

Active control of surface properties and aggregation behavior in amino acid-based Gemini surfactant systems

Haiming Fan^a, Feng Han^a, Zhuang Liu^a, Lang Qin^a, Zichen Li^b, Dehai Liang^b, Fuyou Ke^b, Jianbin Huang^{a,*}, Honglan Fu^c

^a Beijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China

^b Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China

^c College of Life Science, Peking University, Beijing 100871, People's Republic of China

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Abstract

Two types of Gemini surfactants containing a disulfide bond in the spacer, sodium dilauroyl cystine (SDLC) and sodium didecamino cystine (SDDC), were synthesized, and their surface properties and aggregation behavior in aqueous solution were studied by means of surface tension measurements, dynamic light scattering (DLS), transmission electron microscopy (TEM), and fluorescence. During the transition of the Gemini surfactants to their corresponding monomers through the reduction of disulfide bonds, the surface tensions of their aqueous solutions, as well as their aggregation behavior, changed greatly. The reduction of SDLC and SDDC led to disruption of the vesicle, and the oxidation of corresponding monomers to Gemini surfactants led to vesicle re-formation. These results demonstrated the control of surface properties and aggregation behavior by the reversible transition between the Gemini surfactant and its monomer via reduction/oxidation reactions.

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Keywords: Gemini surfactant; Reduction/oxidation reactions; Transition between Gemini and its monomer; Surface tension; Vesicle

1. Introduction

Amphiphiles have the ability to decrease the surface tension at the interface and form various self-organized assemblies, such as micelles and vesicles, in aqueous solution. Because of their capability in controlling the interfacial properties, amphiphiles are widely used in oil recovery, food processing, and pharmaceutical formulation. In addition, their self-assemblies have been widely exploited in the areas of catalysis, biochemistry, material synthesis, and pharmaceutical industries [1–4]. Thus, it is necessary to study the formation and transition of amphiphile self-assemblies which would be helpful to the application in these areas [5,6]. In the past few decades, many efforts have been made to the transformations between surfactant aggregate, especially those induced by adding cosur-

factant [7–9] and salt [10–12], or by varying pH [13–15] and temperature [16–19].

Compared with the changes of the environmental factors, the variation of the molecular structure is more effective for controlling the aggregates formed by the amphiphiles. It provides an approach for obtaining more direct and detailed information on the relationship between the amphiphilic molecular structure and the formation of the aggregates. If the variation of the molecular structure is reversible, the reversible transformation of surface properties and the aggregation behavior can be achieved. One approach is to design molecules containing suitable functional groups. Some light-active and redox-active surfactants have been successfully used to show the reversible changes in aggregation morphology, viscosity, microemulsion separation, and solubilization [20,21]. Besides, research on active control of the interfacial tension has also been reported for designed surfactants using triggers including ultraviolet irradiation [22,23], electrochemical oxidation [24,25] and chemod-

* Corresponding author. Fax: +86 10 62751708.

E-mail address: jbhuang@pku.edu.cn (J. Huang).

egradation [26,27]. In previous investigations, amphiphiles containing disulfide bonds have attracted a great deal of attention [28–33] mainly because of their ability to be reduced chemically, electrochemically, photochemically, and enzymatically [34].

Gemini surfactants have attracted increasing attention over the past years, owing to their superior properties in comparison with those of the conventional single-chained surfactants [35,36]. The most pronounced differences for Gemini surfactants are the lower critical micelle concentration, the higher viscoelasticities, and the higher efficiency in decreasing the surface tension of water than the corresponding monomeric surfactants. The most widely studied Gemini surfactants are dicationic quaternary ammonium compounds, which are referred to as $C_m-C_s-C_m$, where m and s stand for the carbon atom number of the side alkyl chain and the methylene spacer, respectively [36]. Many previous studies have explored the relationship between the surfactant structure and the micellar properties [37–42], with the focus on the effect of spacer length or its flexibility and hydrophobicity. Although there are some works on the synthesis of Gemini surfactant containing disulfide bonds, research on this functional group introduced to the spacer is still rare [43].

Amino acid-based and carbohydrate-based Gemini surfactants represent a class of surfactants with superior properties of biocompatibility and biodegradability. They were also found to be effective as antimicrobials [44,45]. Thus, in this paper, a series of Gemini surfactants derived from cystine, sodium dilauroyl cystine (SDLC), and sodium didecamino cystine (SDDC), as shown in Scheme 1, were systematically investigated. Through the reduction/oxidation reactions between the disulfide bond and the thiol group, the surface tension can be reversibly controlled in these two systems. Moreover, the aggregation abilities of SDLC and SDDC solutions are quite different from those of their monomers. Dynamic light scattering and transmission electron microscopy experiments demonstrated that the reduction of SDLC and SDDC leads to a disruption of the vesicle, and the oxidation of the corresponding monomers to Gemini surfactants leads to the vesicle re-formation. Thus, control of the surface properties and the organized assemblies is achieved by the reduction/oxidation reactions in this series of surfactants.

2. Materials and methods

2.1. Materials

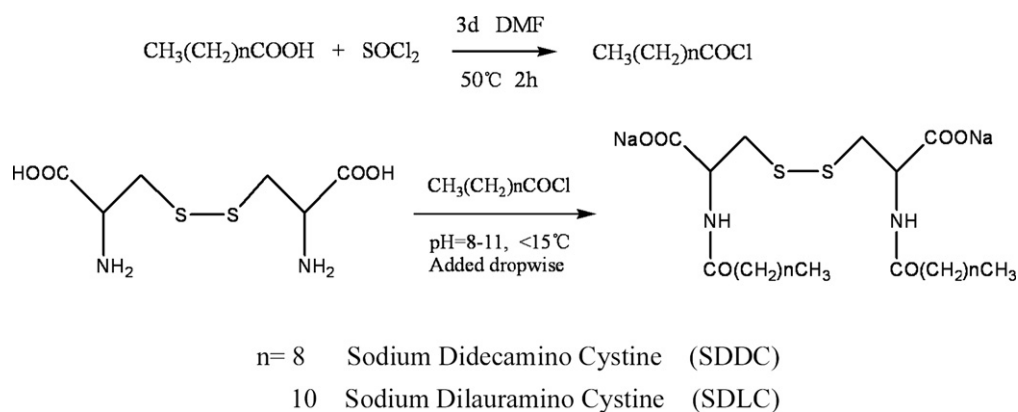
L-Cystine, lauric acid, decanoic acid, thionyl chloride, acetone, ethanol, hydrogen peroxide, sodium hydrogen carbonate, and borax are all A.R. grade and purchased from Beijing Chemical Company. *N,N*-dimethylformamide and sodium hydroxide are all A.R. grade and purchased from Tianjing Chemical Company. Dithiothreitol (DTT, 99%) and mercaptoethanol (ME, 99%) are purchased from Aldrich Company and Farco Chemical Supplies, respectively. Riboflavin is from Sigma Company. All reagents were used without further purification. Water was distilled twice with KMnO_4 to remove the trace amount of organic compounds.

2.2. Synthesis

Compounds SDLC and SDDC were synthesized based on the procedure previously reported [43].

2.2.1. Sodium dilauroamino cystine

Three drops of *N,N*-dimethylformamide were added to the solution containing lauric acid (20.03 g, 100 mmol) and thionyl chloride (50 ml). The mixture was refluxed at 50 °C for 2 h, and the resulting mixture was distilled under reduced pressure to remove most of the thionyl chloride. The solution was then poured into water while stirring. The oil layer was washed first with water and then with 5% sodium hydrogen carbonate (aq) until neutralized to pH 7. The product (lauric acid chloride) was used in the following synthesis without further purification. L-Cystine (4.80 g, 20 mmol) and sodium hydroxide (1.60 g, 40 mmol) were dissolved in 100 ml 2:1 acetone–water mixed solvent. Lauric acid chloride (10.90 g, 50 mmol) was added dropwise while stirring at 10–15 °C, followed by 10% sodium hydroxide solution to keep pH 8–11. Then, the mixture was stirred for 0.5 h. The resulting mixture was filtered and the precipitate was recrystallized four times in the mixture of ethanol/water (v/v, 95/5). ^1H NMR (see Fig. S1a in Supplementary material): δ 4.50 (d, 1H, CHCOONa), 3.27 (d, 1H, SCH_2), 2.93 (t, 1H, SCH_2), 2.30 (d, 2H, COCH_2), 1.62 (s, 2H, COCH_2CH_2), 1.28 (s, 16H, $(\text{CH}_2)_8$), 0.86 (t, 3H, CH_3) ppm;



Scheme 1. Synthesis of SDLC and SDDC.

anal. calc. for $C_{30}H_{54}N_2O_6S_2Na_2$: C, 55.54; H, 8.39; N, 4.32. Found: C, 55.49; H, 8.10; N, 4.16.

2.2.2. Sodium didecamino cystine

The synthesis of SDDC is similar to that of SDLC, except that lauric acid was replaced by decanoic acid. 1H NMR (see Fig. S1b in Supplementary material): δ 4.52 (d, 1H, $CHCOONa$), 3.29 (d, 1H, SCH_2), 2.92 (t, 1H, SCH_2), 2.30 (d, 2H, $COCH_2$), 1.63 (s, 2H, $COCH_2CH_2$), 1.29 (s, 12H, $(CH_2)_6$), 0.88 (t, 3H, CH_3) ppm; anal. calc. for $C_{26}H_{46}N_2O_6S_2Na_2$: C, 52.69; H, 7.82; N, 4.73. Found: C, 52.95; H, 7.87; N, 4.59.

2.3. Methods

2.3.1. Sample preparation

SDLC or SDDC was dissolved in an aqueous buffer containing 10 mM borax (pH 9.2) to avoid hydrolyzation of carboxylate groups. All the measurements for SDDC are conducted at 30.0 ± 0.5 °C, while for SDLC at 40.0 ± 0.5 °C considering that the Krafft temperature of SDLC is higher than 30 °C.

2.3.2. Electrospray ionization mass spectrometry (ESI-MS)

ESI mass spectra and collision-induced dissociation (CID) spectra were obtained using a Finnigan LCQ Deca XP Plus ion-trap mass spectrometer (Thermo Finnigan, San Jose, CA); all experiments were performed in positive mode. A measurement amount of DTT (the molar ratio of DTT versus surfactant equals 100:1) was added into Gemini surfactant solutions to reduce the disulfide bond. Disulfide re-formation was carried out by oxidation with excess hydrogen peroxide. Hydrochloric acid was added to the sodium dilauramino cystine (SDLC) or sodium lauroyl cysteine (SLC) solution to precipitate dilauramino cystine (DLC) or lauroyl cysteine (LC). The precipitate was washed several times by water and used for the ESI-MS measurement in methanol.

2.3.3. Dynamic light scattering (DLS)

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 was used to conduct DLS. All solutions were filtered through a 0.20- μ m membrane filter of hydrophilic PVDF before the measurements. Photon correlation measurements in self-beating mode were carried out at scattering angles of 30°–90° by using a BI-TurboCo Digital Correlator. The intensity autocorrelation functions are analyzed by using the methods of CONTIN [46]. The apparent hydrodynamic radius R_h was deduced from the diffusion coefficient D by the Stokes–Einstein formula $R_h = k_B T / (6\pi\eta D)$.

2.3.4. Transmission electron microscopy (TEM)

Micrographs were obtained with a JEM-100CX transmission electron microscope by the negative-staining method and freeze–fracture technique.

Negative-staining method Uranyl acetate solution (1%) was used as the staining agent. Carbon Formvar-coated copper grid (230 mesh) was laid on one drop of the sample solution for 5 min and the excess solution was absorbed away with filter paper. Then the copper grid was put into one drop of uranyl acetate solution. The excess liquid was also adsorbed away with filter paper. For each solution, at least three TEM samples were prepared and observed independently to exclude the artifacts as possibilities.

Freeze–fracture technique Fracturing and replication were carried out in an EE-FED.B freeze–fracture device equipped with a JEE-4X vacuum evaporator.

2.3.5. Entrapment of riboflavin and gel filtration

Vesicles were prepared in 2×10^{-5} mol L $^{-1}$ riboflavin solution in 10 mM borax buffer (pH 9.2). The amount of 0.50 ml of this solution was loaded onto a preequilibrated Sephadex G-50 column (13 cm \times 1 cm) and eluted with the borax buffer to separate vesicle-entrapped riboflavin from the free riboflavin. The fluorescence emission due to riboflavin was measured at 514 nm on excitation at 374 nm using a Hitachi F-4500 spectrofluorometer. The encapsulation efficiency was determined by measuring the amount of dye encapsulated relative to the initial amount.

2.3.6. Steady-state fluorescence measurements

The micropolarity was investigated by the measurements of the pyrene polarity ratio (I_1/I_3) in the concentration range from below to above the critical micelle concentration (cmc). An ethanol solution of pyrene was added to the surfactant solution. The final pyrene concentration was 5×10^{-7} mol L $^{-1}$. The ethanol volume was less than 1% of the total solution volume. The fluorescence spectra of pyrene solubilized in the investigated solutions were recorded using a Hitachi F-4500 spectrofluorometer in the range of 350–450 nm at an excitation wavelength of 335 nm. I_1/I_3 corresponds to the ratio of the fluorescence intensities of the first ($\lambda = 374$ nm) and third ($\lambda = 384$ nm) vibronic peaks. This value was used to monitor the formation of hydrophobic microdomains.

2.3.7. Surface tension measurements

The dynamic surface tension was measured with a Khan DCA-315 tension meter by the Wilhelmy plate technique. The equilibrium surface tension of aqueous surfactant solution was measured by the drop volume method. The values of critical micelle concentration (cmc) can be determined from the break points in the γ -log C curves. The saturated adsorption amount of surfactants was calculated according to the Gibbs adsorption equation (1) if the ionic strength and $[Na^+]$ were kept constant [2],

$$\Gamma_{\infty} = -d\gamma/2.303RT \, d \log C, \quad (1)$$

where C (mol L $^{-1}$) is the concentration of the corresponding surfactant in the system, and Γ_{∞} is the saturated adsorption amount in mol m $^{-2}$. $\{d\gamma\}/\{d \log C\}$ is the maximal slope in each case. T is the absolute temperature and $R =$

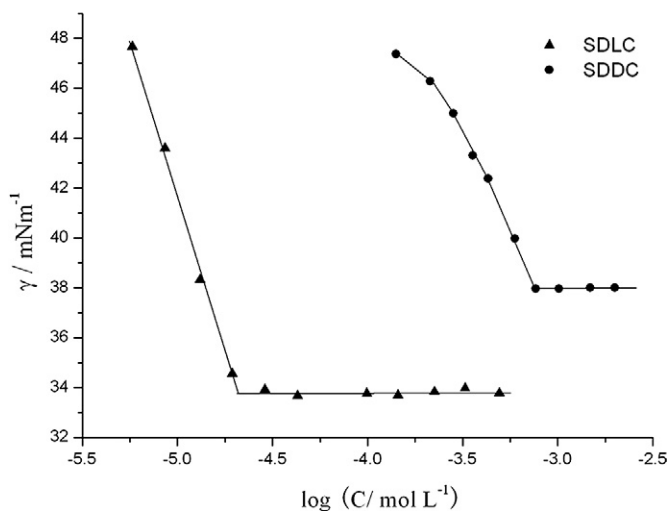


Fig. 1. The surface tension curves of SDLC in borax buffer at 40 °C and SDDC at 30 °C.

Table 1
Comparison of the interfacial properties of SDLC and SDDC with those of other surfactants

Surfactant	cmc (mmol L ⁻¹)	10 ⁶ Γ _∞ (mol m ⁻²)	10 ¹⁸ A _{min} (m ²)	γ _{cmc} (mN m ⁻¹)	Ref.
SDLC	0.0220	3.6	0.46	33.8	
SDDC	0.750	2.8	0.59	38.0	
12-4-12 (Me)	1.00	1.43 (2.15)	1.16 (0.77)	39.8	[47]
12-6-12 (Me)	1.12	1.16 (1.75)	1.43 (0.95)	42.5	[47]
C ₁₁ H ₂₃ COONa	9.55	4.7	0.35	26.2	[48]
C ₉ H ₁₉ COONa	74.5	4.7	0.35	32.6	[48]

8.314 J mol⁻¹ K⁻¹. Then the minimum average area per surfactant molecule A_{\min} (m²) is obtained from the saturated adsorption amount by

$$A_{\min} = 10^{18} / N_A \Gamma_{\infty}, \quad (2)$$

with N_A being the Avogadro constant.

3. Results and discussion

3.1. Reversible control of surface properties in SDLC and SDDC systems

The surface tensions of SDLC and SDDC at pH 9.2 are shown in Fig. 1. To understand the structural effect of these amino acid-based surfactants, some surface chemistry data of SDLC and SDDC systems were compared with those of other surfactants [47,48] in Table 1. The SDLC and SDDC showed superior capability of surface adsorption and micellization. Clearly, the cmc values of SDLC and SDDC were two orders of magnitude lower than those of conventional carboxylic acid surfactants. This indicated that the aggregation ability of Gemini surfactants was far greater than those of the comparable conventional surfactants with the same nature of the hydrocarbon chain. Besides the lower cmc of these systems, A_{\min} s of SDDC and SDLC were also very small and nearly half of 12-s-12 ($s = 4, 6$). These results could be attributed to the fact

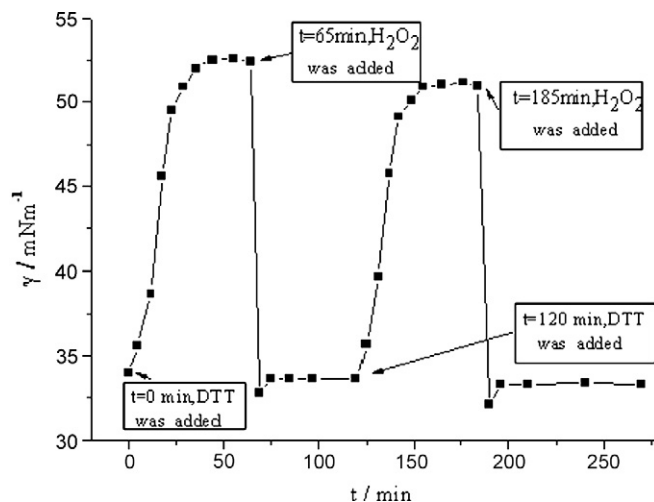


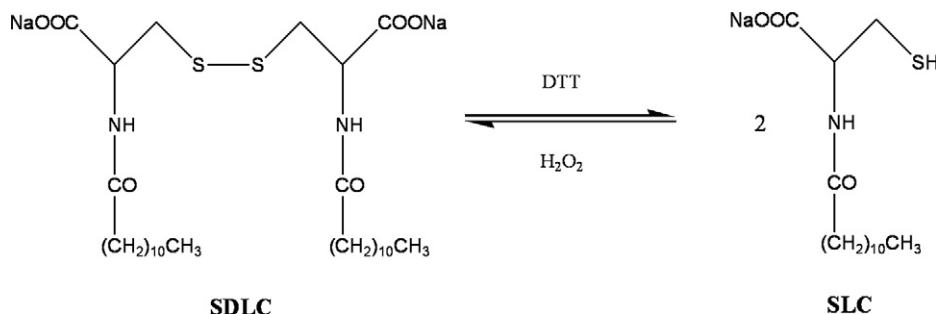
Fig. 2. The surface tension variation in SDLC/SLC transition ($C_{\text{SDLC}} = 0.1 \text{ mmol L}^{-1}$).

that the hydrolyzed carboxylic acid screened the electrostatic repulsion between the polar head groups of the corresponding surfactant systems. It also indicated that the surfactant molecules were packed very tight in the surface adsorption layer, and in the aggregates of SDLC and SDDC systems.

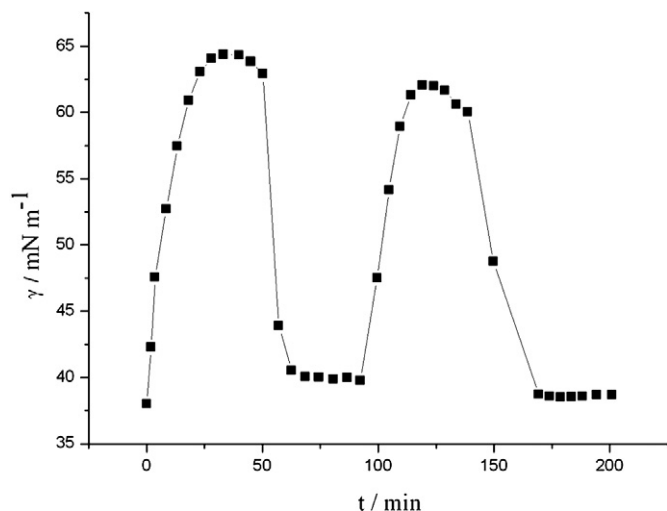
The cmc values of these types of Gemini surfactants were far smaller than those of monomeric surfactants systems. For instance, the cmc of SDLC was 0.02 mmol, while the cmc of its monomeric counterpart, sodium lauroyl cysteine, was about 150 times higher ($\sim 3 \text{ mmol}$ determined by the fluorescence probe method). Therefore, when the disulfide bond was reduced to the thiol group, the surface properties of the aggregates would be greatly changed at the concentration range of original saturation adsorption of Gemini surfactants, although the concentration of monomeric surfactants is twice that of Gemini surfactants. Since the reaction from disulfide bond to thiol group was reversible, the reversible control of the surface properties could be achieved by the transition between Gemini surfactant and its monomeric counterpart.

Dithiothreitol was used to reduce the disulfide bond to the thiol group in SDLC and SDDC systems (Scheme 2) [32]. This thiol–disulfide exchange reaction was confirmed by the ESI-MS measurements (see Fig. S2 in Supplementary material). When DTT was added into the SDLC solution, the disulfide bond in SDLC molecule was broken, and sodium lauroyl cysteine was produced. On the other hand, when H₂O₂ was added into SLC solution, the thiol group was oxidized to the disulfide group, and SDLC was regenerated. This reversible reduction/oxidation cycle could occur several times in our experiments. Thus, the reversible control of the transition between Gemini and its monomer could be achieved.

The surface tension also displayed a reversible variation with the reduction/oxidation reaction circles. As shown in Fig. 2, when DTT was added into SDLC solution at 0.1 mmol L⁻¹ (above its cmc) to reduce SDLC to SLC, the surface tension increased quickly in 20 min, and reached the equilibrium value of 53 mN m⁻¹ in 40 min. When H₂O₂ was added into the solution at 65 min, the surface tension was decreased rapidly. The



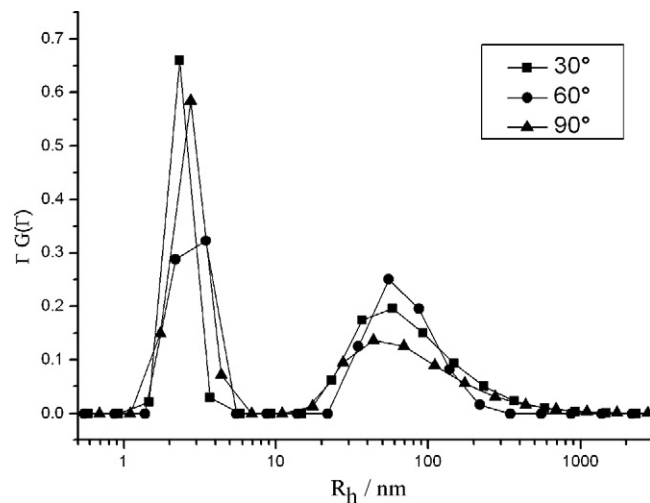
Scheme 2. The reduction/oxidation reaction of SDLC/SLC.

Fig. 3. The surface tension variation in SDDC/SDC transition ($C_{\text{SDDC}} = 1.5 \text{ mmol L}^{-1}$).

oxidation of SLC back to SDLC made the surface tension return to the original value. To further elucidate the reversible control of the surface properties in this system, a second reduction/oxidation circle was consequently performed by subsequent addition of DTT and H_2O_2 into this system, and a similar variation tendency as that of the first circle was observed. Such a variation was also found in the SDDC system (Fig. 3) with the surface tension difference of 25 mN m^{-1} . All these results demonstrate that the reduction/oxidation reactions can be used to reversibly control the surface properties of the system formed by Gemini surfactant and that formed by its monomeric counterpart.

3.2. Reversible control of aggregation behaviors in SDLC and SDDC systems

Organized assemblies in SDLC system was studied by dynamic light scattering and transmission electron microscopy. The curves obtained from the CONTIN analysis of DLS measurements at different scattering angles are shown in Fig. 4, where a well-separated bimodal distribution has been observed. Both the fast and the slow modes did not show any angular dependence (see Fig. S3a in Supplementary material). By using the Stokes–Einstein equation, the corresponding apparent hydrodynamic radius (R_h) values were calculated to be 2.4 and 56.9 nm, respectively. Considering that the molecular length of

Fig. 4. The size distribution at varying scattering angles by using the CONTIN analysis of DLS measurement on 1 mmol L^{-1} SDLC aqueous solution (pH 9.2, 40°C).

SDLC is about 2 nm, it is reasonable to assign the smaller aggregate to a spherical micelle. The obvious peak with $\langle R_h \rangle$ of 56.9 nm represented the typical size of some aggregates. TEM images demonstrated the existence of spherical vesicles with diameters of 60–240 nm in this system (Fig. 5). Combined with the fact that the apparent viscosity of the solution was nearly the same as that of water, the bigger aggregate in the DLS plot should be assigned to vesicles. Thus, it can be concluded that the micelles and vesicles are coexisting in this surfactant system.

When DTT was added into the 1 mmol L^{-1} SDLC solution, SDLC was reduced to SLC. DLS and TEM results demonstrated that no aggregates such as micelles or vesicles were existing in the resulting solution. It was reasonable because the cmc of SLC was larger than 2 mmol L^{-1} . The poor aggregation ability of SLC was understandable, since it was a surfactant with a single hydrocarbon chain. The change in the micropolarity (I_1/I_3 value of pyrene) of SDLC as a function of time is shown in Fig. 6. The increase in the micropolarity with time indicated that the aggregates in SDLC solution were being disassembled. In 80 min, the micropolarity reached the constant value of 1.64, which is close to that of water, confirming that the disassembly process is complete.

As noted above, sodium lauroyl cysteine can be oxidized to SDLC by H_2O_2 . When H_2O_2 (200 mmol L^{-1}) was added

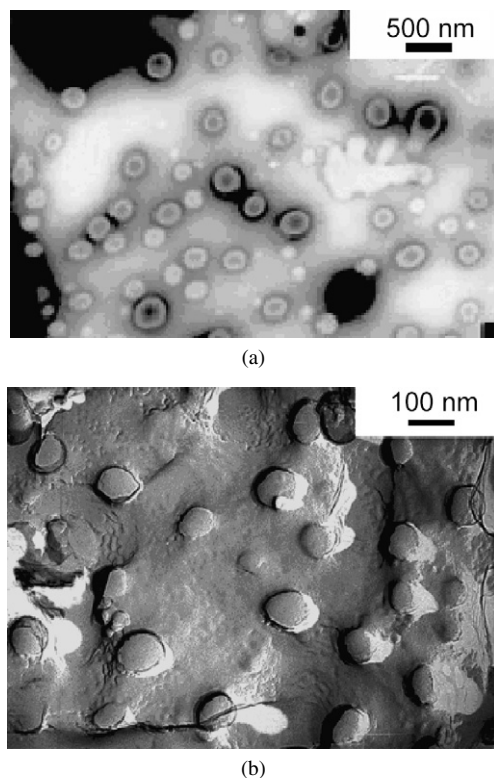


Fig. 5. Micrograph of vesicles by TEM in the SDLC system at the concentration of 1 mmol L^{-1} (pH 9.2, 40°C). (a) Negative-staining method; (b) freeze-fracture method.

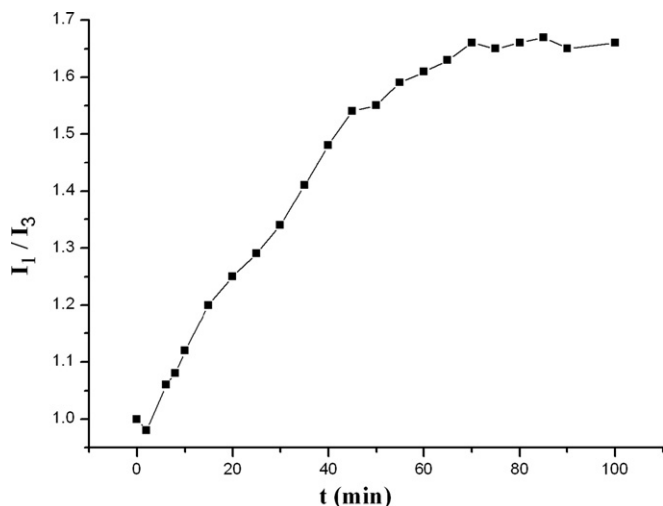


Fig. 6. The curve of micropolarity (I_1/I_3) versus time after DTT addition into the 1 mmol L^{-1} SDLC.

into the resulting SLC solution, the vesicles and micelles appeared again, as demonstrated by the results from DLS (Fig. 7 and Fig. S3 in Supplementary material) and TEM (Fig. 8). Therefore, the reversible control of the disassembly and the re-formation of aggregates of vesicles and micelles were achieved by the transition between Gemini surfactant and its monomer. Again, the reduction/oxidation circle can be carried out several times under our experimental conditions. Fig. 9 shows the TEM images of the SDLC solution after three reduction/oxidation cy-

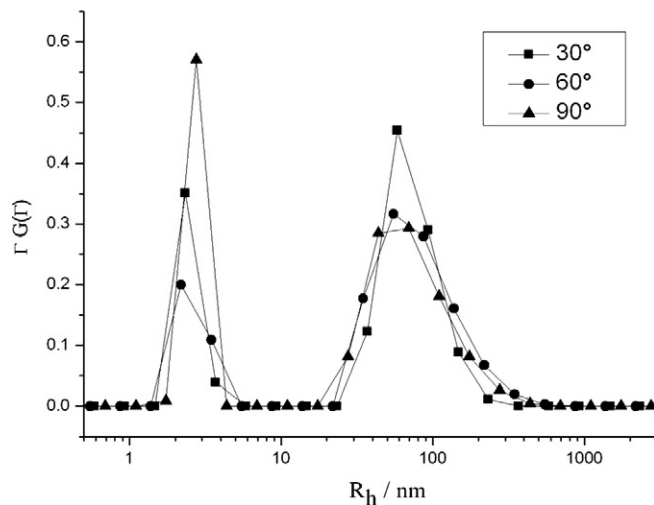


Fig. 7. The size distribution at varying scattering angles by using the CONTIN analysis of DLS measurement on 1 mmol L^{-1} SDLC aqueous solution after one reduction/oxidation cycle (pH 9.2, 40°C).

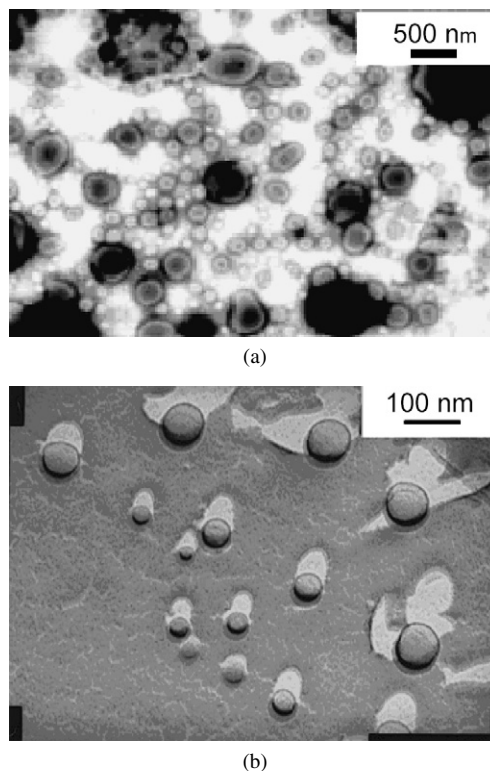


Fig. 8. Micrograph of vesicles by TEM in the SDLC system at a concentration of 1 mmol L^{-1} (pH 9.2, 40°C) after one reduction/oxidation cycle. (a) Negative-staining method; (b) freeze-fracture method.

cles, where a similar result as that in the first cycle was observed in the SDDC system.

The above results illustrated the destruction/re-formation of vesicles in this disulfide-containing Gemini surfactant. The simplicity of triggering the disassembly of vesicles via the reduction/oxidation suggested that this method could be used for target release of the encapsulated molecules of interest. The encapsulation of a water-soluble dye, riboflavin, into the vesicles was studied at 1 mmol L^{-1} SDLC. As shown in Fig. 10,

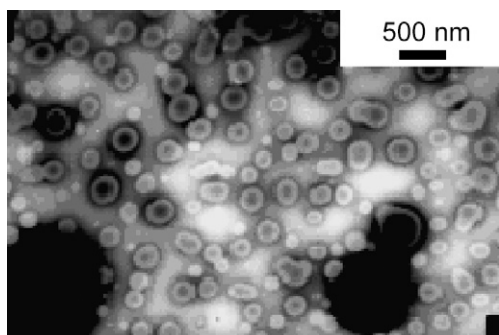


Fig. 9. The TEM result (by negative-staining method) of 1 mM SDLC solution after three reduction/oxidation cycles.

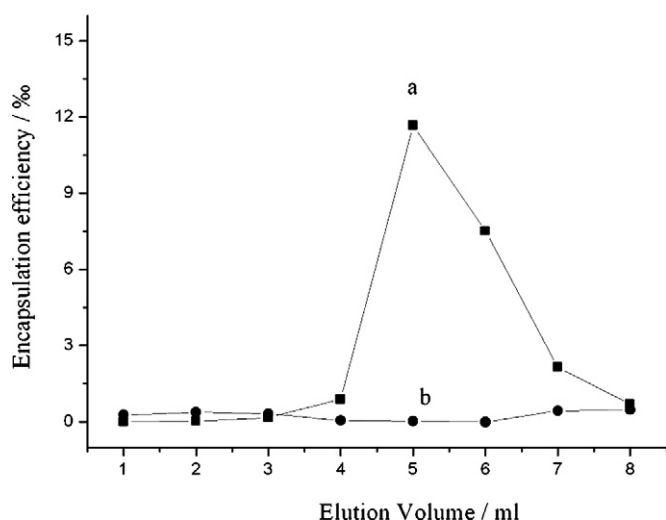


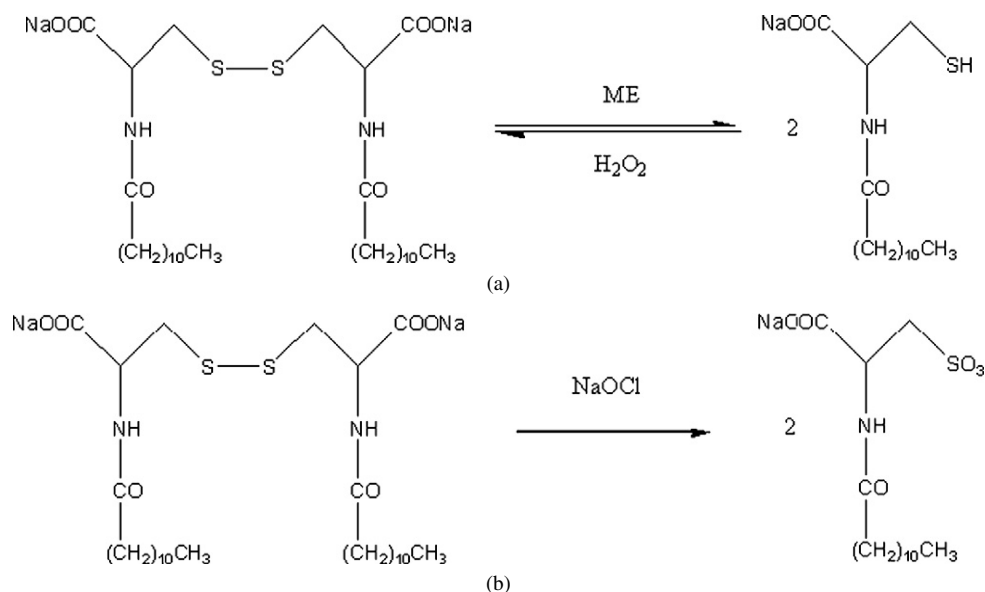
Fig. 10. The riboflavin entrapment results of 1 mM SDLC systems. (a) The riboflavin entrapment results before DTT addition, the entrapment percentage is 1.9%. (b) The riboflavin entrapment results after DTT addition, the entrapment percentage is 0%.

the vesicle peak was clearly observed in the fluorescence plots, indicating that the vesicles were separated successfully in the eluting process. The entrapment percentage was 1.9% before the addition of DTT. After the addition of DTT, the disulfide bond was reduced to a thiol group. Because of the poorer aggregation ability of SLC, the vesicles in the solution were completely destroyed, and no entrapment of riboflavin was observed.

3.3. Other methods to control the surface and bulk properties in this system

Further studies on the reaction of disulfide bond were also performed by other methods. First, thiol–disulfide exchange reaction was achieved by using mercaptoethanol as the reagent (Scheme 3a). When mercaptoethanol was added to 0.1 mmol L⁻¹ SDLC solution, the surface tension increased rapidly from 34 to 53 mN m⁻¹ (see Fig. S4a in Supplementary material), which indicated that the transition of Gemini surfactant to its corresponding monomer had occurred. Secondly, the disulfide bond can also be broken by oxidation reaction. For example, NaClO can oxidize disulfide groups to sulfonic groups (Scheme 3b). After NaClO (5 mmol L⁻¹) was added into 0.1 mmol L⁻¹ SDLC solution, no aggregate was observed in the solution according to the TEM and DLS measurements. In this process, the surface tension was increased from 34 to 60 mN m⁻¹ in 20 min (see Fig. S4b in Supplementary material). However, this process was not reversible because the reduction of the sulfonic group was very difficult under normal conditions.

Electrochemical reduction of SDDC was also studied. The ESI-MS results (see Fig. S5 in Supplementary material) revealed the transformation from Gemini surfactant to monomer. However, there was an obvious peak of SDDC in the ESI-MS spectrum, even after 24 h of electrochemical reduction. This



Scheme 3. Reaction formula of reduction SDLC by ME and NaClO.

indicated that the efficiency of electrochemical reduction was much lower than that of DTT in our system,

4. Summary

The surface properties and aggregation behavior of two Gemini surfactants containing a disulfide group in its spacer were studied. With the reversible transition between Gemini surfactant and its monomer by a reduction/oxidation reaction, the reversible control of surface-chemical properties and aggregation behaviors of surfactant solutions was achieved. We hope that this work is helpful in controlling surface properties and self-assemblies with simple and effective approaches, and provides new further understanding about the amphiphilic assemblies.

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Supplementary material

Supplementary data for this article may be found in the online version on ScienceDirect. Please visit DOI: [10.1016/j.jcis.2008.01.039](https://doi.org/10.1016/j.jcis.2008.01.039). They are the ^1H NMR spectrum of SDLC and SDDC, the ESI-MS results, the plot of the apparent hydrodynamic radius versus scattering angles, and the surface tension variety when SDLC reacts with ME or NaOCl.

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