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Synthesis and properties of novel ester-containing gemini imidazolium surfactants

Ling-Hua Zhuang [a], Kai-Hua Yu [a], Guo-Wei Wang [b], Cheng Yao [a,*]

[a] Department of Applied Chemistry, College of Science, Nanjing University of Technology, Nanjing 211816, PR China
[b] Department of Light Chemical Engineering, College of Food Science and Light Industry, Nanjing University of Technology, Nanjing 211816, PR China

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ABSTRACT

Novel ester-containing gemini imidazolium surfactants were synthesized from various aliphatic acids (C_{12}, C_{14}, C_{16}), 1-methylimidazol, and 2,2-bis (bromomethyl)-1,3-propanediol with a two step reaction. The surfactants are abbreviated as $[C_n\text{im}]_2$ (n = 12, 14, 16). The chemical structures of the prepared compounds were confirmed by ^{1}H NMR, IR spectra, and elemental analysis. Thermal properties of these new surfactants were studied with thermogravimetry (TG) and differential scanning calorimetry (DSC). Their critical micelle concentrations (cmc) in the aqueous solutions were determined by surface tension and electrical conductivity methods. Surface tension parameters including Γ_{cmc}, A_{min}, and γ_{cmc} were obtained. The parameters β (degree of counterion binding to micelles), ΔG^0_{ads} (Gibbs free energy of adsorption), and ΔG^0_{mic} (Gibbs free energy change of micellization) were also derived. The results indicated that these novel gemini surfactants exhibited very low cmcs and a good efficiency in lowering the surface tension of water. Dynamic light scattering (DLS) measurements showed that $[C_{12}\text{im}]_2$ and $[C_{14}\text{im}]_2$ can easily form vesicles at very low concentration, and that the self-assembly of $[C_{14}\text{im}]_2$ is more well-organized than for $[C_{12}\text{im}]_2$. The use of DOSY and DLS as a complementary technique shows that a dynamic micelle-vesicle equilibrium exists in solution.

1. Introduction

Gemini surfactants, which have two hydrophobic tails and two hydrophilic head groups connected by a spacer unit, have attracted considerable attention [1] since the creation of the term by Menger et al. [2]. In comparison with corresponding conventional surfactants, gemini surfactants exhibit superior properties, such as significantly lower critical micelle concentration (cmc), lower surface tension at cmc, unusual aggregation morphologies, and viscosity behavior [3,4]. Therefore, many gemini surfactants have been prepared, and the relationships between structures and properties have been attempted to be illuminated. The mostly widely studied gemini surfactants are dicationic quaternary ammonium compounds. Studies had shown that the variation of the spacer, the tail alkyl chain, and the structure of hydrophilic head group usually affects the aggregation behavior of gemini surfactants [5–8].

In recent years, several new categories of gemini cationic surfactant have been developed and investigated, such as pyridinium [9,10], imidazolium [11–16], and pyrrolidinium [17]. Currently, imidazolium ionic liquids have been widely studied because of their inherent nature and potential applications [18–20]. This fact has attracted surfactant chemists to design and synthesize imidazolium surfactants. Surfactants with imidazolium cations combine the properties of surfactant with those of imidazolium which demonstrates a stronger tendency toward self-aggregation owing to the distinct polarizability of imidazolium head group [11,14]. Therefore, it is significant to study the properties of imidazolium type gemini surfactants.

On the other hand, the majority of the surfactants is discharged after use into industrial effluents and/or sewage and may ultimately reach rivers, lakes, and oceans. Surfactant chemists should pay much attention to the development of biodegradable gemini surfactants for preserving the environment. Cationic surfactants in general have higher aquatic toxicity than anionic and nonionic surfactants, so various approaches are taken to circumvent this problem. One approach is to introduce an easily cleavable bond into the surfactant structure. Many investigations showed ester-containing gemini-type surfactants have good biodegradability [21–26].

Based on the above considerations, we designed and synthesized a new type of cationic gemini surfactant containing diester and bisimidazolium, 2,2-bis (alkanoyloxymethyl)-1,3-bis (3-methylimidazolium)-propane dibromide. In this paper, we report the synthesis, surface activity, and aggregation behavior of these new gemini surfactants.

* Corresponding author.
E-mail address: yaochengnjut@126.com (C. Yao).

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2. Materials and methods

2.1. Materials

2,2-Bis (bromomethyl)-1,3-propanediol was purchased from Leadsh Chemical Co. Ltd., China. Dodecanoic acid (AR), tetradecanoic acid (AR), hexadecanoic acid (AR), and N-methylimidazole (AR) were purchased from Aladdin reagent Co. Ltd., China. These chemicals were used as received. Other chemicals used were of analytical reagent grade. Water used in this work was bisdistilled water.

2.2. Synthesis

Novel gemini surfactants were synthesized by two steps reaction, as shown in Scheme 1.

2.2.1. Synthesis of intermediate diester (compounds 1–3)

2,2-Bis (bromomethyl)-1,3-propanediol (10 mmol) and a catalytic amount of p-TsOH monohydrate (5%w/w relative to the aliphatic acid) were added to a solution of aliphatic acid (22 mmol) in 25 mL toluene. The mixture was heated to reflux. The water formed was removed by reactive distillation and collected in a Dean–Stark trap. The reaction was stopped until no water was generated. After the solvent had evaporated under reduced pressure, methanol (20 mL) was added to the mixture. The white solid product obtained was recrystallized twice from methanol and ethyl acetate. Micro-melting point apparatus X-4 (Shanghai Precision & Scientific Instrument Co. Ltd., China) was used to measure the melting point. NMR Spectrometer (Avance 500, Bruker Corp., Germany), element analyzer (Flash EA-1112A, Thermo Finhigan, Italy), and FTIR-Spectrometer (TENSOR 27, Bruker Corp., Germany) were used to identify the structure of the compounds.

2,2-Bis (dodecanoyloxymethyl)-1,3-dibromopropane (***1***): white solid, yield 87%. mp. 30–32 °C, ^{1}H NMR (500 MHz, DMSO, δ ppm): 0.79–0.85 (t, 6H, 2**CH$_3$**CH$_2$), 1.19–1.24 (m, 32H, 2CH$_3$ **(CH$_2$)$_8$**CH$_2$), 1.51 (m, 4H, 2CH$_3$ (CH$_2$)$_8$**CH$_2$** CH$_2$), 2.21–2.33 (t, 4H, 2**CH$_2$**COO), 3.49–3.59 (s, 4H, 2Br**CH$_2$**), 4.05 (s, 4H, 2COO**CH$_2$**).

2,2-Bis (tetradecanoyloxymethyl)-1,3-dibromopropane (***2***): white solid, yield 89%, mp. 41–43 °C, ^{1}H NMR (300 MHz, CDCl$_3$, δppm): 0.85–0.90 (t, 6H, 2**CH$_3$**CH$_2$), 1.26 (m, 40H, 2CH$_3$ (CH$_2$)$_{10}$-**CH$_2$**), 1.57–1.64 (m, 4H, 2CH$_3$ (CH$_2$)$_{10}$**CH$_2$** CH$_2$), 2.30–2.35 (t, 4H, 2**CH$_2$**COO), 3.50 (s, 4H, 2Br**CH$_2$**), 4.15 (s, 4H, 2COO**CH$_2$**).

2,2-Bis (hexadecanoyloxymethyl)-1,3-dibromopropane (***3***): white solid, yield 73%, mp. 49–50 °C, ^{1}H NMR (500 MHz, CDCl$_3$, δppm): 0.86–0.89 (t, 6H, 2**CH$_3$**CH$_2$), 1.25–1.29 (m, 48H, 2CH$_3$ **(CH$_2$)$_{12}$**CH$_2$), 1.60–1.63 (m, 4H, 2CH$_3$ (CH$_2$)$_{12}$**CH$_2$** CH$_2$), 2.31–2.34 (t, 4H, 2**CH$_2$**COO), 3.50 (s, 4H, 2Br**CH$_2$**), 4.15 (s, 4H, 2COO**CH$_2$**).

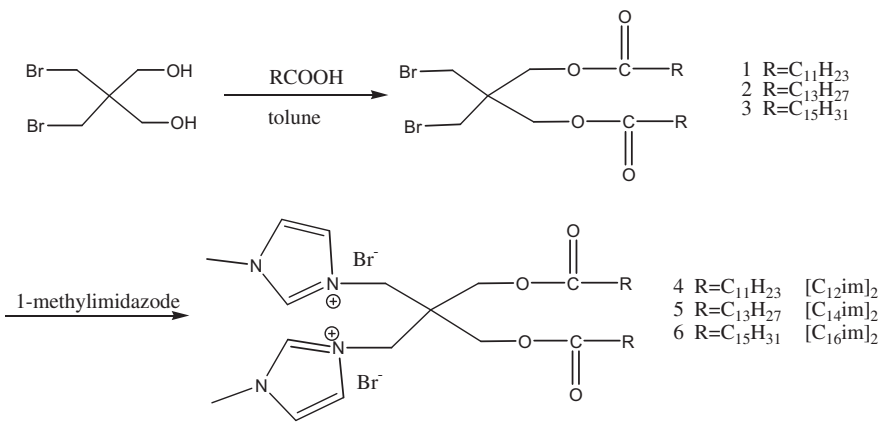
2.2.2. Synthesis of gemini surfactants (compounds 4–6)

The intermediate diester (5 mmol) was added to N-methylimidazole (7 ml). The mixture was stirred at 150 °C for 5 h. After cooling, the solution was filtered and the raw solid product was obtained. Raw solid product was recrystallized twice from chloroform and ether.

2,2-Bis (dodecanoyloxymethyl)-1,3-bis (3-methylimidazolium)-propane dibromide (**4, denoted as [C$_{12}$im]$_2$**): white solid, yield 65%, mp. 171–173 °C, ^{1}H NMR (500 MHz, CDCl$_3$, δppm): 0.86–0.89 (t, 6H, 2**CH$_3$**CH$_2$), 1.26 (m, 32H, 2CH$_3$**(CH$_2$)$_8$**CH$_2$), 1.57 (m, 4H, 2CH$_3$(CH$_2$)$_8$**CH$_2$** CH$_2$), 2.39–2.42 (t, 4H, 2**CH$_2$**COO), 4.06 (s, 6H, 2**CH$_3$**N),4.35 (s, 4H, 2COO**CH$_2$**), 5.09 (s, 4H, 2**CH$_2$**N$^+$), 7.39 (s, 2H, 2—**CH**=CH—N$^+$), 7.83 (s, 2H, 2—CH=**CH**—N$^+$), 10.04 (s, 2H, 2N—**CH**=N$^+$). IR (KBr): 3146.3, 3091.5, 3056.0 (ν = C—H), 2918.0, 2850.6 cm^{-1} (ν C—H), 1743.7 (ν C=O), 1625.1 (ν C—N), 1574.5, 1563.9 (ν C=N and C=C), 1467.7, 1378.3 (δ C—H), 1174.5, 1109.8 (ν C—O—C), 721.0CH$_2$ ($n \geqslant 4$) cm^{-1}. Elemental analysis: calculated (%): C 56.20, H 8.42, N 7.09; found (%):C 56.45, H 8.71, N 7.16.

2,2-Bis (tetradecanoyloxymethyl)-1,3-bis (3-methylimidazolium)-propane dibromide (**5, denoted as [C$_{14}$im]$_2$**): white solid, yield 76%, mp. 171–173 °C, ^{1}H NMR (300 MHz, CDCl$_3$, δppm): 0.90–0.93 (t, 6H, 2**CH$_3$**CH$_2$), 1.29 (m, 40H, 2CH$_3$**(CH$_2$)$_{10}$**CH$_2$), 1.57–1.59 (m, 4H, 2CH$_3$(CH$_2$)$_{10}$**CH$_2$** CH$_2$), 2.41–2.46 (t, 4H,2**CH$_2$**-COO), 4.11 (s, 6H,2**CH$_3$**N),4.38 (s, 4H, 2COO**CH$_2$**), 5.10 (s, 4H, 2**CH$_2$**N$^+$), 7.51 (s, 2H, 2—**CH**=CH—N$^+$), 7.90 (s, 2H, 2—CH=**CH**—N$^+$), 10.01 (s, 2H, 2N—**CH**=N$^+$). IR (KBr): 3146.0, 3091.3, 3055.4 (ν = C—H), 2917.6, 2849.9 cm^{-1} (ν C—H), 1745.9 (ν C=O), 1623.6 (ν C—N), 1574.5, 1563.5 (ν C=N and C=C), 1468.4, 1380.6 (δ C—H), 1174.6, 1108.5 (ν C—O—C), 720.7CH$_2$ ($n \geqslant 4$) cm^{-1}. Elemental analysis: calculated (%): C 58.15, H 8.81, N 6.62; found (%):C 58.42, H 8.95, N 6.53.

2,2-Bis (hexadecanoyloxymethyl)-1,3-bis (3-methylimidazolium)-propane dibromide (**6, denoted as [C$_{16}$im]$_2$**): white solid, yield 91%, mp. 170–172 °C, ^{1}H NMR (500 MHz, CDCl$_3$, δppm): 0.87–0.89 (t, 6H, 2**CH$_3$**CH$_2$), 1.25 (m, 48H, 2CH$_3$**(CH$_2$)$_{12}$**CH$_2$), 1.57–1.59 (m, 4H, 2CH$_3$(CH$_2$)$_{12}$**CH$_2$** CH$_2$), 2.41–2.44 (t, 4H, 2**CH$_2$**-COO), 4.04 (s, 6H, 2**CH$_3$**N), 4.34 (s, 4H, 2COO**CH$_2$**), 5.12 (s, 4H, 2**CH$_2$**N$^+$), 7.31 (s, 2H, 2—**CH**=CH—N$^+$), 7.79 (s, 2H, 2—CH=**CH**—N$^+$), 10.12 (s, 2H, 2N—**CH**=N$^+$). IR (KBr): 3145.9, 3091.4, 3055.2 (ν = C—H), 2916.5, 2850.1 cm^{-1} (ν C—H), 1745.5 (ν C=O), 1623.0 (ν C—N), 1573.4, 1559.8 (ν C=N and C=C), 1467.4, 1378.3 (δ C—H), 1174.9, 1110.0 (ν C—O—C), 720.4CH$_2$ ($n \geqslant 4$) cm^{-1}. Elemental analysis: calculated (%): C 59.85, H 9.15, N 6.20; found (%): C 59.93, H 9.45, N 6.02.



Scheme 1. Synthesis of ester-containing gemini imidazolium surfactants.