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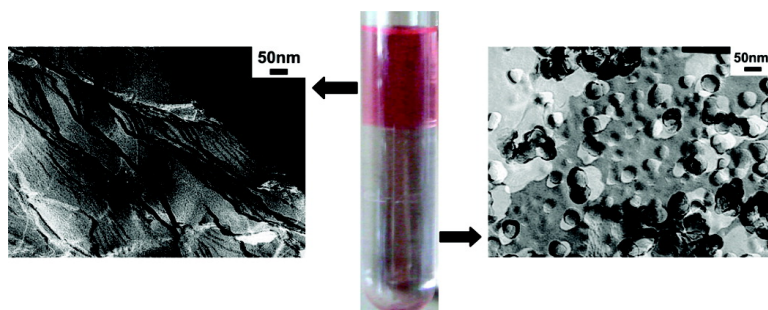# Aqueous Surfactant Two-Phase Systems in a Mixture of Cationic Gemini and Anionic Surfactants

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Aqueous Surfactant Two-Phase Systems in a Mixture of Cationic Gemini and Anionic Surfactants

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The phase behavior as well as the microstructures of the cationic gemini surfactant and anionic conventional surfactant aqueous two-phase system (ASTP) have been studied. The ASTP formation can be attributed to the coexistence of different kinds of aggregates in the upper and lower phases. The effects of temperature, shearing, surfactant concentration and mixing molar ratio on the phase separation of the ASTP-forming systems are systematically investigated. The ASTP can be destroyed by applying shear and increasing temperature. In this process, the lamellar structures (flat bilayers) in the ASTP are transformed into vesicles. Variation of surfactant structure also affects the phase behavior and the aggregates transformation. Appropriate molecular packing is crucial for the formation of ASTP.

Introduction

Phase separation in the mixed surfactant solutions has opened a new vista for isolation and purification of biomaterials while keeping their activities.[1,2] This is known as an aqueous surfactant two-phase system (ASTP),[3,4] which can occur in the aqueous mixture of an ionic surfactant and an oppositely charged polyelectrolyte, or a catanionic surfactant system (i.e., mixture of cationic surfactant and anionic surfactant).[5–8] The phase behavior in the latter system is of special interest owing to its variety.[9–11] So far, according to the structures formed in the surfactant-rich phase (which is always in equilibrium with a surfactant-poor phase), the formation of ASTP in a catanionic surfactant system can be induced by (i) entanglement of rod-like micelles,[12] (ii) formation of lamellar phase,[7] or (iii) dense packing of vesicles.[8,13]

Although there have been many reports dealing with ASTP phenomena in surfactant systems, systematic investigation on their formation mechanism is still rare. It is believed that the phase behavior of surfactant systems is closely related to the structure of aggregates as well as the interactions between the aggregates.[14] Our previous work revealed that the formation of an ASTP strongly depends on the type of surfactant aggregates in it.[4,8,13] To probe the relationship between the macroscopic

phase behaviors with the microstructures of the surfactant aggregates, it is helpful to investigate the influence of various environmental factors, such as temperature and shear on the ASTP formation. Changing temperature is a simple way to tailor assemblies;[15–17] shear force is proven to change the aggregate's morphology.[18–20] In addition, variation of an amphiphilic structure is also important for ASTP investigation, because it plays a key role in the transformation of organized assemblies and phase behaviors.

Here, we report the behavior of an ASTP system formed in a cationic gemini surfactant and oppositely charged conventional surfactant mixed solution. As a novel type of surfactant, gemini surfactants have attracted increasing attention over the past decades because of their many unusual physicochemical properties.[21–23] It is noteworthy that the structure of the gemini surfactant is adjustable owing to the existence of a spacer between the two headgroups. Variation of the spacer in gemini surfactants provides a convenient way to tailor the molecular arrangement and the interaction between molecules, so as to affect the aggregate structures and phase behaviors.[24–26] Our studies have demonstrated that the hydrocarbon parts of the polar headgroup in gemini surfactants also influence the aggregates in aqueous solution.[27] These multiple adjustable factors in gemini surfactants are very convenient for us to understand the effect of molecular structure on the ASTP formation mechanism. However, reported work on

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an ASTP formed in gemini surfactant is very rare.[28,29] In this work, we focus on the phase behavior especially for an ASTP formed by a cationic gemini surfactant hexanediyl-α,ω-bis-(dodecyldiethylammonium bromide) ($C_{12}C_6C_{12}(Et)$) and an anionic sodium laurate (SL). The effects of temperature, shearing and surfactant concentration on the phase separation of the ASTP-forming system are also systematically investigated.

Experimental Section

Materials. SL ($C_{11}H_{23}COONa$) was prepared by neutralizing lauric acid with NaOH in ethanol. Cationic gemini surfactants alkanediyl-α,ω-bis(dodecyldiethylammonium bromide), abbreviated as $C_{12}C_SC_{12}(Et)$ ($S = 4, 6, 12$) and hexanediyl-α,ω-bis(dodecyldimethylammonium bromide), abbreviated as $C_{12}C_6C_{12}(Me)$ were synthesized and purified according to literature methods.[24,27] Conventional cationic quaternary ammonium surfactant dodecyl triethylammonium bromide (DTEAB) was synthesized from 1-bro-mododecane and triethylamine. The purity of all the surfactants was examined, and no surface tension minimum was found in the surface tension curve. The water used was bidistilled from potassium permanganate containing deionized water to remove traces of organic compounds. The pH values of the mixed systems were fixed at 9.2 (0.01 M $Na_2B_4O_7\cdot10H_2O$) to control the hydrolysis of SL.

Sample Preparation and Phase Behavior. Approximately 300 samples (1 mL), were prepared by mixing cationic and anionic surfactants at desired concentrations and mixing molar ratios. Samples were mixed by vortex shaking and allowed to equilibrate in a thermostatic bath at 30.0 °C at least for 72 h. The phase boundaries were assigned by visual inspection. The criterion to determine the presence of an ASTP is the appearance of a clear interface in the system. When the interface is vertical to the tube wall and the volumes of the upper and the lower phase are no longer changed with time, the ASTP has reached equilibrium.

Methods. *Transmission Electron Microscopy (TEM).* Micrographs were obtained with a JEM-100CX II transmission electron microscope both by negative-staining method (with uranyl acetate) and freeze-fracture replication 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 30.0 °C with a ThermoHaake RS300 rheometer (cone and plate geometry of 35 mm in diameter with the cone gap equal to 0.105 mm).

Dynamic Light Scattering (DLS). DLS measurement was 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 scattering angle is 90°, and the intensity autocorrelation functions are analyzed by using the method of Contin.

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

Composition Measurement. First, a certain amount of upper phase solution of the ASTP was weighted and dried in a vacuum desiccator for 48 h, then was weighed and analyzed by elemental analysis (Elementar Bario EL, Germany).

Zeta-Potential Measurement. Zeta-potentials were measured using a temperature-controlled Zetasizer 2000 (Malvern Instruments. Ltd.).

Surface Tension. Surface tension of the surfactant solution was measured by using the drop volume method at 30.00 ± 0.01 °C. The concentration at the break point of the $\gamma-\log C$ curve was denoted as the critical micelle concentration (cmc).

Results and Discussion

ASTP Formation and Properties. At 30.0 °C, a small ASTP region can be observed in the mixed system of $C_{12}C_6C_{12}(Et)$ and

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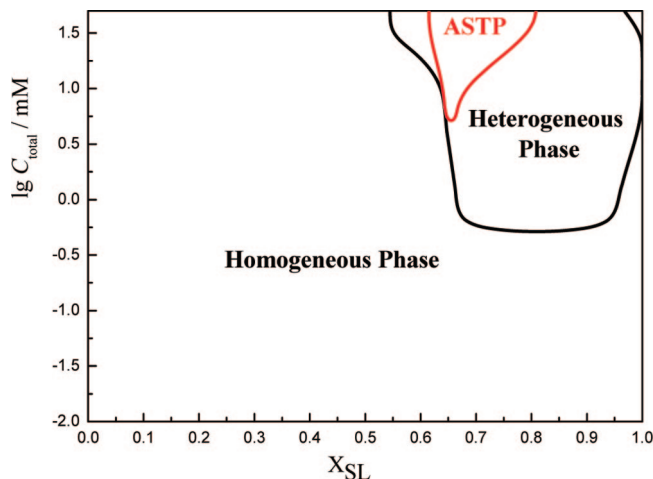
Figure 1. Phase diagram for $C_{12}C_6C_{12}(Et)/SL$ at 30.0 °C.

SL (see Figure 1). The ASTP region is around charge-neutral mixing ($X_{SL} = SL/(SL + C_{12}C_6C_{12}(Et)) \approx 0.67$), as we have expected. The upper phases were always opalescent, whereas the lower phases were transparent. In addition, a large area of heterogeneous region appears on the SL-rich side ($X_{SL} > 0.67$), which obviously deviates from electro-neutral mixing. This can be attributed to the difference of the aggregation capability between the two surfactants. The cmc's for $C_{12}C_6C_{12}(Et)$ and SL are 0.56 mM and 20.4 mM (30.0 °C), respectively, indicating that $C_{12}C_6C_{12}(Et)$ molecules have a stronger tendency to enter the aggregates. As a result, the ratio of $C_{12}C_6C_{12}(Et)/SL$ is larger in the aggregates than that in the bulk solution. This is proven by the result of elemental analysis. The upper phase for a 1:4 ASTP has a composition of 1:3 (C, 64.24; H, 11.10; N, 2.01), i.e., there are more $C_{12}C_6C_{12}(Et)$ molecules in the aggregates than in the bulk solution. Moreover, zeta-potential measurements also delivered similar information. As shown in Table 1, at neutralized mixing, e.g., $C_{12}C_6C_{12}(Et)/SL = 1/2$, the aggregates in the upper phases are positively charged. In a broad range of SL-rich mixing (1:4−1:10), the zeta-potential values of the aggregates do not increase proportionally and show no obvious change in the allowed range of zeta-potential measurement error, which indicates that SL has a weaker ability to enter the aggregates.

At pH 9.2, phase separation occurred in the mixed system $C_{12}C_6C_{12}(Et)/SL = 1/4$ ($C_{total} = 50$ mM) and reached equilibrium within one hour. Similar to other reports,[3,4] the formation of the ASTP in our system was reversible. When the ASTP system was shaken slightly, it became a turbid solution at once, and the turbid solution will return to the ASTP system after aging several minutes. The oil-soluble red dye, Sudan III was added to show more details about the ASTP (Figure 2). It was clearly seen that the color of the upper phase is much darker than that of the lower one, indicating that the upper one is the surfactant-rich phase, whereas the lower is the surfactant-poor phase. Further investigation by the surface tension plots also supported the above conclusion. It was shown in Figure 3 that the surface tension of the upper phase was nearly invariable after the solutions were diluted with buffer, even above 1000 times the volume ratio. In contrast, the surface tension of the lower phase began to rise just after two dilutions. These results indicate that the surfactant concentration of the upper phase is much higher than its cmc, whereas that of the lower one is very close to the cmc.

In Figure 4, we show the viscosity results for the two phases of the ASTP ($C_{12}C_6C_{12}(Et)/SL = 1/4$, $C_{total} = 50$ mM, pH 9.2). It is clearly seen that the lower phase has a viscosity similar to

Table 1. Zeta Potential Results of the Mixed Systems of $C_{12}C_6C_{12}(Et)$/SL with Different Molar Ratios at the Concentration beyond the cmc (pH 9.2, T = 30 °C)

| molar ratio ($C_{12}C_6C_{12}(Et)$/SL)	1:2	1:4	1:6	1:8	1:10	1:12	1:16	1:20
zeta potential (mV)	19	−12	−14	−11	−16	−71	−67	−82

water, but the upper phase is much viscous, and showed a remarkable shear-thinning feature. The rheological property of the two phases is also coincident with the results of dye extraction and surface tension results.

Microstructures in ASTP. Usually, the macroscopic phase behaviors are closely related to the microstructures in the surfactant systems. In order to further probe this relationship, we carried out TEM observations to determine the aggregate structures in the ASTP. In Figure 5a we show a representative micrograph for the upper phase. Lamellar structures (flat bilayers) were observed by freeze-fracture TEM (FF-TEM); in between two polarizers, they were birefringent, and colorful stripes were observed under a polarization microscope (Figure 6a). All these observations confirm the formation of the lamellar structures in the upper phase. In contrast, vesicles with an average diameter of 40 nm were observed in the lower phase (Figure 5b), which is isotropic and shows no birefringence. DLS measurement was used to measure the particle size at 30 °C, and the average

hydrodynamic radius of the aggregates in the lower phase was obtained as 35 nm (Figure 6b), which was almost the same as the size observed by TEM. We believed that the tiny difference in size was brought about by the different measuring methods.

Effect of Temperature. At room temperature, the ASTP is stable for several months or even more than 1 year. However, the ASTP is sensitive to temperature. Upon increasing temperature, the phase boundary became blurry and finally disappeared. For example, the two-phase system of $C_{12}C_6C_{12}(Et)$/SL = 1/4 was substituted by a homogeneous single solution at higher than 70 °C. The microstructures in this single solution were found to be polydisperse vesicles (Figure 7a). If the two phases of the ASTP were separated, then the upper and lower phases were heated to 80 °C, respectively, vesicles were found again (Figure 7b and 7c) in both phases. This indicates that increasing temperature results in the transformation from lamellar structures to vesicles, while the vesicles are superthermally stable under the experimental conditions. The superior thermal stability of the vesicles in the $C_{12}C_6C_{12}(Et)$/SL mixed system may be attributed to the existence of the $C_{12}C_6C_{12}(Et)$ gemini surfactant in the vesicle membrane. It has been reported that vesicles formed by gemini surfactants alone are very thermally stable.[27]

However, it is surprising to find that the microstructure change induced by temperature is not reversible. After the temperature was decreased to the original state, densely packed vesicles, instead of lamellar structures were observed in the upper phase after the system was heated to 80 °C and then cooled to 30 °C (Figure 8a). Meanwhile, the upper phase was no longer birefringent, and no colorful stripes can be observed under a polarization microscope, indicating the absence of lamellar phase. For the lower phase, microstructures did not change when the same treatment was applied. Dispersed vesicles were reserved, regardless of temperature change (Figure 8b). It is obvious that the vesicles are more thermally stable than the lamellar structures, so that the latter is easy to transform into the former upon increasing temperature. However, it seems that both the lamella and the vesicles are kinetically stable. After standing for 1 year at 30 °C, neither the appearance nor the microstructures have changed in the ASTP.
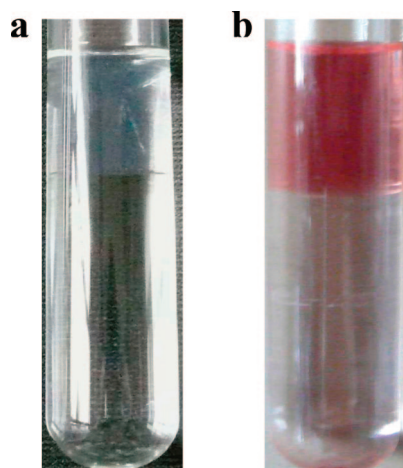
Figure 2. Appearance photographs of a mixed system of $C_{12}C_6C_{12}(Et)$/SL (1/4, C_{total} = 50 mM, pH 9.2) with the oil-solubility dye Sudan III: (a) before the dye addition; (b) after the dye addition.
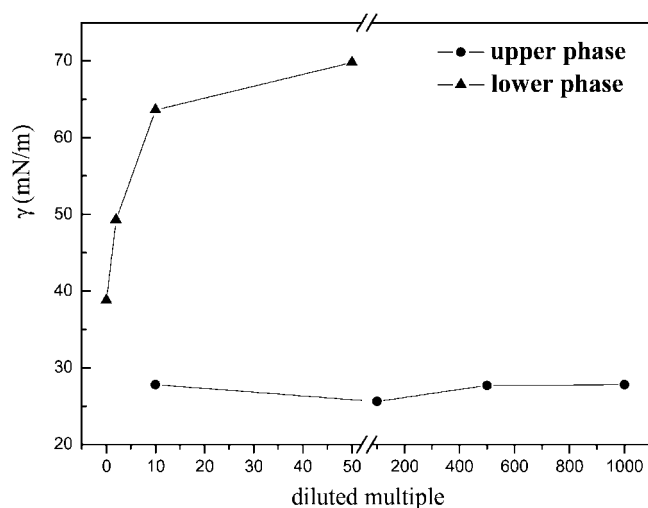
Figure 3. Surface tension of upper and lower phases with diluted multiple in ASTP ($C_{12}C_6C_{12}(Et)$/SL = 1/4, C_{total} = 50 mM, pH 9.2) at 30.0 °C, respectively.
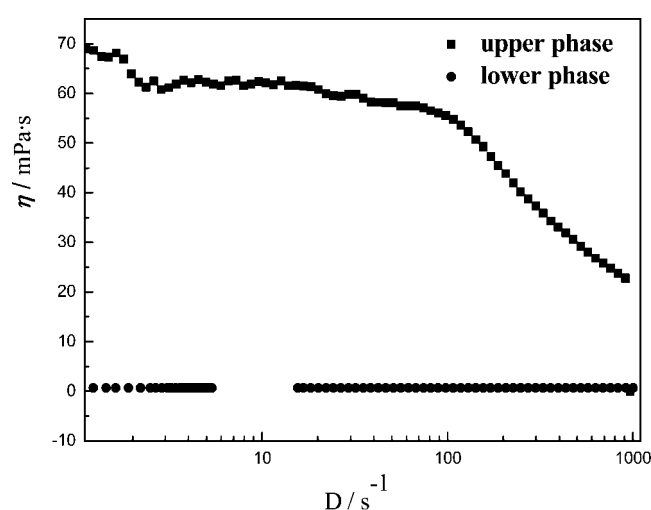
Figure 4. Steady shear viscosity as a function of shear rate of upper and lower phases in ASTP ($C_{12}C_6C_{12}(Et)$/SL = 1/4, C_{total} = 50 mM, pH 9.2) at 30.0 °C, respectively.
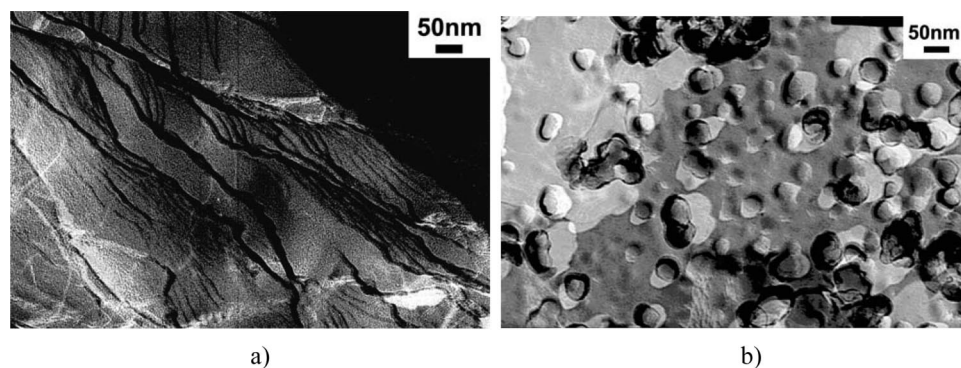
Figure 5. FF-TEM micrographs of ASTP solution in the system of $C_{12}C_6C_{12}(Et)/SL$ (1/4, C_{total} = 50 mM, pH 9.2) at 30 °C: (a) lamellar structures in the upper phase; (b) vesicles in the lower phase.
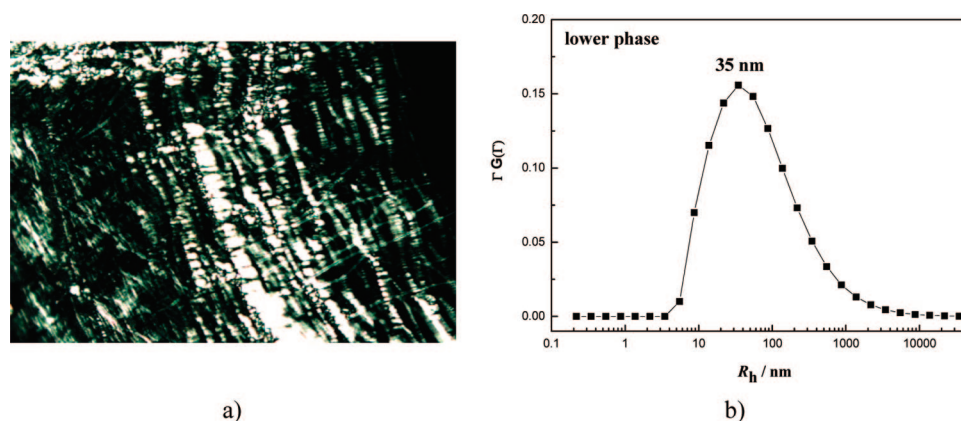

Figure 6. (a) Photograph of upper phase of ASTP ($C_{12}C_6C_{12}(Et)/SL$ = 1/4, C_{total} = 50 mM, pH 9.2) through a polarization microscope; (b) Hydrodynamic radius distribution of the aggregates formed in the lower phase of the ASTP by DLS at 30 °C.
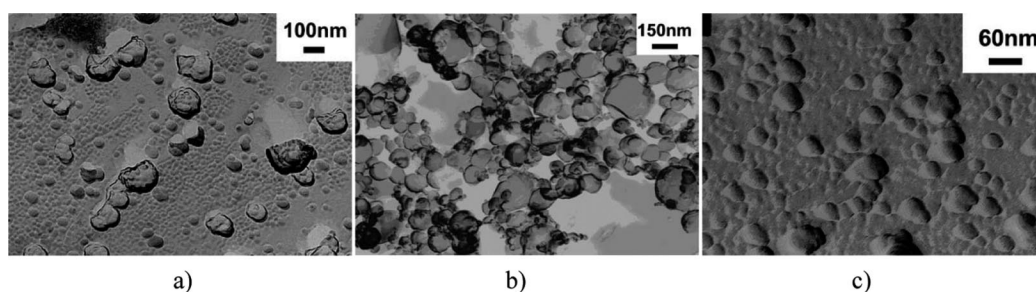

Figure 7. Micrographs by FF-TEM for ASTP solution ($C_{12}C_6C_{12}(Et)/SL$ = 1/4, C_{total} = 50 mM, pH 9.2) at 80 °C: (a) homogeneous phase; (b) upper phase of ASTP; (c) lower phase of ASTP.

Effect of Shearing. It is well-known that the lamellar structures can transform into vesicles under shearing.[19,30,31] This is also the case in the $C_{12}C_6C_{12}(Et)/SL$ system. A transition from lamellar structures to vesicles was observed (Figure 9a) after the upper phase of the ASTP ($C_{12}C_6C_{12}(Et)/SL$ =1/4, C_{total} = 50 mM, pH 9.2) was sheared 10 min at a shear rate of 500 s^{-1}. It seems that shear force has no obvious effect on the microstructures in the lower phase. The vesicles were still there after the system experienced the same shear (Figure 9b). According to the above results, we infer that phase separation would not occur if the whole ASTP is sheared, since the significant difference on the aggregates in upper and the lower phase disappears. This prediction was confirmed both by visual inspection and micrograph observation. After applying shear to the whole ASTP

sample, a homogeneous single solution was observed. The microstructures in this single solution were found to be vesicles (not shown).

Effect of Concentration and Mixing Ratio. The formation of the ASTP depends strongly on the total surfactant concentration. When the total concentration was increased from 50 mM to 100 mM (fixed the mixing molar ratio to 1:4), both the phase behavior and the aggregates were changed. With increasing the concentration, the phase separation gradually disappeared, and a viscous homogeneous phase was observed. TEM result (Figure 10a) revealed the presence of lamellar structures in the system. This demonstrates that increase of concentration favors the formation of lamellar structures. Correspondingly, decrease of concentration should favor the formation of vesicles. Indeed, when the upper phase of the ASTP was separated and diluted with buffer, the lamellar structures were transformed to vesicles (Figure 10b). In addition, the mixing ratio between $C_{12}C_6C_{12}(Et)$ and SL also

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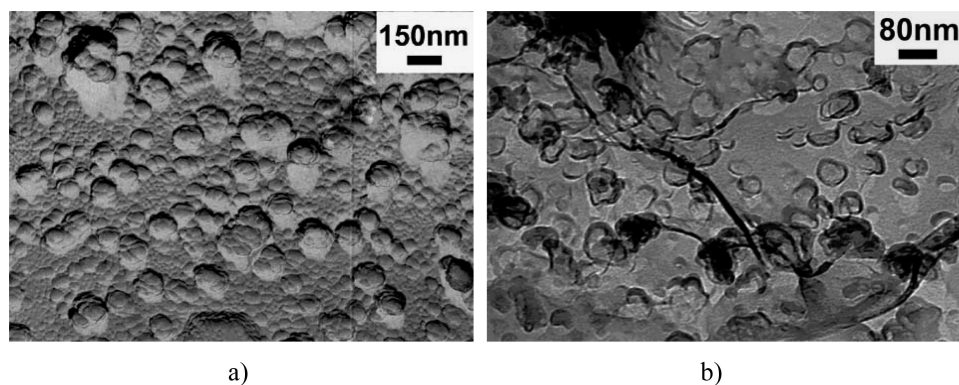
Figure 8. FF-TEM micrographs of ASTP solution in the system of $C_{12}C_6C_{12}(Et)/SL$ (1/4, C_{total} = 50 mM, pH 9.2) experiencing the cycle of heating to 80 °C and then cooling to 30 °C: (a) aggregated vesicles in the upper phase; (b) vesicles in the lower phase.
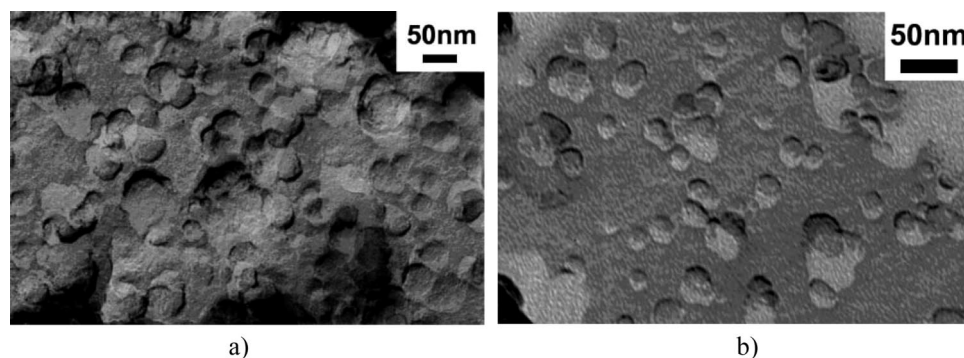

Figure 9. FF-TEM micrographs of ASTP solution ($C_{12}C_6C_{12}(Et)/SL$ = 1/4, C_{total} = 50 mM, pH 9.2) after shearing for 10 min at a shear rate of 500 s^{-1}: (a) upper phase; (b) lower phase.
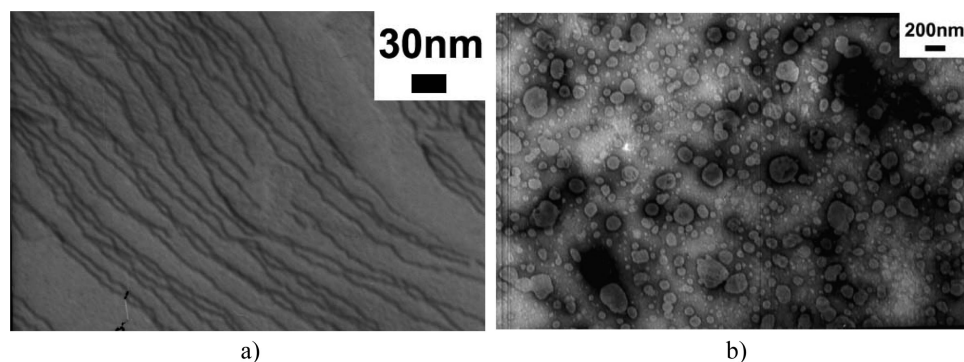

Figure 10. TEM micrographs of the mixed systems of $C_{12}C_6C_{12}(Et)/SL$ at different concentrations: (a) 1/4, C_{total} = 100 mM, pH 9.2 by the freeze-fracture method; (b) upper phase in the $C_{12}C_6C_{12}(Et)/SL$ (1/4, C_{total} = 50 mM, pH 9.2) diluted to the original 5 multiples by the negative-staining method.

Table 2. Volume Fraction of the Upper Phase to the Lower One in the $C_{12}C_6C_{12}(Et)/SL$ ASTP (T = 30 °C, C_{total} = 50 mM, pH 9.2)

molar ratio	1:2	1:3	1:3.3	1:3.5	1:3.7	1:4
V_{upper}/V_{lower}	0.066	0.17	0.21	0.24	0.28	0.43

affects the ASTP formation. In the range of ASTP formation concentration, the volume ratio of the upper and lower phases depends on the mixing ratio. The volume of the upper phase increases with increasing SL content (Table 2), but the microstructures in the upper and lower phases were reserved when changing the mixing ratio.

Effect of Molecular Structures on the ASTP Formation. The special structure of gemini surfactants allows us to adjust their aggregation behaviors conveniently. We found that the ASTP forming ability was affected by the spacer length of gemini surfactants. For example, the ASTP region in the phase diagram of the $C_{12}C_{12}C_{12}(Et)/SL$ mixed system is obviously smaller than that of the $C_{12}C_6C_{12}(Et)/SL$ system (Figure 1 and Figure 11a). That is to say, increasing the spacer from 6 CH_2 to 12, the ability to form ASTP decreased. Decreasing the spacer length to 4 CH_2, ASTP can be obtained in an even smaller region, but the precipitate region was bigger than that of the $C_{12}C_6C_{12}(Et)/SL$ system. According to the above results, the ability to form ASTP follows $C_{12}C_6C_{12}(Et)/SL > C_{12}C_{12}C_{12}(Et)/SL > C_{12}C_4C_{12}(Et)/SL$. This sequence can be related to the different spacer length of the gemini molecules. For the $C_{12}C_{12}C_{12}(Et)/SL$ system, the distance between the two headgroups of the gemini molecule is much longer than that for the $C_{12}C_6C_{12}(Et)/SL$ system. This leads to an increase of the mean area per headgroup and produce a smaller critical packing parameter p (p is defined as $v/a_0 l_c$, where v is
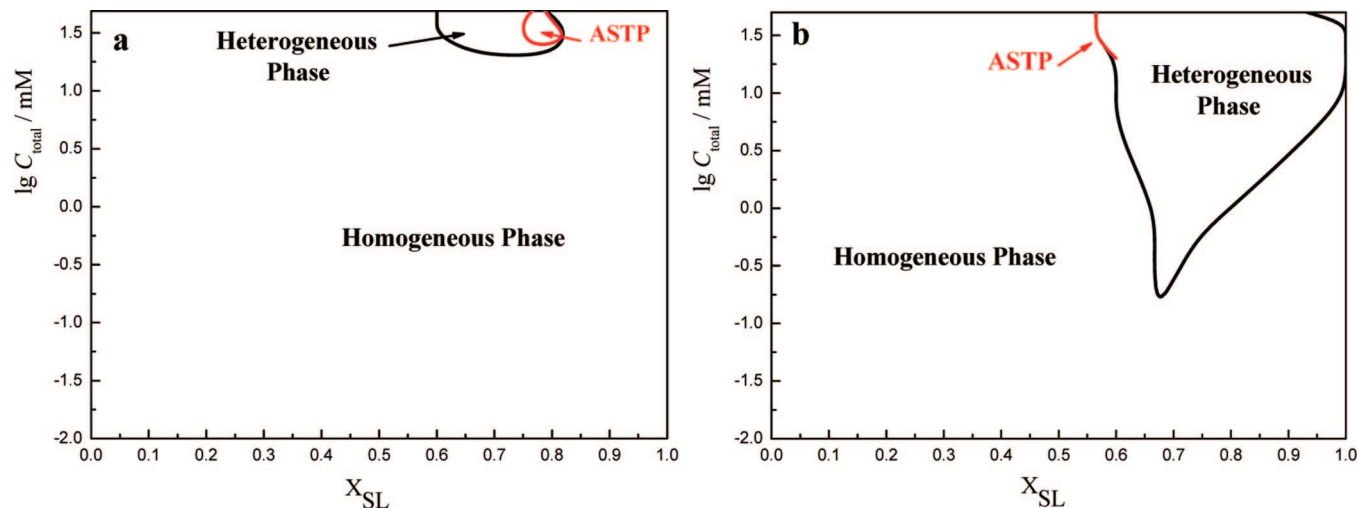
Figure 11. Phase diagrams at 30.0 °C for (a) $C_{12}C_{12}C_{12}$ (Et)/SL and (b) $C_{12}C_6C_{12}$(Me)/SL.

the surfactant tail volume, l_c is the tail length, and a_0 is the equilibrium area per molecule at the aggregate surface; $0 \leq p \leq 1/3$ for sphere micelle, $1/3 \leq p \leq 1/2$ for cylinder micelle, and $1/2 \leq p \leq 1$ for bilayer structure),[32] which results in the small region of heterogeneous phase and ASTP. On the other hand, the shorter spacer in $C_{12}C_4C_{12}$(Et) leads to a smaller headgroup area, which results in larger p. This favors the formation of precipitates, which is disadvantageous to the formation of ASTP. It can be concluded that the geometrical effect plays an important role on the ASTP formation; only an appropriate spacer length favors the formation of ASTP.

Polar headgroup effect on the ASTP formation was also investigated. As shown in Figure 11b, the area of the ASTP region for the mixture of $C_{12}C_6C_{12}$(Me)/SL was much smaller than that of $C_{12}C_6C_{12}$(Et)/SL mixed system, but the area of precipitates region was almost the same in the two systems. This result demonstrates that decreasing the headgroup size of the gemini surfactant is in favor of precipitate, instead of ASTP, formation. As the headgroup size is changed form Et to Me, the p value is increased, so that it is easier to form precipitate rather than ASTP. However, the effect of the polar headgroup on the ASTP formation is different in the conventional mixed surfactant systems. For example, homogeneous phase rather than ASTP formed in the mixed system of DTEAB/SL, in which DTEAB was often considered as the monomer of the gemini surfactant $C_{12}C_6C_{12}$(Et). While for the mixed system of DTAB/SL (dodecyl trimethylammonium bromide), besides homogeneous phase, ASTP and precipitate can also be observed. Combined with the above results, the interaction between the molecules plays an important role in the formation of ASTP, and only the appropriate interaction is optimization for the ASTP formation. Precipitate will be formed if the interaction is too strong, whereas homogeneous solution will be obtained if it is too weak; both of them are disadvantageous for the formation of ASTP. In

addition, it should be noted that the hydrophobic interaction between the aggregates or within the aggregates also plays an important role in the formation of the ASTP. References can be found in our previous work and other literature.[13,33−36]

Conclusions

ASTP and the microstructures in it were systematically studied in a cationic gemini surfactant and a conventional anionic surfactant mixed system. The formation of ASTP can be attributed to the coexistence of different kinds of aggregates in it. Both temperature and shear influence the ASTP formation and induce transformation of the aggregates. Increasing or decreasing the spacer length of the gemini affects the compactness of the molecular packing in the aggregates and, consequently, have an effect on the ASTP formation. The appearance of the ASTP occurs in the region of heterogeneous phase, and only appropriate molecular packing is beneficial to the ASTP formation owing to the geometrical effect and hydrophobic effect. In the mixed system of gemini surfactant and oppositely charged conventional surfactant, our studies on the ASTP may provide further understanding of the molecular organized assembly and the relationship among the macroscopic phase behavior, microscopic structures, and molecular structures, which may advance its applications in correlative fields.

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