



Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Butynediol-ethoxylate based trisiloxane: Structural characterization and physico-chemical properties in water

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ARTICLE INFO

Article history:

Received 25 February 2014

Received in revised form 16 April 2014

Accepted 28 April 2014

Available online xxxx

Keywords:

Trisiloxane surfactant

Surface activity

Absorption kinetics

Aggregation behaviors

Spreading performances

ABSTRACT

A trisiloxane surfactant was synthesized with grafting butynediol ethoxylate onto hydrophobic heptamethyltrisiloxane. The structural analysis of this surfactant was done by ¹H, ¹³C and ²⁹Si NMR. The surface activity, adsorption kinetics, aggregation behaviors in aqueous solutions, and dynamic spreading performances of this siloxane amphiphile were investigated by surface tension, transmission electron microscopy (TEM), dynamic light scattering (DLS) and contact angle techniques at 298 K. The surface tension of this trisiloxane surfactant measured at critical aggregate concentration (CAC) was observed to be significantly lower than that of acetylenic diol based surfactants. Adsorption model for this amphiphile is diffusion-controlled model. Aggregates of this nonionic surfactant formed in aqueous solutions could be assigned as spherical assemblies as suggested by analysis using TEM and DLS. The spreading performances on low-energy Teflon film and paraffin film interface was studied by the contact angle measurement with sessile drop method and proved that it has a potential as spreading agents in industry.

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1. Introduction

Surfactants based on siloxane are widely used in a lot of domains, as polyurethane foam additives, cosmetic formulations, textile manufactures, agricultural adjuvants and paint additives [1]. It has been proved that the surface activity of siloxane-based surfactants mostly surpasses that of conventional hydrocarbon surfactants, and these surfactants can lead to the reduction of surface tension of water to nearly 20–25 mN/m [2]. This property is due to the low cohesive energy and flexibility of siloxane moiety, which enables amphiphilic molecules to adopt proper conformations at air/water interface with a close and efficient packing [3].

Usually, silicone-based surfactants are obtained by attaching one or more hydrophilic polar groups to a silicone chain. Kim et al. [4] synthesized comb rake-type polysiloxane surfactants with multiple hydrophilic groups, allyl-oligo(PO-b-EO) series and allyl-oligo(PO-b-EO)Me series, with hydrosilylation. Luo et al. [5] prepared a hydrolysis resistant

cationic trisiloxane surfactant with heptamethyltrisiloxane attached quaternary ammonium salt. West et al. [6] synthesized tetrasiloxane and trisiloxane compounds by connecting up oligo(ethylene oxide) chains, $-(CH_2CH_2O)_n-$ ($n = 2-7$), via hydrosilylation and dehydrocoupling reactions. One kind of water soluble siloxane amphiphile by grafting the hydrophilic groups of poly(ethylene glycol) onto hydrophobic poly(hydromethyl siloxane) backbone was synthesized by Reddy and co-workers [7]. In our early reports [8–13], a variety of carbohydrate-modified silicone surfactants have been synthesized.

On the other hand, nonionic surfactants based on acetylenic diol represent a unique class of amphiphile with carbon-carbon triple bond and hydroxyl groups [14]. Such a structure, thus, provides these amphiphilic molecules high electron density and hydrophilicity, and also gives the special characteristics of surface wetting/spreading and remarkable defoaming properties for water-based inks and coatings systems [15, 16]. Attachment of an advanced acetylenic glycol to a silicone chain results in novel siloxane surfactants, hence, which will extend a lot of applications in industry. Here, we prepared a novel butynediol-ethoxylate based trisiloxane surfactant through a hydrosilylation procedure between 1,1,1,3,5,5,5-heptamethyltrisiloxane and 1,4-bis(2-hydroxyethoxy)-2-butyne using H_2PtCl_6 [17,18] as a catalyzer. Some of physico-chemical properties of this surfactant, such as surface activity and aggregation behaviors in aqueous solutions, and dynamic spreading performances on low-energy solid interface, were investigated.

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2. Experimental

2.1. Materials

The reagent of 1,4-bis(2-hydroxyethoxy)-2-butyne (BEO) was used as received from Wuhan Loche Technology Development Co., Ltd. (China). 1,1,1,3,5,5,5-Heptamethyltrisiloxane (HMSTs) was from Zhejiang Runhe Organosilicone New Material Co., Ltd. (China). Hexachloroplatinic acid (H_2PtCl_6) was supplied by Nanjing Chemical Reagent Co., Ltd. (China). Isopropanol was purchased from Beijing Chemical Reagent Co., Ltd. (China). All chemicals were used directly as obtained.

2.2. Synthesis of butynediol-ethoxylate modified trisiloxane (BDET) surfactant

A 250 mL four-necked round-bottom flask was equipped with a stirrer, condenser, thermometer, and nitrogen inlet/outlet. BEO (43.5 g, 0.25 mol), HMSTs (55.5 g, 0.25 mol) and 8 mL of the isopropanol solutions of H_2PtCl_6 (1 mg/L) were added to the flask. The mixture was heated to 110 °C and stirred under N_2 for 3 h. The final product was purified by distillation and analyzed satisfactorily by ^1H , ^{13}C , and ^{29}Si NMR.

2.3. Analyses of the structures for BDET

Fourier transform infrared spectroscopy (FT-IR) for BDET was recorded from the compound casting directly onto KBr prisms using a Bruker Vertex-70 spectrometer. ^1H , ^{13}C , and ^{29}Si nuclear magnetic resonance (NMR) spectroscopies were performed in CDCl_3 with a Varian INOVA-400 Hz spectrometer. CDCl_3 was selected as an internal standard for NMR, because of overlapping signals for some methyl groups in the BDET, HMSTs and tetramethylsilane.

2.4. Measurements of the aqueous solution behavior of BDET

All of the surfactant solutions were prepared using the water of double-distilled water with a specific resistance of 18.23 $\text{M}\Omega \cdot \text{cm}$, and care was taken to ensure that all glassware were thoroughly clean. All measurements were performed at 298 ± 0.2 K.

2.4.1. Equilibrium surface tension

Equilibrium surface tension measurements were carried out on a Krüss K122 tensiometer (Krüss Company, Germany) by the duNoüy ring technique. The equilibrium surface tension was determined with a single measurement method. Each measurement was repeated until the standard deviation of three successive readings was <0.20 mN/m. All water used in these measurements had a surface tension of 72.0 ± 0.2 mN/m. The platinum duNoüy ring used in the measurements was cleaned by rinsing with double-distilled water, followed by rinsing with acetone and finally held in a flame until an orange glow was obtained.

2.4.2. Dynamic surface tension

The dynamic surface tension was measured by a Krüss BP100 bubble-pressure tensiometer (Krüss Company, Germany). Prior to the measurements, calibration of the instrument using double-distilled water was performed to ensure that no contamination was present in this system. This measurement was conducted with effective surface ages ranging from 10 to 50,000 ms.

2.4.3. Dynamic light scattering

To investigate the aggregation behaviors of BDET surfactant solutions, the light scattering measurement was made using a Zeta particle size analyzer (Brookhaven, USA). The scattering angle was set at 90°. All analyses lasted for 3 min. Before the measurement, each solution of

BDET was filtered using a mixed cellulose acetate membrane filter with the pore size of 0.45 μm .

2.4.4. Transmission electron microscopy

The technique for investigating the microstructures of surfactant aggregates in aqueous solutions by negative staining has been described in detail elsewhere [9–11]. A small drop of BDET solution was added onto a carbon-coated grid and allowed to equilibrate for 2 min. Excess liquid was removed by blotting using a filter paper, and the grid dried at room temperature. A thin sample film covering the grid was obtained by adding a drop of staining solution (2 wt.% phosphotungstic acid) onto the grid and removing excess liquid by touching one end of the grid with filter paper after 2 min, when the grid was partially dried again. The grid was then transferred to a JEM-1011 (Jeol Co., Japan) transmission electron microscopy operating at an accelerating voltage of 100 kV.

2.4.5. Spreading ability

A set-up [12] was used to measure the spreading ability of prepared surfactant solutions over hydrophobic substrates. Paraffin film and Teflon film were chosen as solid substrates showing different solid–air interfacial energies in terms of contact angles for water [19]: (106 ± 2)° on paraffin, and (117 ± 1)° on Teflon. The film was placed on an aclinic stage in front of a microscope, which was connected to a CCD camera. Using a microsyringe, drops of surfactant aqueous solutions (5 μL) were released and deposited on the film. The contact angle of droplets was estimated with an on-screen protractor software (Powereach Co., Shanghai, China). The environmental humidity was kept constant at $50 \pm 5\%$. To ensure minimal relative error, every experiment was repeated at least three times. The contact angles were the average of values obtained in each set of measurements.

3. Results and discussions

3.1. Syntheses and characterizations

Butynediol-ethoxylate based trisiloxane surfactant was synthesized with hydrosilylation of HMSTs and BEO using H_2PtCl_6 as catalyst (Scheme 1). According to Chalk and Harrod's mechanism [20–22], a complex (I) was formed by the reaction between monomolecular H_2PtCl_6 catalyst and bimolecular BEO. Then another intermediate (II) was formed with chemical incorporation between HMSTs and the previous formed complex (I), and then as the complex (I) was formed again between intermediate (II) and other BEO. The reaction of hydrosilylation was completed and finally compound BDET was obtained.

Fig. 1 shows the FT-IR of HMSTs, BEO, and BDET. The strong and sharp peak at 2150 cm^{-1} , corresponding to typical peak for Si–H of HMSTs, is not observed for BDET. Therefore, complete hydrosilylation is confirmed by the disappearance of this reactive group. The peaks at 1100 and 1090 cm^{-1} are observed in the BDET and indicate the presence of –C–O–C– ether functional groups of EO block, which also appears in Fig. 1, panel (2) observed in the BEO, and –Si–O–Si– group of HMSTs.

Fig. 2 is the ^1H NMR spectra of final product and original reagents. The active hydrogen peak (Si–H) for HMSTs appears at 4.5 ppm. After the completion of hydrosilylation, this peak is not present, as expected, in the spectra of BDET. The chemical shift of new formative hydrogen atom (C=C–H) appears at 6.0 ppm in Fig. 2, panel (3), which is not observed in the spectra of reactants.

Fig. 3 illustrates the ^{13}C NMR spectrum for BEO and BDET. The peaks appear at 81 ppm, which correspond to the carbon atoms of C=C triple bond, are not observed in the spectra for BDET. The chemical shift of new formative carbon–carbon double bond appears at 139 ppm in Fig. 3, panel (2).

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