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Preparation, characterization and properties of anionic gemini surfactants with long rigid or semi-rigid spacers

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ABSTRACT

Four sulfonate-containing gemini surfactants, C_7–M_0–C_7, C_7–M_1–C_7, C_7–M_2–C_7 and C_{11}–M_1–C_{11}, with long rigid or semi-rigid spacer have been synthesized. Fully rigid spacer of C_7–M_0–C_7 is composed two rigid benzene rings and two rigid carbonyl groups. Besides the rigid moieties as C_7–M_0–C_7, the spacers of C_7–M_1–C_7, C_7–M_2–C_7 and C_{11}–M_1–C_{11} contain one or two flexible methylene units. The characterization by ^{1}H NMR, ^{13}C NMR, electrospray ionization/mass spectrometry (ESI-MS) and Fourier transform infrared (FT-IR) verified the structural characters of these new gemini surfactants. The basic surface properties of these novel gemini surfactants were investigated through measuring the relationship between the surface tension of water and the surfactant concentration, and compared with those of the conventional single-chain surfactant sodium dodecylbenzenesulfonate (SDSB). The curves of surface tension versus logarithm of concentration of C_7–M_x–C_7 surfactants were unlike the traditional plot exemplified by SDBS. Above the critical micelle concentration (cmc), the surface tension of aqueous solutions of C_7–M_x–C_7 did not become steady, but still obviously decreased with the concentration increase, which was supposed to be related with the long rigid or semi-rigid spacers. All these gemini surfactants showed lower cmc and C20 (surfactant concentration required for lowering the surface tension of water by 20 mN/m) values, but higher γ_{cmc} (surface tension at cmc) value than SDBS. The gemini surfactants with semi-rigid spacers exhibited superior surface activity to that with fully rigid spacer. The aggregation behavior of C_7–M_x–C_7 in water was investigated using dynamic light scattering (DLS) and transmission electron microscopy (TEM). It was found that the gemini surfactants with long fully rigid spacer preferred to form vesicles, whereas the ones with semi-rigid spacers self-assembled into the mixture of micelles and vesicles at low surfactant concentration and formed vesicles at high surfactant concentration.

1. Introduction

Gemini surfactant represents a new class of surfactant, which consists of two traditional surfactant units connected by a spacer unit. It has been found that gemini surfactants can exhibit superior solution properties to the traditional surfactants, such as lower critical micelle concentration (cmc), better wetting properties, lower limiting surface tensions, unusual aggregation morphologies and low Krafft point [1–3]. Therefore, vast amount of gemini surfactants have been prepared, and the relationships between structures and properties have been attempted to be illuminated [4–11]. Types of back-bones, head-groups and spacers are the main structural factors affecting the properties of gemini surfactants. The backbones of gemini surfactants are usually hydrophobic aliphatic or aromatic chains, whereas, the type of polar head-groups is versatile, such as quaternary ammonium [4,12–15], carboxylate [6,7], sulfate [16,17], sulfonate [11,18–20] and phosphate [2,21]. Among them, sulfonate group has attracted great attention since it renders the surfactant high solubility in the presence of different ions and in wide pH range, which means that sulfonate-containing surfactants can be applied in widely practical fields, such as in tertiary oil recovery and detergents [20]. Unlike the backbone and head-groups, the spacers of gemini surfactants may be hydrophobic [22,23] or hydrophilic [24,25], therefore, they can be altered in a wider range.

The influence of spacer structures on the properties of gemini surfactants have been widely studied [26–29], and it is found that the spacer plays an important role in the aggregation properties of gemini surfactants. Up to date, the ever-studied spacers might be divided into three categories. The first is the flexible spacer that might be hydrophobic saturated aliphatic chain of different length or hydrophilic polyethylene oxide chain [22–25]. This kind of spacer is employed more frequently in the syntheses of gemini surfactants. The second is rigid spacer that contains only a benzene ring or an unsaturated bond [16]. The third is semi-rigid spacer that contains both the rigid and flexible groups [10,27,30]. In the semi-rigid spacer only one benzene

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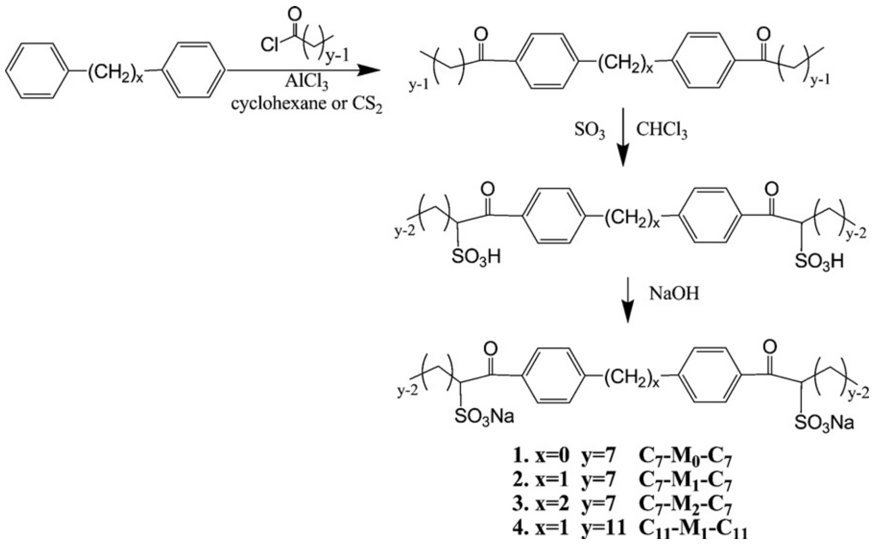

Scheme 1. The synthetic route for the novel gemini surfactants.

ring, double or triple bond has been used as the rigid group. It is clear that in the ever-reported rigid and semi-rigid spacers the rigid moiety is usually short. To our best knowledge, the physicochemical properties of gemini surfactants with long rigid moieties in spacers have never been reported. In this paper, we synthesized four sulfonate-containing gemini surfactants (C_y–M_x–C_y) as shown in Scheme 1, sodium 1,1′-(biphenyl-4,4′-diyl) bis(1-oxooctane-2-sulfonate) (C_7–M_0–C_7), sodium 1,1′-(4,4′-methylenebis(1,4-phenylene))bis(1-oxooctane-2-sulfonate) (C_7–M_1–C_7), sodium 1,1′-(4,4′-(ethane-1,2-diyl)bis(1,4-phenylene))bis(1-oxooctane-2-sulfonate) (C_7–M_2–C_7) and sodium 1,1′-(4,4′-methylenebis(1,4-phenylene))bis(1-oxododecane-2-sulfonate) (C_{11}–M_1–C_{11}). All the spacers of these gemini surfactants contained two rigid benzene rings and two rigid carbonyl groups. Moreover, with respect to the ever-reported gemini surfactants containing both sulfonate and benzene groups, sulfonate groups were usually directly connected to the aromatic ring [11,18,19,23,25], whereas, in the gemini surfactants prepared by us the sulfonate groups lie on the hydrophobic chain instead of the benzene units. The basic physicochemical properties of these novel gemini surfactants were investigated, and compared with those of the conventional sulfonate-containing surfactants.

2. Materials and methods

2.1. Materials

Biphenyl (99%), diphenylmethane (99%) and 1,2-diphenylethane (99%) were received from Alfa Aesar. Octanoyl chloride (98%) and dodecanoyl chloride (98%) were obtained from Shouguang Luyuan Salt Chemical Co., Ltd. Sulfur trioxide, cyclohexane, anhydrous aluminum chloride, aluminum trioxide, chloroform, dichloromethane, ethanol, petroleum ether, ethyl acetate and acetone were purchased from Tianjin Jiangtian Chemical Technology Co., Ltd. We note that the chemicals listed above were of analytical grade and used as received. Double-distilled de-ionized water was used in all experiments.

2.2. Syntheses of C_y–M_x–C_y

Aluminum trioxide (16.5 mmol) was dissolved in 30 mL cyclohexane. Then octanoyl chloride (15.0 mmol) was added dropwise into the mixture. After the solution was heated up to 45 °C under stirring, biphenyl, diphenylmethane or diphenylethane was added dropwise. Subsequently, this reaction was carried out for 2 h. Then the reaction mixture was decomposed using a mixture of ice, water and hydrochloric acid. The solution was filtered and the residue was washed with acetone and ethyl acetate. White crystalline product obtained here was recrystallized from petroleum ether and ethanol, respectively. The final products were purified by silica gel column. The obtained intermediate product (1.6 mmol) was dissolved in 10 mL of chloroform. Then sulfur trioxide (20 mmol) dissolved in 20 mL of chloroform was dropped into the above-mentioned mixture. The solution was heated up to 62 °C for 2 h. After the solvent was removed under reduced pressure, the residue was dissolved in acetone and neutralized with aqueous sodium hydroxide (10%). The raw products were recrystallized from ethanol. The recrystallized products were then further purified through acetone-washing. The three-step overall yields were 16.8, 31.3, 38.0 and 32.0% for C_7–M_0–C_7, C_7–M_1–C_7, C_7–M_2–C_7 and C_{11}–M_1–C_{11}, respectively. C_7–M_0–C_7, FT-IR: 1675 cm^{-1}(υ-C=O), 1603 and 1457 cm^{-1}(υ-C—H in benzene ring), 1219 and 1050 cm^{-1} (υ-S=O), 807 cm^{-1} (υ-1, 4-substituted benzene C—H out-plane bending); ^{1}H NMR (500 MHz, D_2O, δ ppm): 0.18 (br, 6H), 0.42–0.93 (br, m, 16H), 1.92–2.32 (br, 4H), 5.04 (m, 2H), 7.81 (d,4H), 8.13 (d,4H); ^{13}C NMR (125 MHz, D_2O, δ ppm): 13.40, 21.94, 27.16, 28.70, 29.38, 31.34, 65.31, 129.59, 129.92,136.87, 143.99, 197.06; MS (ESI) *m/z*: (M–Na), 587.12 (Calcd. 587.70). C_7–M_1–C_7, FT-IR: 1674 cm^{-1} (υ-C=O), 1603 and 1457 cm^{-1} (υ-C—H in benzene ring), 1226 and 1071 cm^{-1} (υ-S=O), 789 cm^{-1} (υ-1, 4-substituted benzene C—H out-plane bending); ^{1}H NMR (500 MHz, D_2O, δ ppm): 0.24 (br, 6H), 0.53–0.91 (br, 16H), 1.90–2.15 (br, 4H), 4.05 (s, 2H), 4.93 (br, 2H), 7.49 (d,4H), 7.95 (d,4H); ^{13}C NMR (125 MHz, D_2O, δ ppm): 13.44, 21.96, 27.14, 28.61, 29.23, 31.24, 41.71, 65.21, 129.68, 136.47, 147.42, 197.01; MS (ESI) *m/z*: (M–Na), 601.18 (Calcd. 601.72). C_7–M_2–C_7, FT-IR: 1674.35 cm^{-1} (υ-C=O), 1605 and 1457 cm^{-1} (υ-C—H in benzene ring), 1226 and 1071 cm^{-1} (υ-S=O), 782 cm^{-1} (υ-1, 4-substituted benzene C—H out-plane bending); ^{1}H NMR (500 MHz, D_2O, δ ppm): 0.32(br, 6H), 0.55–0.97(br, 16H), 1.89–2.30 (br,4H), 2.90 (s,4H), 4.90 (br, 2H), 7.36 (d,4H), 7.98 (d,4H); ^{13}C NMR (125 MHz, D_2O, δ ppm): 13.49, 21.96, 27.12, 28.63, 29.38, 31.36, 36.90, 65.14, 129.17, 129.40, 136.44, 148.56, 197.28; MS (ESI) *m/z*: (M–Na), 615.22 (Calcd. 615.74). C_{11}–M_1–C_{11}, FT-IR: 1674 cm^{-1}(υ-C=O), 1603 and 1457 cm^{-1}(υ-C—H in benzene ring), 1226 and 1071 cm^{-1} (υ-S=O), 789 cm^{-1}(υ-1, 4-substituted benzene C—H out-plane bending); ^{1}H NMR (500 MHz, D_2O, δ ppm): 0.51 (br, 6H), 0.53–1.50 (br, 32H), 2.04–2.27 (br, 4H), 4.04 (s, 2H), 5.01 (br, 2H), 7.41 (br, 4H), 8.00 (br, 4H); ^{13}C NMR (125 MHz, D_2O, δ ppm):