

Effect of Hydrotropic Salt on the Assembly Transitions and Rheological Responses of Cationic Gemini Surfactant Solutions

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Cationic gemini surfactant dimethylene-1,2-bis(dodecyldiethylammonium bromide), referred to as $C_{12}C_2C_{12}$ -(Et), was synthesized. The effect of sodium salicylate (NaSal) on the assembly formation and transition of this cationic gemini surfactant solution was studied. Addition of NaSal induced rich aggregate morphologies in the $C_{12}C_2C_{12}$ (Et) system. The microstructures and rheological responses resulting from the addition of NaSal were studied systematically to explore the interaction between gemini surfactants and hydrotropic salts. The rich aggregation behavior can be attributed to the special molecular structure of the gemini surfactant and the appropriate interaction between the surfactant and NaSal. The study of gemini surfactant and hydrotropic salt interaction brings promise for applications in materials synthesis as soft templates.

Introduction

In recent years, surfactants have attracted considerable attention in the field of materials synthesis, stemming from their potential applications as a template or designer soft substance for preparation of microstructured functional materials.^{1,2} Considering the rising demand for newer materials with improved and novel properties, studies of the transitions between different surfactant aggregates look more important and have been given more emphasis, because altering the structure of aggregates that serve as templates for the synthesis of mesoporous materials may provide an easy route to tailor the structure and properties of the mesoporous materials.³ Although there are many examples of surfactant aggregates used as templates,^{4,5} the aggregate used is usually one model system, such as micelles or vesicles. So far, few attempts⁶ have been made to synthesize materials in a fixed system providing continuously alterable templates.

As a new type of surfactant, gemini surfactants have attracted increasing attention over recent years, owing to their superior properties in comparison with those of conventional single-chain surfactants, such as much lower critical micelle concentrations, better wetting abilities, and unusual aggregation morphologies.^{7–11} Gemini surfactants have already shown promise in various potential areas of surfactant applications, such as for the synthesis of organized mesoporous silica and gold particles,^{12,13} because of their various microstructures in the aqueous solution. The most widely studied gemini surfactants are dicationic quaternary ammonium compounds which are referred to as $C_M C_S C_M$ (Me), where M and S stand for the carbon atom number in the side alkyl chain and the methylene spacer, respectively.^{14,15} The fact that the properties of gemini surfactants can differ greatly from those of conventional surfactants has been related to the distribution of distances between headgroups,¹⁶ because the spacer groups can overcome the electrical repulsion

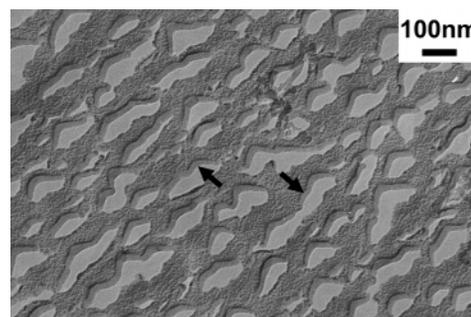


Figure 1. FF-TEM micrograph of the aqueous solution of 20 mM $C_{12}C_2C_{12}$ (Et) at 35 °C.

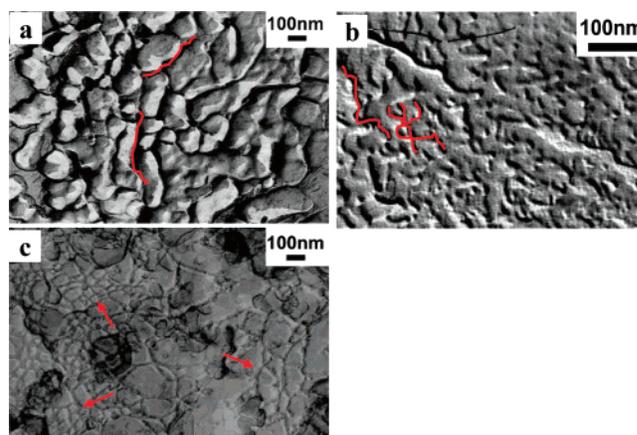


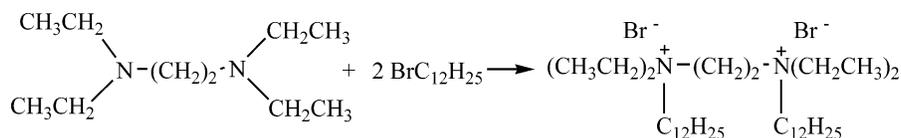
Figure 2. FF-TEM micrographs for 20 mM $C_{12}C_2C_{12}$ (Et) with varying molar ratios of NaSal to $C_{12}C_2C_{12}$ (Et): (a) $R = 0.3$, (b) $R = 0.5$, (c) $R = 0.75$.

between the headgroups and make them closer to each other. Thus, from the point of overcoming the electrical repulsion, gemini surfactants with a short spacer group is better. Recently our work indicated that the influence on the molecular aggregates by the variation of headgroups in gemini surfactant systems is greater than that in a conventional single-chain

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SCHEME 1: Synthetic Routine for the Preparation of Gemini Surfactant C₁₂C₂C₁₂(Et)

surfactant system, and the C₁₂C₅C₁₂(Et) series ([C₁₂H₂₅(CH₃-CH₂)₂N(CH₂)₅N(CH₂CH₃)₂C₁₂H₂₅]_SBr₂, *S* = 4, 6, 8, 10, 12) has better aggregation capability in aqueous solution than that of the C₁₂C₅C₁₂(Me) series ([C₁₂H₂₅(CH₃)₂N(CH₂)₅N(CH₃)₂C₁₂H₂₅]_SBr₂).¹¹ In this paper, we focus on aggregate morphology investigation of the C₁₂C₅C₁₂(Et) series when *S* = 2, i.e., the C₁₂C₂C₁₂(Et) system.

Compared with inorganic salts, organic counterions, or so-called hydrotropic salts, that bind strongly to the micellar surface are highly efficient in promoting micellar growth^{17,18} and induce worm-like micelles at significantly lower ratios of salt to surfactant. There have been numerous studies focused on the effect of hydrotropic salt addition in conventional single-chain surfactant systems;^{19–21} however, few studies²² have focused on the effect of hydrotropic salt addition on the aggregates in gemini surfactant systems. In this paper, we introduce a hydrotropic salt, sodium salicylate (NaSal), into gemini surfactant solutions to extend our understanding of the interaction between gemini surfactants and hydrotropic salts. Actually, interesting aggregation behavior and rheological results were obtained, and the interaction between gemini surfactants and hydrotropic salts is discussed based on the mixed systems of C₁₂C₂C₁₂(Et) and NaSal. Meanwhile, this work can lay a foundation in studying the relationship between the template structures as well as the properties of synthesized materials.

Experimental Section

Materials. Gemini surfactant dimethylene-1,2-bis(dodecyl)diethylammonium bromide (C₁₂C₂C₁₂(Et)) was synthesized as shown in Scheme 1 according to our previous paper.²³ Other C₁₂C₅C₁₂(Et) series (where *S* = 4, 6, 8, 10, 12) and C₁₂C₂C₁₂(Me) were synthesized according to published papers, respectively.^{11,15} Conventional cationic quaternary ammonium surfactant dodecyl triethylammonium bromide (DTEAB) was synthesized from 1-bromododecane and triethylamine. Hydrotropic salts sodium salicylate (NaSal), 2-naphthalenesulfonic acid sodium (SNS), and tetrabutylammonium bromide (Bu₄NBr) were from Aldrich Co. and used as received. The water used was redistilled from potassium permanganate-containing deionized water to remove traces of organic compounds.

Sample Preparation. The solutions of the mixed systems were prepared by simply dissolving C₁₂C₂C₁₂(Et) in NaSal stock solutions. Samples were vortex mixed and equilibrated in a thermostatic bath before investigation. It was found that the addition of NaSal made the krafft temperature of C₁₂C₂C₁₂(Et) (32 °C)²³ lower, which is beneficial to the actual study. Consequently, all the reported measurements of the mixtures of NaSal/C₁₂C₂C₁₂(Et) were performed at 30 °C. The C₁₂C₂C₁₂(Et) concentration [C₁₂C₂C₁₂(Et)] was fixed at 20 mM. The NaSal concentration [NaSal] was varied with the molar ratio, *R* = [NaSal]/[C₁₂C₂C₁₂(Et)].

Dynamic Light Scattering (DLS). DLS measurements were performed with a commercialized spectrometer (Brookhaven Instruments Corporation, Holtsville, NY) equipped with a 100 mW solid-state laser (GXC-III, CNI, Changchun, China) operating at 532 nm. The intensity autocorrelation functions were analyzed by using the methods of Contin and Cumulant.

Transmission Electron Microscopy (TEM). Micrographs were obtained with a JEM-100CX II transmission electron microscope by the freeze-fracture technique: Fracturing and replication were carried out in an EE-FED.B freeze-fracture device equipped with a JEE-4X vacuum evaporator.

Rheology. The rheological properties of the samples were measured at 30 °C with a ThermoHaake RS300 rheometer (cone and plate geometry of 35 mm in diameter with the cone gap equal to 0.105 mm). Frequency-sweep experiments were performed at a constant stress (chosen in the linear viscoelastic range) over a frequency range of 0.01 to 20 rad/s.

XRD Measurements. Self-supported cast films for the XRD studies were prepared by dispersing the sample solutions in precleaned quartz slides. Reflection XRD studies were carried out with a model XKS-2000 X-ray diffractometer (Scintaginc). The X-ray beam was generated with a Cu anode, and the wavelength of the KR1 beam was 1.5406 Å. The X-ray beam was directed toward the film edge, and the scanning was done up to the 2θ value of 10°.

Polarization Microscopy. Photographs of birefringence were taken by polarization microscope (OLYMPUSBH-2) with Kodak-400 color films. The intensity of incident light as well as the time of exposure remained constant.

NMR Spectroscopy. NMR measurements were performed on a Bruker NMR spectrometer (resonance frequency of 300 MHz for ¹H) operating in the Fourier transform mode. For NMR measurements, samples were prepared in D₂O.

Results and Discussion

Molecular Assemblies in Pure C₁₂C₂C₁₂(Et) Solution. The molecular assemblies formed in a pure solution of 20 mM C₁₂C₂C₁₂(Et) was studied by freeze-fracture transmission electron microscopy (FF-TEM). By TEM observation, elongated micelles with a diameter of 20–30 nm were observed (Figure 1). Further investigation by dynamic light scattering measurement (Figure 1 in Supporting Information) indicated that the elongated micelles coexisted with the spherical micelles, and the spherical micelles were dominant compared with the elongated micelles. It has shown that the bigger aggregate peak which was assigned to elongated micelles appeared only when the scattering angle was small enough and its contribution to the scattering light strength was relatively small. The above-mentioned opinion can also be proved from the result of the apparent viscosity measurement of the solution. It is well-known that surfactant solutions containing spherical micelles are isotropic in nature and have low viscosity.²⁴ Since the apparent viscosity (η_a) of the above solution was quite close to the water viscosity and there was no rheological response under shearing, it indicated that the elongated micelles were small in quantity. In previous studies, C₁₂C₂C₁₂(Me) exhibited more elongated micelles and a shear thickening phenomenon in the rheological experiment,^{25–26} and that therefore the size of polar headgroups may play an important role in the micelle morphology.

Micelle Growth and Transitions by NaSal Addition into C₁₂C₂C₁₂(Et) Systems. However, the addition of NaSal into C₁₂C₂C₁₂(Et) induced rich aggregation behavior in aqueous solutions. Figure 2 showed that both the micelle growth and

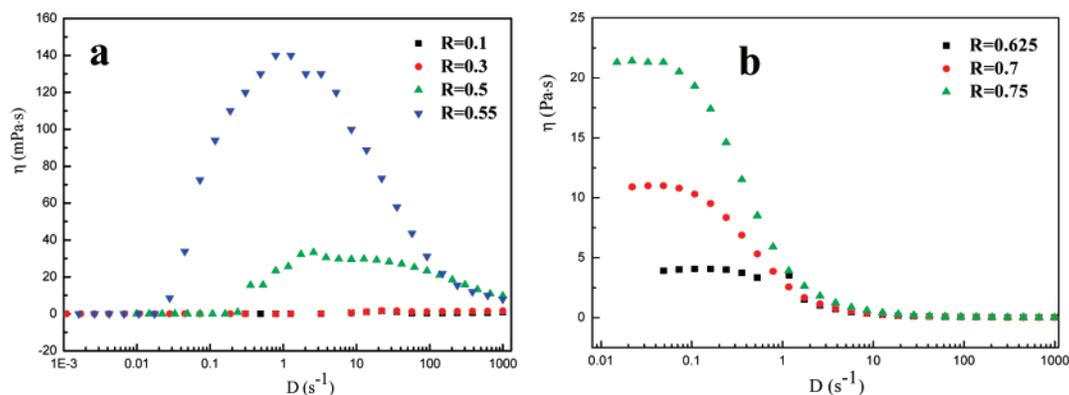


Figure 3. Steady shear viscosity as a function of shear rate in the presence of NaSal for various molar ratios (R), $[C_{12}C_2C_{12}(Et)] = 20$ mM at 30 °C.

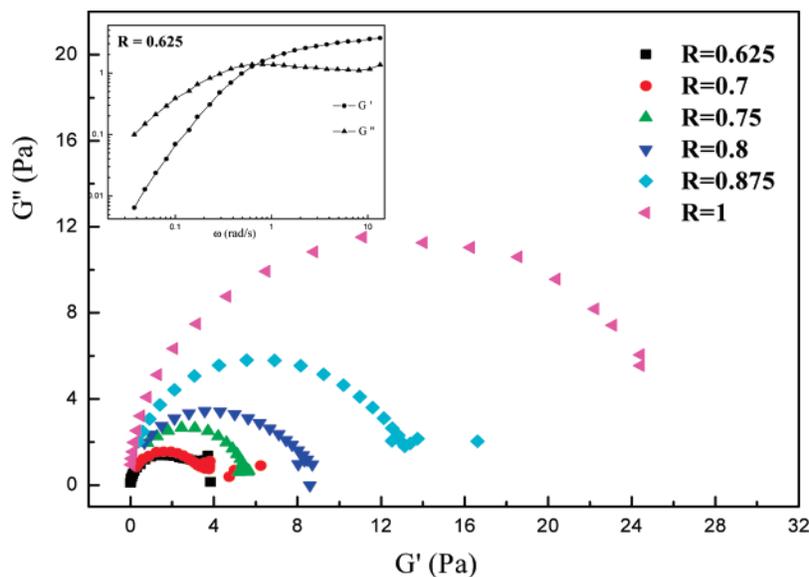


Figure 4. Cole–Cole plots of the NaSal/ $C_{12}C_2C_{12}(Et)$ mixtures at various molar ratios (R) at 30 °C. The inset is the representative curve of the variation of storage modulus (G'), loss modulus (G'').

transitions were dependent on the different molar ratios of NaSal (R) to the surfactant. At low NaSal concentration, the elongated micelles became slightly longer (Figure 2a) compared with the case without NaSal addition. As the molar ratio of NaSal increased, the micelles began to overlap and entangle each other slightly (Figure 2b). When the molar ratio R reached 0.75, the micelles eventually developed into long, flexible entities, and an entangled three-dimensional network formed.

Rheology measurements were also performed in the process of micelle growth in the $C_{12}C_2C_{12}(Et)$ system. With the increase of the molar ratio of NaSal (R), the systems changed from Newtonian fluid to non-Newtonian fluid, and the shear thickening phenomenon was obvious in the flow curve when R reached 0.5 (Figure 3a), indicating the existence of asymmetric aggregates. It is well-known that the elongated or flow alignment of cylindrical micelles is responsible for the shear thickening behavior in dilute surfactant solutions.^{27–29} Combined with the former result of a 20 mM $C_{12}C_2C_{12}(Et)$ solution in which the elongated micelles were small in quantity, it can be concluded that the spherical micelles have transformed into elongated micelles after NaSal addition. Further addition of NaSal ($R \geq 0.625$), the systems showed shear thinning behavior (Figure 3b) and dynamic rheological response appeared (Figure 4). It is worth to note that the biggest value of zero shear viscosity (η_0) was obtained at $R = 0.75$, in which the network of micelles formed in the system as observed by TEM. Combined the results

of TEM and rheology measurement, it can be concluded that the progressive addition of NaSal promotes micellar growth in the $C_{12}C_2C_{12}(Et)$ system.

Figure 4 shows the normalized Cole–Cole plots of the $C_{12}C_2C_{12}(Et)$ system at various molar ratios of NaSal. It can be seen that, from $R = 0.625$ to 1.0, the behavior of G' and G'' showed the characteristics of a viscoelastic surfactant solution. It was also found that the data followed a Maxwellian behavior at lower frequency, and deviation from the Maxwellian behavior occurred at a higher frequency, which was in agreement with the theory of Cates et al.³⁰

Complex aggregation behavior occurs at a higher molar ratio of NaSal. When the molar ratio further increased to $R = 1$, densely packed vesicles were observed (Figure 5a), indicating that the three-dimensional network of micelles has transformed into vesicles. Beyond $R = 1$, NaSal is not an additive but becomes the major component of the system. With further addition of NaSal, a birefringent phase formed at R of 1.4–4.2. Under a polarization microscope, colorful stripes were observed at $R = 2$ (Figure 2 in Supporting Information), indicating the formation of the lamellar structures in this case. Furthermore, lamellar structures were confirmed by FF-TEM (Figure 5b). Meanwhile, small vesicles were also observed for the same molar ratio of $R = 2$ (the inset in Figure 5b). From the XRD result (Figure 6), it can be seen that the sample exhibited two groups of periodic peaks (3.2 nm, 1.6 nm, 1.1

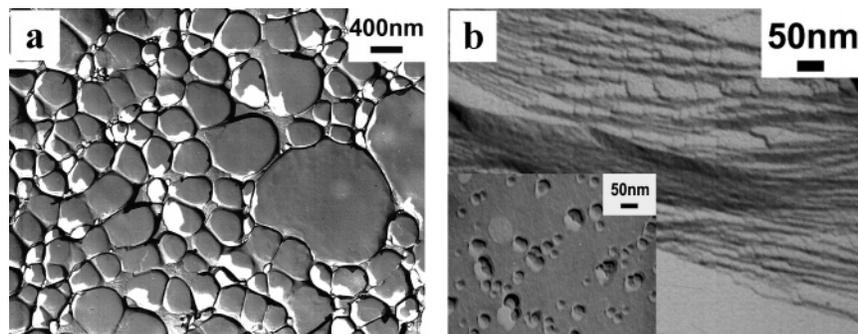


Figure 5. FF-TEM micrographs for 20 mM $C_{12}C_2C_{12}(Et)$ with varying molar ratios of NaSal. (a) $R = 1$, densely packed vesicles, (b) $R = 2$, lamellar structures coexisting with dispersed small vesicles.

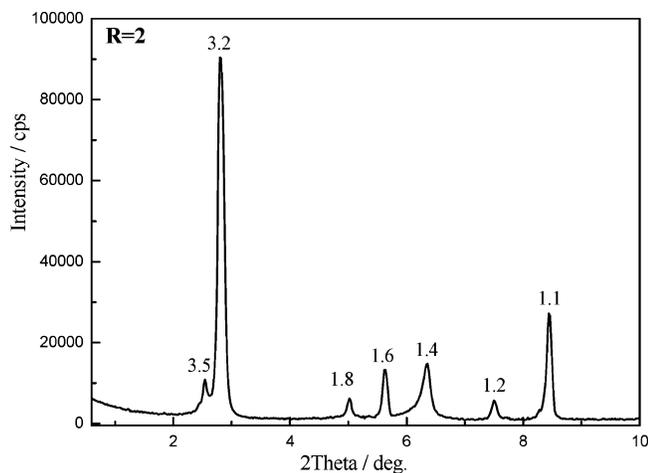


Figure 6. XRD diagram for 20 mM $C_{12}C_2C_{12}(Et)$ with the molar ratio $R = 2$ of NaSal.

nm; 3.5 nm, 1.8 nm, 1.2 nm) corresponding to the thickness of the membranes, indicating the formation of two kinds of molecular assemblies. The different spacings of the two microstructures may be attributed to the different proportion of NaSal held in the aggregates, which resulted in the different molecular packings.

In summary, the progressive addition of NaSal to the aqueous solution of $C_{12}C_2C_{12}(Et)$ leads to a consecutive decrease in the aggregate curvature. The aggregates undergo transitions from spherical micelles to elongated micelles, a network of micelles, and subsequently to densely packed vesicles and then to lamellar structures, as illustrated in Figure 7. The rich aggregation behavior is the result of cooperation between $C_{12}C_2C_{12}(Et)$ and NaSal. The aromatic counterion is more effective to penetrate into the headgroup region which leads to the reduction of headgroup repulsions and facilitates micellar growth.²² The orientation of the hydrotropic counterion on $C_{12}C_2C_{12}(Et)$ micelles was determined by NMR spectroscopy (Figure 3 in Supporting Information). It was clear from comparison of NaSal spectra with and without $C_{12}C_2C_{12}(Et)$ addition that signals of protons in the 2-, 3-, and 4-positions have shifted to higher field, indicating the nonpolar environment of the aggregate, while the signal of the proton in the 1-position did not significantly change in shift and continued to remain in the same polar environment. This implies that the aromatic counterion was adsorbed at the micelle–water interface with its aromatic ring intercalated in the hydrophobic interior of the aggregate, which is in accordance with the results of previous reports.^{20,31} Additionally, NaSal increases the critical packing parameter p^{18} because of its hydrophobic part; as a result, the aggregates have a lower curvature (as long as the packing parameter does not exceed 1).³² Further investigation indicated that only the oppositely

charged hydrotropic salts can induce such microstructure transitions in these gemini surfactant systems. For example, the oppositely charged 2-naphthalenesulfonic acid sodium (SNS) brought nearly the same effect to the $C_{12}C_2C_{12}(Et)$ system, only with lower efficiency relative to NaSal. However, the addition of NaBr or tetrabutylammonium bromide (Bu_4NBr) did not bring such an effect on the assembly transitions but only made the krafft temperature of $C_{12}C_2C_{12}(Et)$ higher, which is inconvenient for the actual study. In fact, the gemini molecular structures also play an important role in this transition, which will be discussed later.

In the application of template synthesis of mesoporous materials, our work may provide a simple method to realize a fixed system that provides continuously alterable templates. Spherical and elongated micelles, vesicles, and lamellar structures in the solutions of gemini surfactants generated by addition of hydrotropic salts could act as templates for the synthesis of different morphological materials. Kaler et al. have prepared hollow silica spheres by templating cationic vesicles.³³ Zhao et al. have found that a multi-headgroup bolaform surfactant was beneficial to the formation of low-symmetry mesoporous silica structures.³⁴ So it is hopeful that worm-like micelles in our systems may be used in the preparation of one-dimensional nanowires. Moreover, the transition of different aggregate templates can be easily obtained by gradual addition of hydrotropic salts, and thus the relationship between the template structures as well as the properties of synthesized materials can also be systemically investigated, which may help to understand the complex template mechanism.

Effect of the Surfactant Structures. The effect of NaSal addition on the conventional surfactant dodecyl triethylammonium bromide (DTEAB) was also studied in order to compare with gemini surfactant. No obvious viscosity change was observed with DTEAB solution even when the concentration of DTEAB was increased to 200 mM, indicating that the NaSal addition cannot induce micelle growth in the DTEAB system. When the length of the hydrophobic carbon chain was increased to cetyl, i.e., cetyltrimethylammonium bromide (CTAB) which was studied extensively in many studies,^{21,35} the addition of NaSal cannot bring an aggregation behavior as rich as that of $C_{12}C_2C_{12}(Et)$, thus revealing the unique characteristic of the gemini surfactant.

Furthermore, it is found that the polar headgroups play an important role in the phase behavior of gemini and NaSal mixed systems. When the headgroups of $C_{12}C_2C_{12}(Et)$ changed from ethyl to methyl, i.e., $C_{12}C_2C_{12}(Me)$, it can be seen that shear thickening phenomena appeared at $R = 0.1$ and then shear thinning behavior at $R = 0.3$ accompanied with dynamic rheological responses (Figure 8). The above-mentioned rheological responses appeared earlier than that of $C_{12}C_2C_{12}(Et)$ with

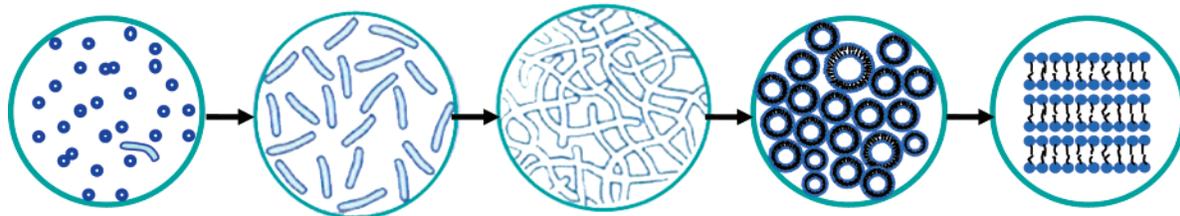


Figure 7. Illustration of the formation and transformation of various aggregates in the 20 mM $C_{12}C_2C_{12}(Et)$ aqueous solution with the continuous addition of NaSal.

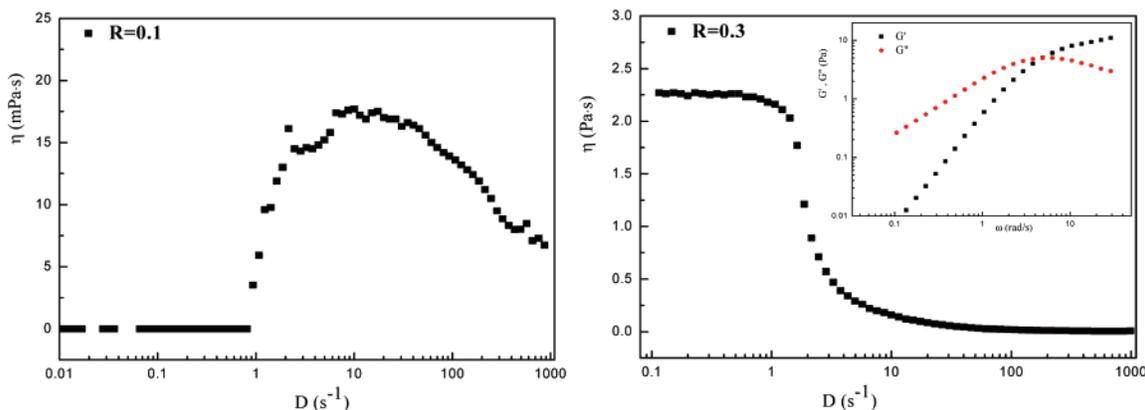


Figure 8. Steady shear viscosity as a function of shear rate in the presence of NaSal for various molar ratios (R), $[C_{12}C_2C_{12}(Me)] = 20$ mM at 30 °C.

the addition of NaSal, and they only appeared at a smaller range of $R < 0.35$. With further addition of NaSal, precipitation occurred before $R = 1$, in contrast to the case of $R = 4.5$ in the $C_{12}C_2C_{12}(Et)$ system, indicating that the interactions between surfactant–salt complexes of NaSal/ $C_{12}C_2C_{12}(Me)$ are stronger than those of NaSal/ $C_{12}C_2C_{12}(Et)$. However, just because the interactions are too strong, as a result, the precipitate occurs earlier, and it does not show the gradual transition of the aggregates, contrary to the case of $C_{12}C_2C_{12}(Et)$. On the other hand, a higher R for $C_{12}C_2C_{12}(Et)$ indicates that interactions between surfactant–salt complexes are gentle, and only these appropriate interactions ensure the rich aggregate transitions.

On the other hand, the spacer effect of gemini surfactants on the microstructure was also studied by a rheology experiment in the $C_{12}C_S C_{12}(Et)$ series ($S = 4, 6, 8, 10, 12$) with the presence of NaSal. It was found that with the spacer increasing, the viscosity obviously decreased with NaSal addition. For example, when $S = 4$, i.e., $C_{12}C_4C_{12}(Et)$, only the concentration reached 40 mM, the obvious viscosity value can be obtained (Figure 9). In other words, even though the surfactant concentration and R were high, no rheological transition was observed and the viscosity value was smaller, contrary to the case of $C_{12}C_2C_{12}(Et)$. For other spacers ($S = 6, 8, 10, 12$), apparent viscosity (η_a) of the 20 mM gemini solutions was quite close to the water viscosity, and no rheological response under shearing with the addition of NaSal could be observed. It can be attributed to the steric effect caused by an increasing flexibility of the spacer bridge. With the spacer increasing, the two ammonium head-groups of the surfactant molecule tend to reduce the tendency of micellar growth.³⁶ In addition, compared with the system of NaSal/ $C_{12}C_2C_{12}(Et)$, other long spacer gemini surfactant systems of the NaSal/ $C_{12}C_S C_{12}(Et)$ series ($S = 4, 6, 8, 10, 12$) did not show dynamic rheological responses even though the concentration increased to ten-fold that of $C_{12}C_2C_{12}(Et)$. All of these indicated that the spacer length of gemini surfactants play an important role in studying the interaction of gemini surfactants and hydrotropic salts, and only the gemini surfactants with very

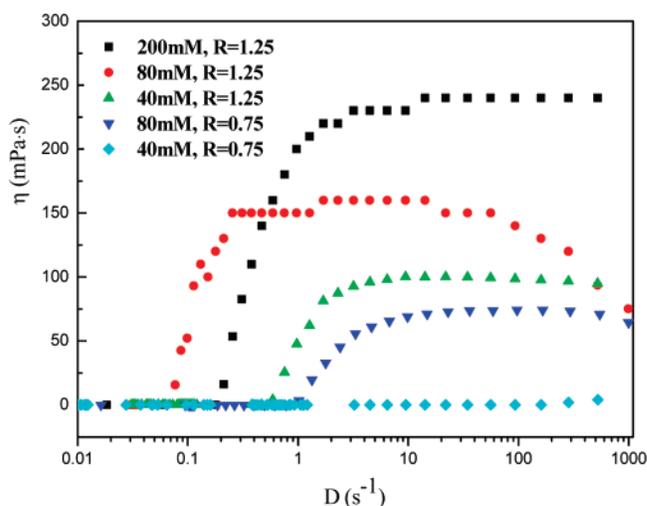


Figure 9. Steady shear viscosity as a function of shear rate in the presence of NaSal for various concentration of $C_{12}C_4C_{12}(Et)$ at 30 °C.

short spacers, such as $C_{12}C_2C_{12}(Et)$, can show such interesting aggregate transition with the addition of NaSal.

Conclusion

The hydrotropic salt addition to gemini surfactant system brings richer microstructure transitions compared with the conventional surfactant system. The interaction between gemini surfactants and hydrotropic salts is closely related to the charge of the hydrotropic salts and the structure of the gemini surfactants, including the polar headgroup and spacer. Moreover, it provides a simple method to obtain different kinds of surfactant aggregates including symmetrical and asymmetrical aggregates which can be used in materials synthesis as soft templates. This work may advance further understanding of interaction between hydrotropic salts and surfactants, especially for gemini surfactants, and promote their applications in other fields.

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Supporting Information Available: DLS results of the aqueous solution of 20 mM C₁₂C₂C₁₂(Et), polarization microscopy photograph for molar ratio $R = 2$, and NMR measurements for C₁₂C₂C₁₂(Et) with the addition of NaSal. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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