



## Synthesis and aggregation behaviors of disulfonate gemini surfactant with double hexadecyl tails



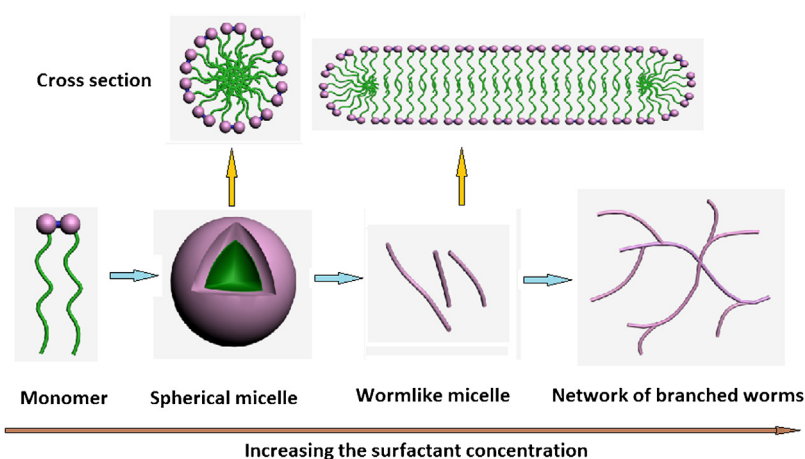
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### HIGHLIGHTS

- Wormlike micelles are formed by disulfonate gemini surfactant without additive.
- The synthesis method is simple and suitable for industrial production.
- Low aggregation number values indicate the existence of premicellar aggregates.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Dihexadecyl diphenyl ether disulfonate ( $C_{16}$ -DADS) was synthesized via three-step reactions: Friedel-Crafts alkylation, sulfonation and neutralization.  $^1H$  NMR and ESI-MS were used to characterize the structure of target products. The aggregation behaviors of  $C_{16}$ -DADS in aqueous solutions were investigated by electrical conductivity, steady-state fluorescence, dynamic light scattering, transmission electron microscopy and rheological measurements. The results show that spherical micelles, wormlike micelles, wormlike micellar gels and network of branched worms are formed with increasing the surfactant concentration. The electrical conductivity data show that  $C_{16}$ -DADS possess a relatively low critical micelle concentration (0.105 mM, 30 °C) and the micellization process is primarily driven by the entropy. Transmission electron microscopy images demonstrate the existence of spherical micelles in  $C_{16}$ -DADS solutions with 0.8 mM and 2 mM surfactant concentrations. The average aggregation number values of  $C_{16}$ -DADS are low because of the formation of premicellar aggregates. Wormlike micelles formed by  $C_{16}$ -DADS without additive are proved by rheological experiments, particularly fascinating is the formation of wormlike micellar gels and network of branched worms with the increase of  $C_{16}$ -DADS concentration.

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## 1. Introduction

Gemini surfactants are generally composed of two hydrophilic head groups and two alkyl chains, linked by a rigid or flexible spacer.

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These surfactants possess unusual aggregation morphologies, lower critical micelle concentration (cmc), and higher efficiency in reducing the oil/water interfacial tension than their corresponding monomeric surfactants. Due to these advantages, gemini surfactants have various application prospects such as cosmetic, biological, and petrochemical systems [1–5].

It is well-known that surfactant molecules have the ability to form varieties of micellar structures by self-assembly in aqueous solution, such as spherical micelles, vesicles and wormlike micelles [2,6–8]. Among these aggregates, wormlike micelles have attracted much attention over the past few decades because of their unique micellar structures and rheological response. In general, wormlike micelles can be formed via different ways. Small spherical micelles may assemble into wormlike micelles and further grow into entangled linear worms and even network of branched worms by appropriate special temperature, concentration, and other conditions [9,10]. External stimuli, such as salinity, pH, CO<sub>2</sub>, UV/vis light and hydrocarbon, would also induce instantaneous and radical changes of macroscopic physicochemical properties of wormlike micelles [10–15]. These wormlike micelles possess remarkable viscoelastic properties while they exist in a dynamic equilibrium between breaking down and reforming, which is different from polymers. Because of these unique properties, wormlike micelles show great potential in versatile applications such as daily care products, biomimetic materials and tertiary oil recovery [16,17].

Numerous previous articles have reported that wormlike micelles can be formed by single or mixed surfactants systems with or without additives. For example, Mu et al [18] discovered that wormlike micelles were formed by anionic surfactant sodium dodecyl trioxyethylene sulfate solutions in presence of AlCl<sub>3</sub>. Chu et al [19] reported that C22-tailed amidosulfobetaine surfactants could assemble into branched worms, which showed various advantages such as low overlapping concentration, insensitive to inorganic salt and stable over the whole pH range. Moreover, Rodriguez et al [20] showed that wormlike micelles were formed by sodium dodecyl sulfate and alkanoyl-*N*-methylethanolmine systems. However, to the best of our knowledge, few studies have focused on wormlike micelles self-assembled by disulfonate gemini surfactants without additive.

In this work, dihexadecyl diphenyl ether disulfonate (C<sub>16</sub>-DADS) was synthesized by three-step reactions which are similar to the previous article [21]. This method is simple and suitable for industrial production. The aggregation behaviors of C<sub>16</sub>-DADS with increasing the surfactant concentration were investigated systematically. Electrical conductivity measurements were performed to investigate the micellization of C<sub>16</sub>-DADS. The aggregation number and aggregate morphologies at low concentrations were studied by steady-state fluorescence measurements and transmission electron microscopy, respectively. The wormlike micelles formed at relatively high concentrations were analyzed by rheological measurements.

## 2. Experimental

### 2.1. Materials

Zirconium oxychloride octahydrate ( $\geq 99.0\%$ ) was purchased from Sinopharm Chemical Reagent Co. (China). Ammonia solution (25%), sodium hydroxide (98%), 1, 2-dichloroethane (98.0%) and 1-hexadecene (95.0%) were obtained from Kermel Chemical Reagent Co. (Tianjin, China). Diphenyl oxide (99%) was purchased from Chengdu Kelong Chemical Co. (Chengdu, China). Sulfuric acid ( $\geq 98.0\%$ ) was obtained from Beijing Chemical Reagent Co. (Beijing, China). Triply distilled water was used as solvents in all experiments.

### 2.2. Preparation of C<sub>16</sub>-DADS

The sulfated zirconia catalyst was prepared according to the methods reported previously [21,22]. C<sub>16</sub>-DADS was synthesized by a multistep reaction, as shown in Scheme 1. The Friedel-Crafts alkylation of diphenyl oxide (30 g) with 1-hexadecene (100 g) in presence of sulfated zirconia catalyst (2 g) was carried out at 120 °C for 4 h. Then the catalyst was separated from the mixture by vacuum filtration and the unreacted materials were removed by reduced pressure distillation. The dihexadecyl diphenyl ether was purified by chromatography on a silica gel column using petroleum ether as the mobile phase. The dihexadecyl diphenyl ether (20 g) was sulfonated by fuming sulfuric acid (50 g) at 50 °C for 50 min and neutralized with sodium hydroxide aqueous solution (30 wt%). The raw product was desalted in anhydrous ethanol and unreacted alkylated diphenyl oxide was removed by extraction with petroleum ether. The aqueous layer was dried and the product was obtained as a light yellow powder. The purity of C<sub>16</sub>-DADS, determined by two-phase titration method, was 98.8%.

### 2.3. Analyses of the structures for C<sub>16</sub>-DADS

<sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) spectroscopy of dihexadecyl diphenyl ether was performed with a JEOL JNM-GSX400 spectrometer. The sample was placed in 5 mm BBO probe with CDCl<sub>3</sub> as solvent and the measurements were conducted at 25 °C. The electrospray ionization-mass spectrometry (ESI-MS) analysis of C<sub>16</sub>-DADS was carried out using a Waters ZQ2000 mass spectrometer with an electrospray interface and recorded in negative mode.

### 2.4. Electrical conductivity measurements

The electrical conductivity of surfactant solutions was performed using a conductivity analyzer (model DDS-307, Shanghai INESA & Scientific Instrument Co., Ltd., Shanghai, China). The temperature was maintained at constant values (20, 30, 40 and 50 °C). The temperature of electrical was controlled by a constant-temperature bath within  $\pm 0.1$  °C and each electrical conductivity data point was recorded with an uncertainty of less than 0.5%.

### 2.5. Steady-state fluorescence measurements

The fluorescence spectra were recorded with a Hitachi F-4600 spectrofluorometer (Hitachi, Co., Ltd., Tokyo). The fluorescence excitation wavelength was focused at 335 nm. The emission spectra wavelength ranged from 350 to 500 nm, Slit widths for emission and excitation were fixed at 2.5 and 10 nm, respectively. Pyrene and benzophenone were used as fluorescence probe and quencher, respectively. The concentration of pyrene was kept constant at  $5 \times 10^{-7}$  mol/L and all the fluorescence spectral measurements were conducted at 30 °C.

### 2.6. Equilibrium surface tension measurements

Surface tension measurements were carried out using a KRÜSS K12 Processor Tensiometer by the Wilhelmy plate method at  $30 \pm 0.1$  °C. The length and thickness of the platinum plate was 19.9 mm and 0.2 mm, respectively. Surfactant solutions were prepared at least one day before the determinations. Each surface tension value was determined until the change in the surface tension was less than 0.2 mN/m.

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