of both and thus to a strong association in solution [1]. Strong interaction causes an increase in the hydrophobic tail volume of the surfactant ion pair and a decrease in the head group area [2,3]. According to the surfactant packing theory [4], this yields a large molecular packing parameter P that is defined as v/al, where v is the hydrophobic volume of surfactant unit, a is the head group area, and l is the hydrophobic chain length. Thus they are favorable for forming long and flexible wormlike micelles. On the other hand, reduction in the electrostatic repulsion energy between the charged head groups facilitates micellar growth along a one-dimensional direction [5]. That is why screening salts or hydrophobic salts (classified as hydrotropes) were often added into the ionic surfactant solutions to help the construction of wormlike micelles [6–10]. Combing the two factors, cationic and anionic surfactant mixtures become important systems producing spontaneously wormlike micelles [11–15]. Up to now, however, all the systems were made up of oppositely charged traditional single-chain surfactants.

Gemini surfactant consists of two hydrophilic head groups, two hydrophobic tails, and a spacer linked at or near the head groups. Among the constituted groups in gemini molecules, spacer is the most unique and its chemical nature and length have been known to strongly affect the self-assembly of gemini surfactants [16–20]. Alkanediyl-α,ω-bis(dimethyldodecylammonium bromide), generally referred to as 12-s-12, where s represents the number of carbon atoms in the spacer group, is a common family of gemini surfactants investigated extensively [16]. It was known that 12-2-12 and 12-3-12 can spontaneously form wormlike micelles without the addition of any salts due to their columnar-like molecular geometry [21–23]. On the basis of 12-3-12 and 12-4-12, the bis(quaternary ammonium halide) gemini surfactants with a hydroxyl-substituted spacer were synthesized and their properties were investigated in several groups [24–28]. In the very recent work [29], we found that in the system of 2-hydroxyl-propanediyl-α,ω-bis(dimethyldodecylammonium bromide) that was referred to as 12-3(OH)-12 (Scheme 1), the hydrogen bonds can be formed between the hydroxyl-substituted spacers of the gemini molecules. Intermolecular hydrogen-bonding interaction is a kind of directive force. As a supplementary and effective contribution besides a generally hydrophobic effect between the alkyl...
tails, intermolecular hydrogen bonding has been verified to greatly promote the growth of 12-3(OH)-12 micelles [29]. In fact, in some amphiphile systems, the significance of hydrogen-bonding interactions was also emphasized in the construction of supramolecular self-assemblies such as gel [30] or lamellar phases [31].

Among the homologues of 12-2-12, 12-3-12, and C12/C12, focusing on their wormlike micelles. As the first mixed example, we hoped to obtain knowledge how to fully utilize the superior, particularly for their spacer groups, in the construction of complicated aggregates. In this system, the hydrogen-bonding interactions between the hydroxyl-substituted spacers of 12-3(OH)-12 were expected to provide a supplementary contribution to micellar growth besides a generally hydrophobic effect and electrostatic attraction, which are very interesting but given little attention in wormlike micellar systems up to now. In addition, we wanted to explore an effective approach further strengthening the hydrogen-bonding interactions, in which a few oppositely charged C12φC12 were added to construct mixed wormlike micelles and the surfactant molecules within the aggregates were thus packed more tightly. To better understand the additional contributions as noted above, the mixed system of unsubstituted 12-3-12 and C12φC12 was also examined at the identical level.

2. Materials and methods

2.1. Materials

Two cationic gemini surfactants, 2-hydroxyl-propanediyl-α-xo-bis(dimethyldodecylammonium bromide) and propanediyl-α-xo-bis(dimethyldodecylammonium bromide), referred to as 12-3(OH)-12 and 12-3-12, respectively, and an anionic gemini surfactant, O,O-bis(sodium 2-dodecylcarboxylate)-p-benzenediol, referred to as C12φC12, is an anionic gemini surfactant with a p-benzenediol spacer (Scheme 1). Due to the rigid characteristic of aromatic rings, a pseudo volume is yielded between the two tails, which hinders the alkyl tails drawing close and thereby also leads to a columnar-like molecular geometry. In our previous work, similar carboxylate gemini surfactants with an azobenzene spacer have been confirmed to spontaneously form wormlike micelles in the absence of salt [32,33].

In the present work, we were interested in the mixed cationic and anionic gemini surfactant system of 12-3(OH)-12 and C12φC12, focusing on their wormlike micelles. As the first mixed example, we hoped to obtain knowledge how to fully utilize the superiority of the gemini molecular structures, particularly for their spacer groups, in the construction of complicated aggregates. In this system, the hydrogen-bonding interactions between the hydroxyl-substituted spacers of 12-3(OH)-12 were expected to provide a supplementary contribution to micellar growth besides a generally hydrophobic effect and electrostatic attraction, which are very interesting but given little attention in wormlike micellar systems up to now. In addition, we wanted to explore an effective approach further strengthening the hydrogen-bonding interactions, in which a few oppositely charged C12φC12 were added to construct mixed wormlike micelles and the surfactant molecules within the aggregates were thus packed more tightly. To better understand the additional contributions as noted above, the mixed system of unsubstituted 12-3-12 and C12φC12 was also examined at the identical level.

2.2. Methods

Rheological measurements were performed on a stress-controlled rheometer (AR2000ex, TA Instruments) with a cone-plate sensor. The cone is made of standard ETC. steel with a diameter of 20 mm and the cone angle of 2°. The gap between the center of cone and the plate is 50 µm. Each sample was kept for 5 min on the plate to reach the equilibrium before testing. A strain sweep was performed at a frequency of 6.28 rad s⁻¹ (1 Hz) before the test. A strain value was then decided to make sure the sample was in the linear viscoelastic region during the following oscillatory measurements. The temperature was kept at 25 ± 0.1 °C throughout the experiments. All the solutions were prepared using Milli-Q water with a resistivity of 18.2 MΩ cm.

3. Results and discussion

3.1. Steady-state viscosity

The total concentration of the mixed systems was fixed at 80 mmol L⁻¹. On the addition of C12φC12, all the mixed samples show a low shear Newtonian plateau, followed by shear thinning at higher shear rates (Fig. 1). This behavior has been taken as evidence for the formation of wormlike micelles [15]. The zero-shear viscosity (η₀) can be obtained according to the Carreau model. Fig. 2 shows the variation of η₀ with molar fraction x₁ of C12φC12 on a surfactant-only basis. On the increase in x₁, the η₀ of 12-3(OH)-12/C12φC12 increases rapidly, indicating the one-dimensional growth of the micelles and the more structured system [15]. A maximum of 261 Pa s yields at x₁ = 0.045.

The maximum in η₀ may be a common phenomenon as extensively seen in many systems such as single ionic surfactant with [35] or without salt [36], mixed cationic/anionic [12,13,15], cationic/nonionic [37], etc. For mixed cationic/anionic systems, the micellar branching was suggested as the mechanism producing the viscosity maximum [12,14], which was also supported by direct observation from cryo-TEM [38]. This was considered as the consequence of a maximum in contour length due to a balance between the micellar growth and the variations in the electrostatic screening as the oppositely charged surfactant concentration increases. These intermicellar junctions can effectively slide along the micellar body and serve as stress-release points and thus the multifunctional network displays a reduced viscosity compared to entangled micelles.

Among the homologues of 12-s-12, 12-2-12 was known to have the strongest ability of wormlike micelle forming [21,22]. This surfactant produces a viscosity maximum of 226 Pa s in the salt-free system at 25 °C [21]. Comparatively, 12-3(OH)-12 alone has only a viscosity of 0.8 Pa s at 80 mmol L⁻¹, and C12φC12 alone shows shear thinning behavior even at C > 250 mmol L⁻¹. However, the mixture of 12-3(OH)-12/C12φC12 achieves a maximum viscosity of 261 Pa s higher than that of 12-2-12. This indicates that the mixture produces quite strong synergism. The present maximum viscosity is comparable with other typical cationic/anionic systems such as cetyltrimethylammonium iodide (CTIA)/sodium dodecylbenzene sulfonate (SDBS) [12] or N-dodecylglutamic acid (LAD)/cetyltrimethylammonium bromide (CTAB) in the presence of 2,2'-dinitrolitriethanol (TEA) [15] but smaller than the mixture of sodium oleate (NaOA)/octyltrimethylammonium bromide (C8TAB). The latter has a high viscosity of about 1800 Pa s [13], perhaps relating to long hydrophobic chains of NaOA.

For the present system, the addition of C12φC12 neutralizes a part of the head group charge of 12-3(OH)-12 and reduces the electrostatic repulsion. This must be a cause of promoting the micellar growth. However, for the similar mixture of 12-3-12/C12φC12, its η₀
bonds at 3429 and 3231 cm\(^{-1}\) through lapping (KBr pellet method) exhibited two characteristic
gates of 12-OH-12\[39\]. The IR spectrum of 12-OH-12 solid
evidence for the intermolecular hydrogen bonding within the aggre-
gates. Furthermore, IR measurement provided direct evi-
suggested the hydrogen-bonding interactions between 12-OH-12
sharp contrast with that of unsubstituted 12-OH-12 and strongly

has only a very small increase from 0.6 to 14.2 Pa s over a broader range of \(x_1\) compared with that of 12-3(OH)-12/C\(_{12}\)\(\phi\)C\(_{12}\) and the maximum (14.2 Pa s at \(x_1 = 0.09\)) is also far smaller than that of 12-3(OH)-12/C\(_{12}\)\(\phi\)C\(_{12}\). Since 12-3-12/C\(_{12}\)\(\phi\)C\(_{12}\) produces the maximum viscosity at larger \(x_1\) than 12-3(OH)-12/C\(_{12}\)\(\phi\)C\(_{12}\), the head group charge of 12-3-12 must be neutralized to a greater extent. This clearly indicates that besides electrostatic energy, other factors must play a more important role for the growth of 12-3(OH)-12/C\(_{12}\)\(\phi\)C\(_{12}\) micelles. That is the interaction between the hydroxyl-substituted spacers of 12-3(OH)-12 since it is the sole difference of the two systems. In our previous work, the hydro-
gen-bonding interactions between 12-3(OH)-12 molecules have been verified to occur in both the disperse state of surfactant mol-
ecules in dilution and the aggregates in concentrated solution. In the dilute solution, dynamic surface tension and differential con-
ductivity measurements gave out clear information for the formation of oligo-aggregate ions of 12-3(OH)-12 in solution prior to
their adsorption and aggregation \[29\]. The phenomena were in sharp contrast with that of unsubstituted 12-3-12 and strongly suggested the hydrogen-bonding interactions between 12-3(OH)-12 molecules. Furthermore, IR measurement provided direct evidence for the intermolecular hydrogen bonding within the aggregates of 12-3(OH)-12 \[39\]. The IR spectrum of 12-3(OH)-12 solid through lapping (KBr pellet method) exhibited two characteristic bands at 3429 and 3231 cm\(^{-1}\), respectively, which were assigned
to the hydroxyl group in an associated state since both are remark-
ably lower than the general 3650–3580 cm\(^{-1}\) for free hydroxyl
\[40\]. Obviously, this associated state was certainly induced by the intermolecular hydrogen bonding in dried 12-3(OH)-12 solid. For 12-3(OH)-12 in liquid CDCl\(_3\) with a concentration as high as 1 mol L\(^{-1}\), which yielded a somewhat viscous solution, both bands at 3410 and 3226 cm\(^{-1}\) were obviously spread out and slightly shifted to lower wavenumbers compared with those at solid state, confirming the existence of strong intermolecular hydrogen-bonding interactions within 12-3(OH)-12 aggregates. As a directive force, intermolecular hydrogen-bonding interaction can promote micellar growth along a one-dimensional direction. In the present mixed system, electrostatic attraction between the oppositely charged head groups brings about tighter packing of molecules in the aggregates. This is favorable for the formation of intermole-
cular hydrogen bonds and thus favorable for micellar growth.

Even though the intermolecular hydrogen bonds have partly ex-
isted in the aggregates of 12-3(OH)-12 alone \[29,39\], its viscosity is only 0.8 Pa s at 80 mmol L\(^{-1}\) (Fig. 2). This indicates that the addition of the oppositely charged C\(_{12}\)\(\phi\)C\(_{12}\) is very efficient for promot-
ing the hydrogen-bonding interactions, which suggests a simple approach for enhance the hydrogen bonding by utilizing cationic/anionic surfactant mixtures.

Interestingly, for the 12-3(OH)-12/C\(_{12}\)\(\phi\)C\(_{12}\) system, the range of the molar ratio responding to rapid raise of \(\eta_0\) is very narrow \((x_1 = 0.02–0.06, \text{Fig. 2})\) compared with the mixtures of CTAT/SDBS \[12,14\], alkyltrimethylammonium bromide (C\(_n\)TAB)/NaOA \[13\], and LAD/CTAB \[15\]. By the mechanism noted above, one may easily understand this characteristic phenomenon. Since enhanced intermole-
cular hydrogen-bonding interaction is the main contribution for the present micellar growth, excessive molecules of C\(_{12}\)\(\phi\)C\(_{12}\) inserting in the mixed micelles certainly hinder instead of rein-
force intermolecular hydrogen bond formation.

Based on the uncharged polymer solution, the scaling behavior of rheological parameters is generally represented as a function of surfactant volume fraction. Nevertheless, the validity of the scaling relationships to a wormlike micellar system has been tested in io-

surfactants or cationic/anionic surfactant mixtures \[12,14,15,21,41\]. Since the weight fraction is almost proportional to the volume fraction, the scaling relationships were also often obtained by the weight fraction of a certain surfactant in mixed surfactant systems \[14,15\], For the 12-3(OH)-12/C\(_{12}\)\(\phi\)C\(_{12}\) system, the scaling law gives the relationship of \(\eta_0 \propto w^{3.58}\), where w represents the weight fraction of C\(_{12}\)\(\phi\)C\(_{12}\). The exponent of 3.58 well agrees with the predicted value of 3.5 by scission–recombination
theory [42] and thus the wormlike micelles look as if “living” polymers.

3.2. Viscoelastic spectra of mixed systems

Fig. 3 shows the dynamic rheological spectra of some typical mixed systems at different molar fractions. At low frequencies, elastic or storage modulus ($G'$) is always smaller than viscous or loss modulus ($G''$). As frequency increases, both $G'$ and $G''$ increase and cross at a frequency $\omega_c$, after which $G''$ decreases to a minimum, showing a typical characteristic of viscoelastic solution.

At low shear frequencies, viscoelastic micellar solution generally follows Maxwell fluid behavior with a single stress relaxation time ($\tau_R$) [43], and $G'$ and $G''$ are related to the shear frequency, $\omega$, by the following relations [44,45]:

$$G' = \frac{(\omega \tau_R)^2}{1 + (\omega \tau_R)^2} G'_\infty$$  \hspace{1cm} (1)

$$G'' = \frac{\omega \tau_R}{1 + (\omega \tau_R)^2} G'_\infty.$$  \hspace{1cm} (2)

Fig. 4 represents good fitting results for two typical cases of 12-3(OH)-12/C12/C12 at $\alpha_1 = 0.045$ (squares) and 12-3-12/C12/C12 at $\alpha_1 = 0.09$ (cycles) as shown by solid lines, according to the Maxwell model.

Combining Eqs. (1) and (2), a new relation can be obtained:

$$G'^2 + (G' - G'_\infty/2)^2 = (G'_\infty/2)^2.$$  \hspace{1cm} (3)

Thus, the plot of $G'$ as a function of $G''$, i.e., so-called Cole–Cole plot, becomes another way of verifying viscoelastic wormlike micellar behavior [45]. Fig. 5 illustrates the Cole–Cole plots of two typical cases as shown in Fig. 4, in which the shape of the curves follows perfectly a semicircular behavior in the range of low and medium frequencies. This indicates that both viscoelastic wormlike micellar solutions follow the Maxwell model with a single relaxation time [45].

3.3. Discussion on viscoelastic properties of mixed systems

As seen in Fig. 3, around the molar fraction yielding maximum $\eta_0$, the $\omega_c$ of the 12-3(OH)-12/C12/C12 system is always lower than that of the 12-3-12/C12/C12 system. Since relaxation time, $\tau_R$, can be estimated as $\omega_c^{-1}$ [46], the 12-3(OH)-12/C12/C12 system has a longer $\tau_R$ than the 12-3-12/C12/C12 system (Table 1). According to the Maxwell model, $\tau_R$ is associated with the length of the wormlike micelles undergoing stress relaxation by reptation. Thus, on the addition of C12/C12, 12-3(OH)-12/C12/C12 may form longer wormlike micelles than 12-3-12/C12/C12. This corresponds to the former stronger network structure than the latter [47].

Fig. 3. Dynamic rheological spectra of some typical mixed systems of 12-3(OH)-12/C12/C12 (a) and 12-3-12/C12/C12 (b), where filled and open symbols present elastic modulus ($G'$) and viscous modulus ($G''$), respectively.
This is also reflected in another characteristic parameter, i.e., plateau modulus, $G'_\text{c}$, at high frequencies. In surfactant systems where the $G$ does not give a constant limiting value, the $G'_\text{c}$ may be estimated from the modulus value at $\omega_1$, using the relation $G'_\text{c} = 2G_\text{max}$, where $G_\text{max}$ is the viscosity modulus at shear frequency $\omega_1$ [46]. The data concluded in Table 1 indicate that at a comparable concentration, the $G'_\text{c}$ of 12-3(OH)-12/C12@C12 is always obviously larger than that of 12-3-12/C12@C12. Generally, $G'_\text{c}$ depends on the number density of the aggregates. Therefore, the larger $G'_\text{c}$, which reflects more entanglements between the micelles, is related to the longer micelles, agreeing with the result of $\tau_b$.

More directly, according to the Maxwell model, the micellar contour length ($L$) can be estimated by the relation [45]

$$L \approx \frac{I_l}{G'_\text{min}},$$

where $I_l$ is the average length between two entanglement points and $G'_\text{min}$ is the minimum value of loss modulus at the high-frequency region. Fig. 6 shows the ratio of $G'_\text{c}$ to $G'_\text{min}$ as a function of $x_1$. Similar to the situation in $G'_\text{s}$, at a comparable concentration, the $G'_\text{c}/G'_\text{min}$ of 12-3(OH)-12/C12@C12 is always larger than that of 12-3-12/C12@C12, clearly indicating that the micelle of the former is longer. Though the $I_l$ is not currently available, however, as a comparison, a typical value of $I_l$ (80–150 nm) for wormlike micelles can be adopted [42] and thus $L$ corresponds to roughly 0.5–0.9 μm for 12-3(OH)-12/C12@C12 and 0.3–0.6 μm for 12-3-12/C12@C12, respectively, at each maximum. Compared with the reported results for various single or mixed surfactant systems, the length of a 12-3(OH)-12/C12@C12 wormlike micelle is only moderately long. This may relate to the addition of too small amount of C12@C12, which cannot effectively neutralize the charge of cationic head groups. Similarly, for a single component 12-2-12 system in the absence of salt, the wormlike micelle is about 1 μm in length at 25 °C [21]. However, in the cationic/anionic mixed CTAT/SDBS system at a total surfactant concentration of 1.5 wt.%, the maximum ratio of $G'_\text{c}/G'_\text{min}$ is about 20 at the SDBS weight fraction of 5 [12]. This ratio of $G'_\text{c}/G'_\text{min}$ is 3-fold larger than that of 12-3(OH)-12/C12@C12, indicating that much longer wormlike micelles formed in the CTAT/SDBS system. Obviously, the participation of a great amount SDBS in the mixed micelles leads to effective neutralization of the charge of ionic head groups.

Let us return to the discussion on plateau modulus $G'_\text{c}$. As seen in Table 1, after the molar ratio which produces the maximum of $G'_\text{c}$ of 12-3(OH)-12/C12@C12 continuously increases, and on the contrary, that of 12-3-12/C12@C12 decreases. This gives important information for judging the micellar structure even though the solution viscosity of both shows a similar descent in appearance after the maximum in $G'_\text{c}$ (Fig. 2). As stated above, $G'_\text{c}$ can be related to the number density of the aggregates. Thus, for the 12-3(OH)-12/C12@C12 system, the descent in $G'_\text{c}$ after its maximum accompanying the increase in $G'_\text{c}$ can be attributed to the micellar branching as discussed in Section 3.1. For the 12-3-12/C12@C12 system, however, the decrease of $G'_\text{c}$ over this region implies the transition of a part of the micelles from long wormlike to short rodlike type [15]. In fact, the molecular geometry of 12-3-12 is not the most suitable for forming wormlike micelles compared with 12-2-12 of this homologous series. If a methylene group is further increased in the spacer, 12-4-12 only forms spherical micelles over a rather large range of concentrations [22]. Therefore, the addition of a somewhat great amount of C12@C12 may influence the molecular geometry to a certain extent. Compared with 12-3-12, the hydrogen-bonding effect between 12-3(OH)-12 molecules certainly plays a key role for the wormlike micelle formation. This effect dominates the whole range of the examined molar ratio, promoting the micelles always toward growth.

The living polymer model proposed by Cates [44] describes the dynamics of the viscoelastic micellar system by combining the reptation model of polymer dynamics with the effect of reversible scission on viscoelastic properties. The model involves two time scales of stress relaxation, namely reptation time ($\tau_{\text{rep}}$), which corresponds to the curvilinear diffusion of a chain of the mean length along its own contour, and breaking time ($\tau_b$). When breaking occurs over the time scale of reptation ($\tau_b < \tau_{\text{rep}}$), as in a typical wormlike micellar system, the chain undergoes many breakages and recombinations before a chain segment relaxes by reptation. The stress relaxation is characterized by a new time scale given by $\tau_s = (\tau_b\tau_{\text{rep}})^{1/2}$, and the solution behaves as a Maxwell fluid with single relaxation time, $\tau_s$. The average scission time for the micelle, $\tau_{\text{rep}}$, is approximately equal to the inverse of $\omega$ corresponding to the minimum of $G'_\text{min}$ in the high-frequency region. For the present systems, the $\tau_b$ at the maximum of $\eta_0$ is estimated to be 0.028 s for 12-3(OH)-12/C12@C12 and 0.018 s for 12-3-12/C12@C12. Obviously, a longer scission time of the former corresponds well to the intermolecular hydrogen-bonding interaction. Moreover, the 12-3(OH)-12/C12@C12 system also shows quite a long reptation time than the 12-3-12/C12@C12 system, agreeing with the estimation of the former’s longer wormlike micelles.

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$s_1$ represents the molar fraction of C12@C12 in mixed systems.

Fig. 6. The ratio of $G'_\text{c}$ to $G'_\text{min}$ as a function of $x_1$ for 12-3(OH)-12/C12@C12 (O) and 12-3-12/C12@C12 (C) systems.
4. Conclusions

In this paper, we report for the first time wormlike micelles formed by mixed cationic/anionic gemini surfactants, 12-3(OH)-12 and 12-3(OH)-12 in the presence of C12, which can produce intermolecular hydrogen bonding within the aggregates. For the system of 12-3(OH)-12 alone, this supplementary interaction promotes micellar growth [29]. On the addition of a small amount of C12, the intermolecular hydrogen-bonding interaction is greatly enhanced, resulting in longer wormlike micelles and far viscous solution compared with that formed by unsubstituted 12-3-12 and C12. The present results emphasize the important role of intermolecular hydrogen bonding for constructing wormlike micelles. Different from the general hydrophobic effect, intermolecular hydrogen bonding is a kind of directive driving forces and therefore is particularly favorable for the construction of long wormlike micelles. Moreover, the intermolecular hydrogen bonding can be conveniently and efficiently enhanced by adding a small amount of the oppositely charged surfactant to form the mixed micelles. It is possible that the approach utilizing the effect of intermolecular hydrogen bonding can further be used for the construction of other dissymmetry self-assemblies, which will be very interesting and significant.

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Appendix A. Supplementary material


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