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Synthesis and surface activities of a novel di-hydroxyl-sulfate-betaine-type zwitterionic gemini surfactants

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ABSTRACT

A series of novel di-hydroxyl-sulfate-betaine-type zwitterionic gemini surfactants of 1,2-bis[*N*-ethyl-*N*-(2-hydroxyl-3-sulfopropyl)-alkylammonium] alkyl betaines (DBA_{s-n}, where *s* and *n* represent the spacer length of 2, 4 and 6 and the hydrocarbon chain length of 8, 12, 14, 16 and 18, respectively) were synthesized by reacting alkylamine with sodium 3-chloro-2-hydroxypropanesulfonate (the alternative sulphonated agent), followed by the reactions with a,ω-dibromoalkyl and then ethyl bromide. Their adsorption and aggregation properties were investigated by means of equilibrium surface tension, dynamic light-scattering (DLS) and transmission electron microscopy (TEM). DBA_{s-n} gemini surfactants showed excellent surface activities and packed tightly at the interface. For example, the minimum CMC value for DBA_{s-n} series was of the order of 10^{-5} M and the surface tension of water can be decreased as low as 22.2 mN/m. It was also found that the aggregates of DBA_{s-n} solutions were significantly dependent on their hydrocarbon chain lengths. The aggregates changed from vesicles to entangled fiber-like micelles as the chain length increased from dodecyl to tetradecyl.

1. Introduction

Gemini surfactants that contain two hydrophobic chains and two hydrophilic groups in a molecule can be described as an equimolar combination of two single-chain surfactants which are chemically bonded together by a spacer at or near their headgroups [1]. Such unique structure makes gemini surfactants exhibit superior surface-activities in comparison with conventional monomer surfactants such as remarkably low critical micelle concentration (CMC), high capability in reducing the surface tension of water, good water solubility, abnormal micelle aggregate formation at concentrations below the CMC, unique rheological properties and low krafft point. Because of these excellent properties, gemini surfactants have been continuously gaining widespread interest in the scientific community and for various applications [2–4].

The zwitterionic surfactants incorporating both negative and positive charges in the molecular exhibit pH-dependent behavior and are less irritating to skin and eyes than anionic and cationic surfactants [5]. However, there have been few reports on zwitterionic gemini surfactants until recently, and most of the work are concerned on zwitterionic gemini surfactants possessing nonidentical hydrophilic headgroups such as ammonium-phosphodiester [6–8] and sulfate-polyoxyethylene [9–11]. Only a few reports are available with regard to the ones which incorporate two identical zwitterionic headgroups in a molecular such as pair betaines or pair sulfobetaines [12]. Yoshimura and Ichinokawa [13] synthesized sulfobetaine-type zwitterionic gemini surfactants $2C_nSb$. Such surfactants exhibited unusual physicochemical properties. However, 1,3-propanesultone, which was used in his paper for sulfonating, is relatively unavailable and hazardous to the health. So it is of great scientific and industrial importance to design and synthesize such pair sulfobetaines zwtterionic surfactants with an alternative of 1,3-propanesultone and investigate their properties.

In this work, using the sodium 3-chloro-2-hydroxypropanesulfonate as the alternative sulphonated agent, a series of novel di-hydroxyl-sulfate-betaine-type zwitterionic gemini surfactants were synthesized and designated as DBA_{s-n}. To study their adsorption and aggregation properties at the air/water interface and in the bulk solution, we performed measurements of equilibrium surface tension, dynamic light-scattering (DLS) and transmission electron microscopy (TEM). In this study we also discussed the effects of the hydrocarbon chain length, spacer chain length as well as the surfactant concentration on their adsorption and aggregation behavior. Scheme 1 shows the synthesis route of the novel DBA_{s-n} zwitterionic gemini surfactants.

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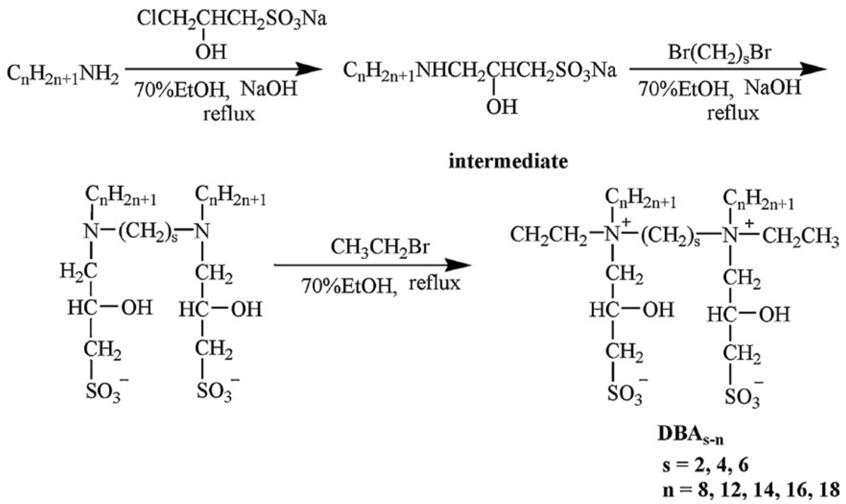

Scheme 1.

2. Experimental methods

2.1. Materials

N-octylamine (99%), *n*-dodecylamine (98%), *n*-tetradecylamine (96%), *n*-hexadecylamine (90%), *n*-octadecylamine (90%), 1,2-dibromoethane (99%), 1,4-dibromobutane (99%) and 1,6-dibromohexane (97%) were purchased from Aladdin Co. (Shanghai, China) and used without further purification. All organic solvents (Chemical Pure) were purchased from KeLong Co. (Chengdu, China). Sodium 3-chloro-2-hydroxypropanesulfonate was prepared in the same manner as the literature [12].

2.2. Synthesis

2.2.1. Synthesis of sodium 2-hydroxy-3-sulfopropylalkylamine (intermediate) [14]

Sodium 3-chloro-2-hydroxypropanesulfonate (4.90 g, 0.025 mol) was dropped into a stirred solution of alkylamine (3.23–6.90 g, 0.02 mol) [alkyl = octyl (*n* = 8), dodecyl (*n* = 12), tetradecyl (*n* = 14), hexadecyl (*n* = 16), octadecyl (*n* = 18)] in 100 mL 70 wt% ethanol aqueous. The mixture was refluxed for 13–16 h under an alkaline condition by adding Na_2CO_3. Then the hot mixture was filtered to remove the insoluble inorganic salt formed. After the filtrate was cooled to room temperature, the precipitation obtained was collected by filtration, washed three times with benzene to remove the unreacted alkylamine, recrystallized twice from 250 mL 70 wt% ethanol aqueous at room temperature, and dried under reduced pressure to give sodium 2-hydroxy-3-sulfopropylalkylamine as white powder. The yields were 49.0, 40.0, 45.1, 43.2 and 38.7% for *n* = 8, 12, 14, 16 and 18, respectively. IR (Paragon 1000, Germany, KBr), ν, cm^{-1}, 3438–3479 (O—H stretching), 3292–3367 (N—H stretching), 2923–2925, 2850–2854 (C—H stretching), 1465–1469 (—CH_2 bending in-plane), 1380–1419 (—CH_3 bending in-plane), 1190–1214 (C—N stretching), 1157–1197 (S=O asymmetrical stretching), 1091–1093 (S=O symmetric stretching), 1041–1052 (C—O stretching), 719–725 ($(CH_2)_{n\geq 4}$ rocking), 613–630 (S—O stretching) [15,16]. HRMS (ESI, Agilent 6224 TOFLC/MS) *m*/*z*: Calcd for $C_{11}H_{25}NO_4S$ (M+H) 268.1538, found 268.1578; Calcd for $C_{15}H_{33}NO_4S$ (M+H) 324.2164, found 324.2206; Calcd for $C_{17}H_{3}7NO_4S$ (M+H) 352.2477, found 352.2524; Calcd for $C_{19}H_{41}NO_4S$ (M+H) 380.2790, found 380.2834; Calcd for $C_{21}H_{45}NO_4S$ (M+H) 408.3103, found 408.3148. ^1H NMR (Bruker, AM-300, 300 MHz, D_2O, TMS): δ 0.765–0.796 (t, 3H, $\boldsymbol{CH_3}CH_2$), 1.19–1.22 [m, (2*n* – 6)H, $CH_3(\boldsymbol{CH_2})_{n-3}CH_2$], 1.40–1.41 [m, 2H, $(CH_2)_{n-3}\boldsymbol{CH_2}CH_2NH$], 2.51–2.64 [m, 2H, $(CH_2)_{n-3}CH_2\boldsymbol{CH_2}NH$], 2.82–2.93 [m, 2H, $NH\boldsymbol{CH_2}CH(OH)CH_2SO_3^-$], 2.94–3.06 [m, 2H, $NHCH_2CH(OH)\boldsymbol{CH_2}SO_3^-$], 4.07–4.12 [m, 1H, $NHCH_2\boldsymbol{CH}(OH)CH_2SO_3^-$], 4.70 (s, DOH).

2.2.2. Synthesis of 1,2-bis[N-ethyl-N-(sodium 2-hydroxyl-3-sulfopropyl)-alkyl-ammonium] ethane betaine (DBA_{2-n})

A 1.5-fold molar excess of 1,2-dibromoethane (1.40 g, 0.0075 mol) was added to a stirred solution of intermediate (2.90–3.00 g, 0.01 mol) in 150 mL 70 wt% ethanol aqueous. The mixture was refluxed for 48–60 h under an alkaline condition by adding Na_2CO_3, and then 3-fold molar excess of ethyl bromide (1.63 g, 0.015 mol) was added to the mixture and refluxed again for another 48 h. The hot mixture was filtered to remove the insoluble inorganic salt formed. The crude product precipitated from the filtrate at 0 °C after standing for 10–12 h. The precipitation was collected by filtration, washed three times with acetone or diethyl ether, recrystallized three times from 250 mL mixture of methanol and acetone (V:V = 1:5) at room temperature, and dried under reduced pressure to give 1,2-bis[*N*-ethyl-*N*-(sodium 2-hydroxyl-3-sulfopropyl)-alkylammonium] ethane betaine (DBA_{2-n}) as white powder. The yields were 45.6, 41.0, 39.2, 40.3 and 34.7% for *n* = 8, 12, 14, 16 and 18, respectively. IR (KBr), ν, cm^{-1}, 3365–3469 (O—H stretching), 2917–2925, 2850–2854 (C—H stretching), 1454–1469 (—CH_2 bending in-plane), 1380–1047 (—CH_3 bending in-plane), 1199–1204 (C—N stretching), 1176–1199 (S=O asymmetrical stretching), 1091–1095 (S=O symmetric stretching), 1045–1056 (C—O stretching), 719–723 ($(CH_2)_{n\geq 4}$ rocking), 622–632 (S—O stretching). HRMS (ESI): Calcd for $C_{28}H_{62}N_2O_8S_2/2$ (M−2Br+2H)/2 309.1991, found 309.1939; Calcd for $C_{36}H_{78}N_2O_8S_2/2$ (M−2Br+2H)/2 365.5716, found 365.5746; Calcd for $C_{40}H_{86}N_2O_8S_2/2$ (M−2Br+2H)/2 393.6247, found 393.6079; Calcd for $C_{44}H_{94}N_2O_8S_2/2$ (M−2Br+2H)/2 421.6779, found 421.6723; Calcd for $C_{48}H_{102}N_2O_8S_2/2$ (M−2Br+2H)/2 449.7311, found 449.7697. ^1H NMR (CD_3Cl, TMS) for DBA_{2-14}: δ 0.883 [t, 6H, $2\boldsymbol{CH_3}(CH_2)_{n-3}$], 1.27 [m, (4*n* – 12)H, $2CH_3(\boldsymbol{CH_2})_{n-3}CH_2$], 1.56–1.62 (t, 6H, $2\boldsymbol{CH_3}CH_2N^+$), 1.78 [m, 4H, $2(CH_2)_{n-3}\boldsymbol{CH_2}CH_2N^+$], 3.06 [d, 4H, $2N^+CH_2CH(OH)\boldsymbol{CH_2}SO_3^-$], 3.21 (m, 4H, $2CH_3\boldsymbol{CH_2}N^+$), 3.29 [t, 4H, $2(CH_2)_{n-3}CH_2\boldsymbol{CH_2}N^+$], 3.60 [d, 4H, $2N^+\boldsymbol{CH_2}CH(OH)CH_2SO_3^-$], 3.75 (t, 4H, $N^+\boldsymbol{CH_2CH_2}N^+$), 4.62 [m, 2H, $2N^+CH_2\boldsymbol{CH}(OH)CH_2SO_3^-$], 8.10–8.29 [d, 2H, $2NHCH_2CH(\boldsymbol{OH})CH_2SO_3^-$].