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Synthesis and physicochemical properties of star-like cationic trimeric surfactants

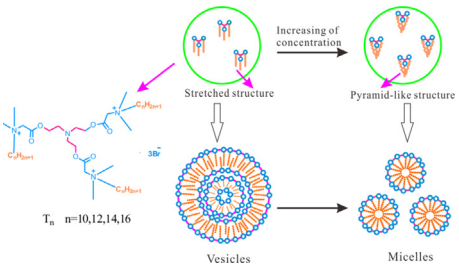
Xue-Guo Liu[a,b], Xiao-Jing Xing[b], Zhi-Nong Gao[a,b,*]

[a] Key Laboratory of Biomedical Polymers (Ministry of Education of China), Wuhan 430072, Hubei, PR China
[b] College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, Hubei, PR China

HIGHLIGHTS

- Efficient synthesis of four star-like cationic trimeric surfactants has been achieved.
- Systemic surface-active properties were investigated.
- Aggregations change from vesicles to micelles with increasing surfactant concentrations.

GRAPHICAL ABSTRACT



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ABSTRACT

Efficient synthesis of four star-like triethanolamine based cationic trimeric surfactants T_n (where n is the tail chain length, n = 10, 12, 14, and 16) with ester groups in spacers has been successfully achieved, where mild reaction conditions were employed by substituting triethylamine (TEA) with potassium carbonate as the acid binding agent. The physicochemical properties of these surfactants were investigated by means of surface tension, electrical conductivity, and steady-state fluorescence measurements. The trimeric surfactants have been found to be capable of adsorbing to the air/water interface and orienting themselves through the interactions among the hydrocarbon chains. The conductivity measurement revealed the formation of premicellar aggregations in the T_{16} solution. It is noteworthy that the micropolarity of the surfactant aggregations decreased with the elongation of the hydrophobic chain length. Typically, dynamic light scattering and transmission electron microscopy studies showed that the aggregations of the four surfactants changed from larger ellipsoidal vesicles to smaller globule micelles with the increase of the surfactant concentration. It is assumed that this unusual aggregation behavior is related to the transformation of molecular conformation from stretched configuration to a pyramid-like shape.

1. Introduction

As a new generation of amphiphilic molecule, oligomeric surfactants characterized by two or more hydrophobic chains and polar head-groups covalently linked through spacer groups, have attracted great research attention. Gemini surfactants consisting of two hydrophobic chains and two polar head-groups are the simplest oligomeric surfactant. Since the first reported in 1971, various kinds of gemini surfactants have been synthesized [1,2] and substantial investigations have proved that they are superior in many

* Corresponding author at: College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, Hubei, PR China. Tel.: +86 2768752701; fax: +86 2768754067.
E-mail addresses: huanliu1987@126.com (X.-G. Liu), xingshujing2005@163.com (X.-J. Xing), gzn@whu.edu.cn (Z.-N. Gao).

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aspects, such as lower critical micelle concentration (cmc), higher surface activity, richer aggregation morphologies, and stronger hydrophobic microdomains, compared with the monomeric surfactants [3,4]. Consequently, the outstanding properties of gemini surfactants drive people to synthesize other higher oligomeric surfactants, such as trimeric surfactants.

Zana et al. [5] conducted the pioneering work in the development of trimeric surfactants, where they synthesized two quaternary ammonium-type surfactants with three dodecyl chains and three ammonium headgroups connected by two propylene spacer groups. They found that the cmc values of the trimeric surfactants were well below those of the corresponding monomeric and dimeric surfactants and unique branched threadlike micelles formed in their aqueous solution. Up to now, different types of trimeric surfactants with varying properties have been synthesized and investigated, including cationic [6–10], anionic [11–13], and nonionic trimeric surfactants [14,15], among which the cationic trimeric surfactants are particularly interesting and have been intensely researched. For example, Laschewsky et al. [16] reported the synthesis of three series of cationic trimeric surfactants, and subsequently investigated the micelle aggregation numbers of these trimeric surfactants [17]. More recently, Yoshimura et al. [8] synthesized a series of star-type cationic trimeric surfactants with a tris(2-aminoethyl)amine spacer and researched the growth mechanism of the wormlike micelles [18]. However, the studies on trimeric surfactants are still at the beginning and there are not enough information on the relationship between their structures and properties, probably owing to the great difficulty with synthesis. Thus, it would be inspiring and important to design, synthesize and fundamentally research new kinds of trimeric surfactants.

In this paper, we synthesized four star-like trimeric surfactants T_n (where n is the tail chain length, $n = 10$, 12, 14, and 16) with ester groups in spacers through a simple two-step reaction. Their physicochemical properties were studied by surface tension, electrical conductivity and steady-state fluorescence measurements. The preliminary examinations of the aggregation behaviors were carried out by dynamic light scattering (DLS) and transmission electron microscopy (TEM).

2. Experimental

2.1. Materials

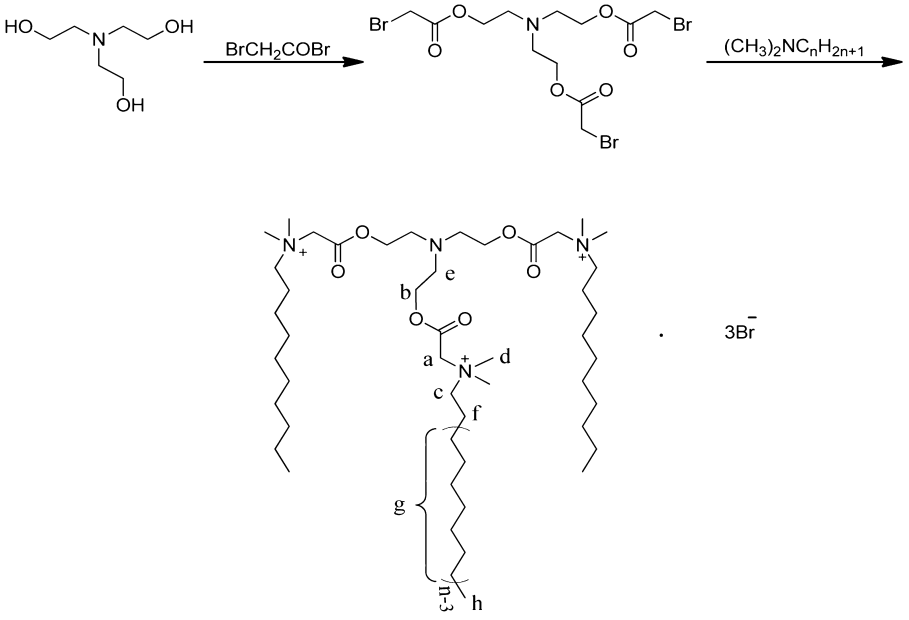
Triethanolamine and bromoacetyl bromide were purchased from Aladdin chemical reagent corporation (Shanghai, China) and used as received. All other chemicals used in the synthesis process were purchased from Sinopharm chemical reagent corporation (Shanghai, China) unless otherwise noted. Potassium carbonate (K_2CO_3) was dried at 100 °C overnight and then cooled down under vacuum. Pyrene (Alfa Aesar, USA) was 99% pure and recrystallized three times from ethanol. Ultrapure water was used in all experiments.

2.2. Synthesis and characterization

The synthesis of the trimeric cationic surfactants T_n is illustrated in Scheme 1. The preparation is based on a previously reported approach by Menger and Migulin [19] with some modifications. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded at a Mercury VX 300 MHz spectrometer (Varian, USA). ESI mass spectra (ESI-MS) were obtained on a P/ACE MDQ CEMS spectrometer (Beckman Coulter, USA). FT-IR spectra were recorded on a model 5700 FT-IR spectrometer (Thermo Nicolet Corporation, USA), and KBr pellets of the samples were used. Elemental analysis was determined on a Vario EL (Elementar, Germany) elemental analyzer.

2.2.1. Triethanolamine tris(bromoacetate)

Bromoacetyl bromide (24.35 g, 0.16 mol in 20 ml dichloromethane) and K_2CO_3 solution (20.00 g, in 25 ml of water) were simultaneously added dropwise into a solution of triethanolamine (4.00 g, 0.027 mol in 20 ml dichloromethane) at room temperature with vigorous stirring for 5 h. Afterwards, the organic layer was washed three times with water and dried with magnesium sulfate. After removing the solvent in vacuum, the crude product was purified via column chromatography (petroleum ether–ethyl acetate, 2:1, v/v) to afford a colorless and



Scheme 1. The synthetic procedure of T_n.