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Synthesis and surface-active property of bis-quaternary ammonium-sodium sulfate Gemini surfactant

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Abstract N,N-dimethyldodecylamine, hydrochloride and epichlorohydrin (molar ratio is 2:1:1) were used to synthesize bis-quaternary ammonium Gemini surfactant with a hydroxyl in its spacer group by the one-pot method. This hydroxyl was sulfonated by chlorosulfonic acid and then neutralized to bis-quaternary ammonium-sodium sulfate zwitterionic Gemini surfactant. The yield of the final product was 78%, and the melting point was 231–233°C. Its structure was characterized by IR, ¹H-NMR, MS, and elemental analyses. The critical micelle concentration (cmc) and surface tension of the novel zwitterionic Gemini surfactant in aqueous solution at 15°C are 7.2×10^{-5} mol/L and 34.5 mN/m, respectively.

Keywords Gemini, surfactant, synthesis, surface activity

1 Introduction

Gemini surfactant is a novel type of surfactant synthesized during the recent ten years. Its advent has greatly broadened the perspective of interface science [1–3]. Compared with the conventional surfactants, Gemini surfactants are more efficient in lowering surface tension and have much lower critical micelle concentration (cmc). Gemini surfactants, despite their recent development, are already a hot subject in colloids and surface sciences and are hoped to be one type of surfactants that will be most widely used in the twenty-first century [4–7].

In 1998, Renouf and coworkers synthesized a type of asymmetric Gemini surfactant with two different head groups [8]. Compared with the symmetric Gemini surfactants

[4] reported before, this kind of surfactant possesses many unique properties and has greatly roused the concern of chemists. However, it is difficult to synthesize asymmetric Gemini surfactants; only a few have been reported. Gemini surfactants with a special structure have always shown more satisfying properties than the symmetric ones [9–12]; hence more and more researchers are beginning to design and synthesize Gemini surfactants with unusual structures. Considering this point, we synthesized a type of bis-quaternary ammonium with a spacer group containing a hydroxyl group, and then introduced a sulfate through to the hydroxyl group. A Gemini surfactant with three hydrophilic groups and two hydrophobic chains was synthesized. Although the structure of the molecule is still symmetric, its spacer group has changed largely. The introduction of sulfate makes the molecule more hydrophilic, and results in much better surface-active properties.

2 Experimental

2.1 Materials and methods

N,N-dimethyldodecylamine (industrial reagent), chlorosulfonic acid (chemical purity), and other reagents (analysis reagent) were all purchased from commercial suppliers.

The ¹H-NMR spectra were recorded in CDCl₃ on a VX 300 MHz Spectrometer, with TMS as internal reference. FTIR spectra were taken on a Nicolet 360 FT-IR Spectrometer in KBr pellets. Elemental analyses were carried out through a Flash 1112-series Instrument. Mass spectra were obtained by ZAB-3F Spectrometer. All the melting points were determined on an electrothermal apparatus without correction.

The equilibrium surface tension was measured using a Jzhy1-180 Surface Tension Meter. All the measurements were carried out at 15°C, and redistilled water was used as solvent (conductivity: 1.07 μs/cm).

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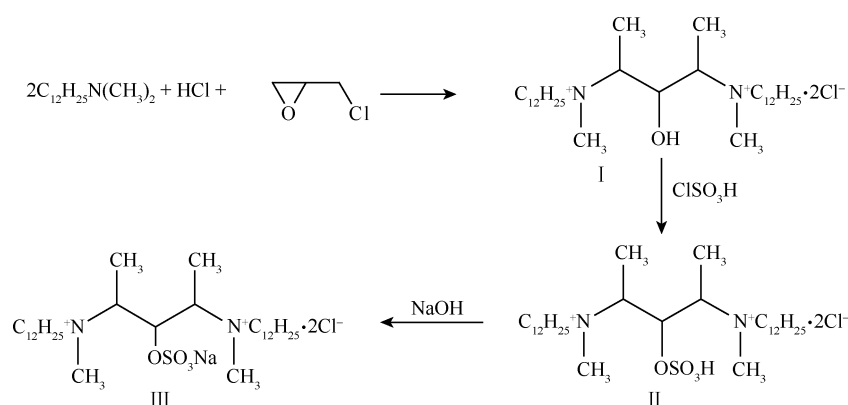


Fig. 1 Synthesis route of Gemini (III)

2.2 Synthesis method

The synthesis route of bis-quaternary ammonium-sulfate zwitterionic Gemini surfactant with three head groups is shown in Fig. 1.

2.2.1 Synthesis of bis-quaternary ammonium cationic Gemini (I)

The molar ratio of N, N-dimethyldodecylamine: hydrochloride: epichlorohydrin was 2:1:1, and the mixture was refluxed in ethanol for 12 h. The solvent was removed under reduced pressure, and then the raw material was recrystallized thrice in acetone. White solid product was collected. The yield was 72%, m.p.: 87–88°C (ref [13]: 86–87°C). The data of $^1\text{H-NMR}$ were 0.88 (t, 6H), 1.20–1.45 (m, 36H), 1.78 (m, 2H), 1.87 (m, 2H), 3.39 (s, 6H), 3.42 (s, 6H), 3.52 (t, 4H), 3.67 (t, 2H), 4.32 (d, 2H), and 5.19 (m, 1H). The result was in accordance with ref [13].

2.2.2 Synthesis of bis-quaternary ammonium-sulfate Gemini (II)

A quantity of 5.55 g (0.01 mol) Gemini (I) was resolved in 20 mL dichloromethane in a 100 mL flask equipped with a condenser and a drying tube. Then 1 mL (0.015 mol) chlorosulfonic acid dissolved in 10 mL dichloromethane was added to the solution of Gemini (I) through a tipping funnel. The mixture was stirred for 3 h at 30°C, then N_2 was added to the flask to remove HCl until plenty of precipitation appeared. The white product was collected and washed with acetone twice; the yield was 82%, m.p.: 174–176°C.

2.2.3 Synthesis of bis-quaternary ammonium-sulfate Gemini (III)

A quantity of 3 g Gemini (II) was resolved in 30 mL ethanol; then 30% NaOH aqueous solution was added until the pH

was 9–10. The mixture was refluxed for 0.5 h, then the NaCl was filtered and the ethanol was removed under reduced pressure. A quantity of 2.95 g white product zwitterionic Gemini (III) was collected, and the yield was 95%, m.p.: 231–233°C.

Note: The final product Gemini (III) could be synthesized from Gemini (I) without separation of Gemini (II). In this article, step-by-step method was used to identify the structure of the product exactly.

3 Results and discussion

3.1 Characterization of bis-quaternary ammonium-sulfate Gemini (II)

IR spectra of Gemini (I) and (II) are shown in Fig. 2. From Fig. 2 we can see that the peaks at 3,424 and 3,323 cm^{-1} in the spectra of Gemini I indicate the existence of $-\text{OH}$, but in the spectra of Gemini II, the peaks both disappeared and two strong peaks appeared at 1,222 and 1,189 cm^{-1} , which indicates the existence of $-\text{OSO}_3\text{H}$. FAB-MS: 581 ($[\text{M-HCl-OH}]^+$), 469, 270, 256. Elemental analyses (%) provided the following results: C: 58.55, H: 10.78, N: 4.41, S: 5.04; values found were C: 56.68, H: 10.55, N: 4.60, S: 5.41.

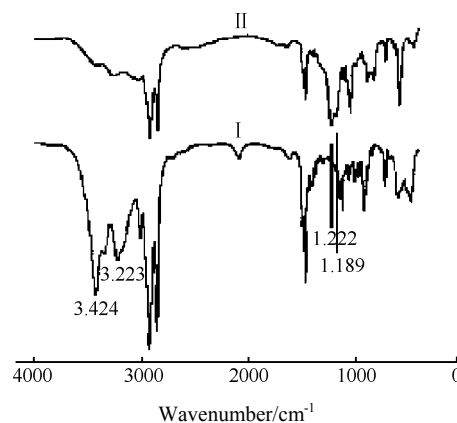
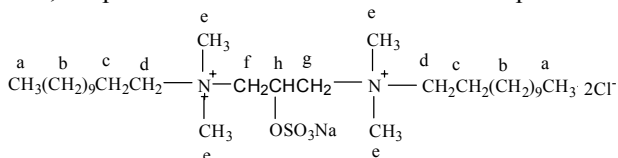


Fig. 2 IR spectra of Gemini (I) and (II)

3.2 Characterization of zwitterionic Gemini (III)

$^1\text{H-NMR}$: 0.88 (t, 6H,Ha), 1.20–1.45 (m, 36H,Hb), 1.78–1.87 (d, 4H, Hc), 3.52 (t, 4H,Hd), 3.39–3.42 (d, 12H,He), 3.76 (t, 2H,Hf), 4.34 (d, 2H,Hg), 5.35 (d, 1H,Hh). Elemental analyses (%) provided the following results: C: 56.62, H: 10.19, N: 4.26, S: 4.87; values found were C: 55.23, H: 9.86, N: 4.26, S: 4.71. The experimental results and the calculated results are in accordance with each other; hence, the product obtained is what we had anticipated.



3.3 Surface activity of synthesized products

Surface tension of Gemini surfactants I, II, and III were measured at 15°C. To compare Gemini and traditional surfactants, the surface tension of N, N-dimethylammonium chloride was also measured. The results are shown in Fig. 3.

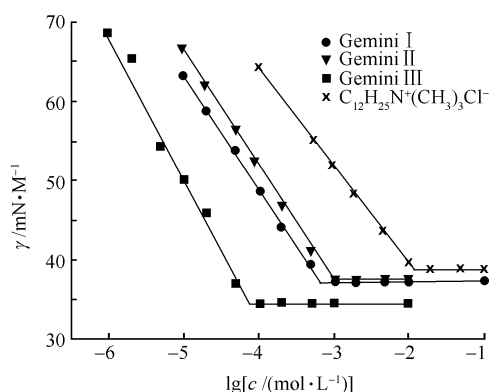


Fig. 3 The γ -lg c curve of three Geminis and a conventional surfactant

The breakpoints at the curve of the surface tension (γ)-logarithm of the concentration (lg c) were taken as cmc. Table 1 lists the cmc and the surface tension at cmc (γ_{cmc}) of different surfactants.

From Table 1, we can see that the Gemini surfactants can self-assemble at concentrations almost 100–1000 fold lower than the corresponding conventional surfactant and exhibit lower surface tension at cmc. Because of the existence of the spacer group, the Gemini surfactants show better surface activity. The spacer group connected head groups through chemical bonds; thus, the repulsion between head groups was strongly decreased. As for different Gemini surfactants, their surface activity changes largely with different spacer groups. When it comes to Gemini I, II, III, the hydroxyl on the spacer group was changed into SO_3H , and then to $-\text{OSO}_3^-\text{Na}^+$. Thus, the hydrophilic ability of the spacer becomes smaller firstly, and then becomes much stronger; meanwhile the spacer group becomes even more rigid. All

these factors result in the cmc and γ_{cmc} changing from smaller to bigger, and then becoming even lower. The excellent surface activity of Gemini III is not only due to the transformation of the spacer group but also due to the change of head groups. Because of its zwitterionic structure with three head groups, the pulling force between counter ions makes the repulsive force between the head groups strongly decrease, so the surfactants molecules are more likely to self-assemble, resulting in much higher surface activity.

Table 1 The cmc and γ_{cmc} of three Geminis and a conventional surfactant

Compounds	$c_{\text{cmc}}/\text{mol}\cdot\text{L}^{-1}$	$\gamma_{\text{cmc}}/\text{mN}\cdot\text{m}^{-1}$
$\text{C}_{12}\text{H}_{25}\text{N}^+(\text{CH}_3)_3\text{Cl}^-$	1.2×10^{-2}	39.0
Gemini I	6.9×10^{-4}	37.3
Gemini II	8.8×10^{-4}	37.9
Gemini III	7.2×10^{-5}	34.5

4 Conclusion

A new type of bis-quaternary ammonium zwitterionic Gemini surfactants with three hydrophilic head groups and two hydrophobic chains was synthesized with N,N-dimethyldodecylamine, epichlorohydrin, hydrochloric acid, chlorosulfonic acid, and sodium hydroxide as reagents. The structure was identified by IR, $^1\text{H-NMR}$, MS, and elemental analyses. The results of cmc and γ_{cmc} indicate that the product has excellent surface activity. Further researches on this kind of Gemini surfactants, especially the schemes about their high surface activity, will be helpful in understanding the relationship between the structure of Gemini surfactants and their properties.

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References

- Menger F. M., Littau C. A., Gemini surfactants: synthesis and properties, *J. Am. Chem. Soc.*, 1991, 113(4): 1451–1452
- Menger F. M., Littau C. A., Gemini surfactants: a new class of self-assembling molecules, *J. Am. Chem. Soc.*, 1993, 115: 10083–10090
- Menger F. M., Keiper J. S., Gemini surfactants, *Angew. Chem. Int. Ed.*, 2000, 39: 1906–1920
- Yao Zhigang, Li Ganzuo, Dong Fenglan, Hu Aixi, Progress in synthesis in Gemini surfactants, *Progress in Chem.*, 2004, 16(3): 349–364 (in Chinese)
- Tan Zhongliang, Han Dong, Yang Puhua, Recent development in molecular structure of Gemini surfactants, *Advances in Fine Petrochemicals*, 2003, 4(12): 20–26 (in Chinese)
- Rosen M. J., Geminis: a new generation of surfactants, *Chemtech*, 1993, 23(3): 30–32
- Zana R., Gemini (dimeric) surfactants, *Current Opinion in Colloid*

- & Interface Science, 1996, 1(5): 566–571
8. Renouf P., Mioskowski C., Lebeau L., Dimeric surfactants: first synthesis of an asymmetric Gemini compound, *Tetrahedron Lett.*, 1998, 39: 1357–1360
 9. Maja S., Ines P., Nada F., Adsorption and association in aqueous solutions of dissymmetric Gemini surfactant, *J. Colloid & Interface Sci.*, 2002, 250: 221–229
 10. Han F., Zhang G. Y., New family of Gemini surfactants with glucosamide-based trisiloxane, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 2004, 237: 79–85
 11. Tracy D. J., Li R. X., Yang J., Nonionic Gemini surfactants of aromatic compounds having three hydrophilic heads and two lipophilic tails, USP 5846926, 1998-12-08
 12. Alami E., Holmberg K., Heterogemini surfactants, *Advances in Colloid and Interface Science*, 2003, 100–102: 13–46
 13. Kim T. S., Hiral T., Ikeda I., Preparation of bis-quaternary ammonium salts from epichlorohydrin, *J. Am. Oil Chem. Soc.*, 1996, 73: 67–71