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Synthesis and properties of novel gemini surfactant with short spacer

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Cationic gemini surfactant dimethylene-1,2-bis(dodecyldiethylammonium bromide), referred to as $C_{12}C_2C_{12}$(Et) was synthesized, and its surface property and aggregation behavior in aqueous solution were studied. The value of γ at the critical micelle concentration (γ_{cmc}) is much smaller than that of the surfactant homologues with longer spacer. Spherical and elongated micelles were formed in the aqueous solution of this gemini surfactant, and the spherical micelles were absolutely dominant compared to the elongated micelles at our studied concentration quantitatively.

gemini surfactant, synthesis, elongated micelles

As a new type of surfactants, gemini surfactants have attracted increasing attention over the last years, owing to their superior properties in comparison with those of conventional single-chain surfactants[1−4]. The most widely studied gemini surfactants are di-cationic quaternary ammonium compounds referred to as $C_MC_SC_M$ (Me), where M and S stand for the carbon atom number in the side alkyl chain and the methylene spacer, respectively[5−7]. Compared to $C_{12}C_SC_{12}$(Me), when the headgroups changed to ethyl, i.e. $C_{12}C_SC_{12}$(Et), it is found that the $C_{12}C_SC_{12}$(Et) serials (S = 4, 6, 8, 10, 12) have better aggregation capability in the aqueous solution than that of $C_{12}C_SC_{12}$(Me) serials[8]. As for gemini surfactants, the most pronounced changes in the properties were reported for rather short spacer groups[9], because the short spacer can overcome the electrical repulsion between the headgroups and make them more closer to each other. Usually, the short-spacer gemini surfactant favors the one-dimensional growth and trends to the formation of wormlike micelles[10]. However, the research on the $C_{12}C_SC_{12}$(Et) series when S = 2 is not mentioned in the published papers. While the synthesis method for $C_{12}C_2C_{12}$(Et) is different from other $C_{12}C_SC_{12}$(Et) series (S = 4, 6, 8, 10, 12), having its own difficulty and character.

In this work, dimethylene-1,2-bis(dodecyldiethylammonium bromide), referred to as $C_{12}C_2C_{12}$(Et) was synthesized. It was revealed that the $C_{12}C_2C_{12}$(Et) with short spacer was different from its homologues with long spacer.

1 Experimental and methods

1.1 Materials

1-Bromododecane, and *N*,*N*,*N*′,*N*′-tetraethylethylenediamine were purchased from Aldrich Chemical Co. and were used without further purification. Other reagents of AR grade were from Beijing Chemical Co. The water used was redistilled from the potassium permanganate containing deionized water to remove traces of organic compounds.

1.2 Methods

1.2.1 Krafft temperature. The Krafft temperature for $C_{12}C_2C_{12}$(Et) was obtained with a TU-1810 spectropho-

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tometer at 530 nm and assisting with visual observation method. The temperature was controlled by an external thermostatic bath.

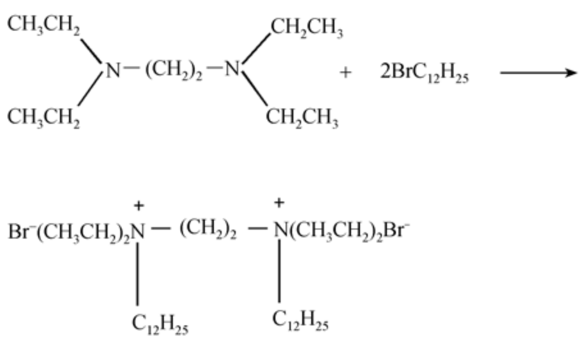
1.2.2 Surface tension. The surface tension measurement was conducted using the drop volume method at 35.00 ± 0.01℃. The critical micelle concentration (cmc) was determined from the break point of the surface tension and logarithm of concentration curve.

1.2.3 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.

2 Results and discussion

2.1 Synthesis and characterization

Cationic gemini surfactant $C_{12}C_2C_{12}$(Et) (dimethylene-1,2-bis(dodecyldiethylammonium bromide)) was synthesized as shown in Scheme 1. 16.42 g 1-bromododecane was dissolved in 25 mL acetonitrile by heating, and then it reacted with the mixture of 5.15 g *N*,*N*,*N'*,*N'*-tetraethylethylenediamine(Aldrich, 98%) and 12 mL acetonitrile under reflux (T≈80℃) for 48 h. The solvent was removed and brown solid was gained. The reaction product was recrystallized in ethanol-ethyl acetate for at least 6 times to ensure the purity of the surfactant. The purity of the surfactant was checked by ^{1}H NMR ($CDCl_3$, 400 MHz, Buker) and elemental analysis (Elementar Bario EL, Germany).



Scheme 1 Synthetic routine for the preparation of gemini $C_{12}C_2C_{12}$(Et).

The ^{1}H NMR sample of the obtained surfactant gave identical spectra, and the integrated spectra gave the expected proton contents, which indicated that the surfactant was well purified. ^{1}H NMR ($CDCl_3$, 400 MHz), δ 0.88 (t, 6H, CH_3-), 1.2-1.4 (m, 50H), 1.7 (m, 4H, N^+-$(CH_2)_{10}$-$\underline{CH_2}$-CH_3), 2.0 (m, 4H, N^+-CH_2-$\underline{CH_2}$-C), 3.6 (m, 4H, N^+-$\underline{CH_2}$-CH_2-C), 3.8 (d, 8H, $(CH_3$-$\underline{CH_2})_2N^+$), 4.4 (s, 4H, N^+-$\underline{CH_2}$-$\underline{CH_2}$-N^+). Anal. Calcd for $C_{34}H_{74}N_2Br_2$: C, 60.88; H, 11.12; N, 4.18. Found: C, 60.93; H, 10.73; N, 4.05. Other $C_{12}C_SC_{12}$(Et) series (S = 4, 6) gemini surfactants were synthesized according to our previous paper[8].

2.2 Surface and micellization

The Krafft temperature determined by UV observation and assisting with visual observation method of the aqueous solutions of $C_{12}C_2C_{12}$(Et) surfactant is about 32℃, higher than the other $C_{12}C_SC_{12}$(Et) serials (S = 4, 6, 8, 10, 12). All the reported measurements of $C_{12}C_2C_{12}$(Et) were performed at 35℃ to ensure the complete dissolution of the surfactant.

The equilibrium surface tension vs. concentration isotherm of $C_{12}C_2C_{12}$(Et) surfactant at 35℃ is presented in Figure 1. The values of the critical micelle concentration (cmc), and surface tension at the cmc (γ_{cmc}) of $C_{12}C_2C_{12}$(Et) are listed in Table 1. For the sake of comparison, the data of the $C_{12}C_4C_{12}$(Et) and $C_{12}C_6C_{12}$(Et) were also presented. First, the cmc value of $C_{12}C_2C_{12}$(Et) is much lower than the conventional cationic quaternary ammonium surfactants dodecyl triethylammonium bromide which is regarded as the monomer of the gemini

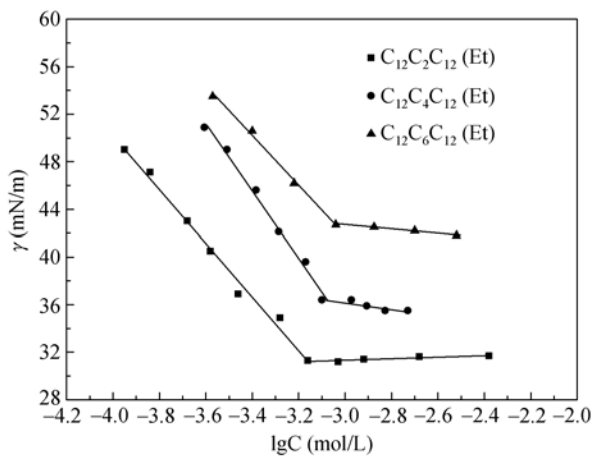


Figure 1 Variation of the surface tension with the concentration of the $C_{12}C_SC_{12}$(Et) series at 35.0℃, where S = 2, 4, 6.

Table 1 Values of the cmc and γ_{cmc} of $C_{12}C_SC_{12}$(Et) series at 35.0℃, where S = 2, 4, 6

S	2	4	6
cmc (mmol/L)	0.66	0.85	0.91
γ_{cmc} (mN/m)	31.1	36.3	42.7

(DTEAB, cmc = 1.3×10^{-2} mol/L). Then, it is worth noting that the cmcs show specific dependence on the spacer carbon number S in the range of S = 2, 4, 6. Table 1 shows for the $C_{12}C_SC_{12}$(Et) surfactants an increase of cmc upon increasing S in the range of S = 2, 4, 6, indicating that $C_{12}C_2C_{12}$(Et) has stronger aggregation capability than $C_{12}C_4C_{12}$(Et) and $C_{12}C_6C_{12}$(Et) in the aqueous solution.

It is noteworthy that the value of γ at the critical micelle concentration (γ_{cmc}) of $C_{12}C_2C_{12}$(Et) is much smaller than that of the surfactants homologues with longer spacer (Table 1). It can be attributed to that the short spacer can react against the strong electrical repulsion between the headgroups, so that the headgroups are closer to each other. Indeed, a short spacer means that the two quaternary ammonium headgroups in a gemini surfactant are separated by a fixed distance shorter than the distance resulting from thermodynamics in conventional surfactants[11]. As a result, the molecules arranged compactly on the surface, leading to positive effect on reducing surface tension.

2.3 Aggregation in aqueous solution

The molecular organized assembly formed in the aqueous solution of $C_{12}C_2C_{12}$(Et) was also studied. By TEM observation, elongated micelles with the diameter of 20—30 nm were observed in the aqueous solution of 20 mmol/L $C_{12}C_2C_{12}$(Et) (Figure 2) using freeze-fracture method, but vesicles were not found for $C_{12}C_2C_{12}$(Et). It is different from other surfactants of $C_{12}C_SC_{12}$(Et) series (S = 4, 6, 8, 10, 12) in which spherical micelles and vesicles are formed[8]. The formation of the elongated micelles can be attributed to the special molecular structure especially for short spacer of $C_{12}C_2C_{12}$(Et). The average optimal surface area occupied by a short spacer gemini surfactant at the water-micelle interface is smaller, and the spontaneous curvature is reduced and happens to be just appropriate to inducing the one-dimensional growth that leads to wormlike micelles[11]. Further investigation by dynamic light scattering measurement indicated that the elongated micelles coexisted with the spherical micelles in the aqueous solution of 20 mmol/L $C_{12}C_2C_{12}$(Et), and the spherical micelles were absolutely dominant quantitatively compared to the elongated micelles. Recently, our other results indicate that the addition of organic counter-ion will induce the transition from spherical micelles into rod-like micelles, and make the viscosity of the solution increase remarkably. Furthermore, it will bring rich phase behavior for the system of $C_{12}C_2C_{12}$(Et) with further addition of the organic counter-ion. Further studies are still going on in our laboratory.

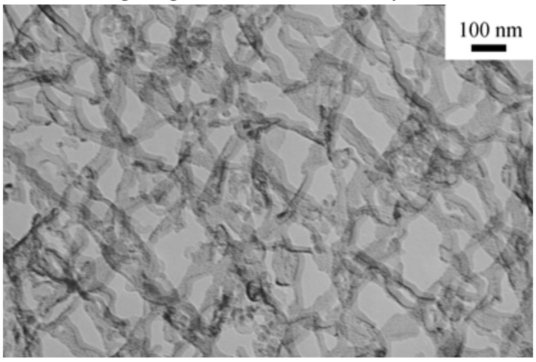


Figure 2 TEM micrograph for $C_{12}C_2C_{12}$(Et) of 20 mmol/L aqueous solution by the freeze-fracture method.

3 Conclusions

The cationic gemini surfactant $C_{12}C_2C_{12}$(Et) was synthesized. The surface tension measurement indicated that the short spacer is beneficial to reducing surface tension. Furthermore, $C_{12}C_2C_{12}$(Et) has good ability to form elongated micelle in the aqueous solution due to its special molecular structure especially for short spacer.

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