



Synthesis and properties of a branched short-alkyl polyoxyethylene ether alcohol sulfate surfactant



Wanxu Wang, Jianbo Li, Xiaoyi Yang*, Ping Li*, Chaohua Guo, Quanhong Li

China Research Institute of Daily Chemical Industry, Taiyuan Shanxi 030001, PR China

ARTICLE INFO

Article history:

Received 12 August 2015

Received in revised form 16 September 2015

Accepted 21 September 2015

Available online xxxx

Keywords:

Branched tail

Polyoxyethylene groups

SO₃ vapor

Krafft point

Surface activity

ABSTRACT

A branched alkyl polyoxyethylene ether alcohol sulfate, sodium isooctyl polyoxyethylene ether sulfate (i-OE₃S), was synthesized and its physico-chemical properties were investigated systematically. The experiment on Krafft point gave a result that the Krafft temperature of i-OE₃S was below 0 °C. The measurement of static surface tension showed that the critical micelle concentration (cmc) and surface tension at cmc (γ_{cmc}) of i-OE₃S were 21.67 mmol·L⁻¹ and 27.4 mN·m⁻¹, respectively. From the results of dynamic surface tension (DST) measurements, we could obtain that the adsorption of i-OE₃S at air/liquid interface is controlled by the mixed diffusion–kinetic mechanism. Spherical assemblies with a diameter in the range of 263 to 606 nm in water were observed by transmission electron microscopy (TEM). The spreading performance of i-OE₃S aqueous solution on paraffin film was investigated by dynamic contact angle and the results demonstrated that i-OE₃S possessed an excellent spreading ability.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Anionic–nonionic surfactants are widely used in the field of petroleum recovery, washing industry, environmental improvement of water, coatings technology and other similar areas owing their excellent properties in salt tolerance, Krafft points, surface properties and biodegradability [1–3]. Alkyl polyoxyethylene ether alcohol sulfates (AES) are the most popular domains in anionic–nonionic surfactants. The strong and close relationships between the structure of AES and their physicochemical properties have been studied in recent years [3–7]. For instance, compared with common alkyl sulfates, both of the cmc and Krafft points of the anionic–nonionic surfactants are much smaller due to the existence of poly (ethylene oxide) groups, while their temperature tolerance, salt tolerance and solubility are quite larger [3, 7–11]. Weil et al. [12] synthesized a series of sulfated ethenoxylated tallow alcohols by esterifying ether alcohol with chlorosulfonic acid as the sulfating agent. They found that the increase of average number of ethylene oxide (EO) units (less than 5) led to a decrease in the cmc, Krafft point, foam height and detergency of long straight chain ether alcohol sulfates. Shinoda and co-workers [9,13] obtained a variety of dodecyl polyoxyethylene sulfuric acid and discovered that the introduction of EO groups could observably reduce the Krafft points of these surfactants in the presence of multivalent cations and the variation of cmc coincided with Weil's conclusion. Chen and Xu [14] researched

that the introduction of EO units in the anionic surfactants might enhance the Ca²⁺-tolerance of original surfactants through molecular dynamics simulation.

Compared to straight chain surfactants, the branched tail surfactants possess excellent properties, including lower γ_{cmc} and Krafft points which favor the practical applications [8,15]. The branched hydrophobic groups are highly resistant to electrolyte, which results in an excellent salt tolerance [16]. In addition, the branched products show superior performance in the efficiency of decreasing surface energy and have good natural biodegradation behavior at low temperature. These advantages above make the branched alkyl ethoxy sulfates become research hotspots in a number of fields. Varadaraj et al. [5,8,17,18] synthesized a series of alkyl-branched ethoxy sulfates and studied their static surface tensions, DST, dynamic contact angles, Krafft point and other interfacial properties in details. In addition, they discussed the structure–activity relationships of different surfactants through studying thermodynamics of adsorption and micellization to answer their superior surface properties and lower Krafft points. Huang et al. [19] synthesized Guerbet hexadecyl sulfate by esterifying branched alcohol with liquid sulfur trioxide (SO₃) solution in dichloroethane as the sulfating agent. They noted that the branched tail surfactant showed better surface-active property, wetting ability and emulsifying ability than sodium dodecyl sulfate (SDS). Jin et al. [20] discovered that Guerbet tetradecyl polyoxyethylene ether sulfates possessed higher surface activities than linear chain surfactants. They also showed that the surfactant, with branched lipophilic chain and EO units being chosen as hydrophobic and hydrophilic groups at the same time, possess even more excellent surface activity than surfactants with only branched tail but without EO groups.

* Corresponding authors at: China Research Institute of Daily Chemical Industry, 34 Wenyuan Street, Taiyuan, Shanxi Province 030001, PR China.

E-mail addresses: yxywlyzx@163.com (X. Yang), yipingli_@126.com (P. Li).

The surfactants involving in the reports above are all focus on the long hydrophobic chain. But for the synthesis of sulfated ether alcohols, long chain alcohols are easy to be oxidized or may present solid phase at room temperature, which make the insertion of EO or propylene oxide more different than that of branched short-tail alcohols [21]. Furthermore, the sulfating agents mentioned in the literatures above are chlorosulfonic acid or liquid SO_3 dissolving into dichloroethane. The residues such as waste acid or chlorine-containing compounds can cause a burden to the environment and economy. Hence, a new sulfating method for the synthesis of branched short-tail AES becomes a challenged and meaningful research.

In this article, a branched short-tail AES, sodium isooctyl polyoxyethylene ether sulfate ($i\text{-OE}_3\text{S}$) was synthesized using bubbling SO_3 vapor as the sulfating agent, and in doing so, the problem caused by waste acid or chlorine-containing compounds can be alleviated greatly. The structure and physicochemical performances of $i\text{-OE}_3\text{S}$ were investigated systematically by various measurements. Sodium octyl ethoxy sulfate (OE_3S) and sodium isooctyl sulfate ($i\text{-OS}$) were also synthesized for comparing with $i\text{-OE}_3\text{S}$ on Krafft point, static surface tension, and dynamic contact angle. Moreover, DST and aggregation behavior of aqueous solution of $i\text{-OE}_3\text{S}$ were measured by bubble pressure and TEM, respectively.

2. Experimental

2.1. Materials and characterization

Isooctyl alcohol, n-octanol, sodium hydroxide, absolute ethanol and petroleum ether were from Tianjin Kermel Chemical Reagent Co., Ltd. (China). Acetone and fuming sulfuric acid (65%) were supplied by Tianjin Shentai Chemical reagent Co., Ltd. (China). EO was from Sinopec Yanshan Co., Ltd. (China). The chemicals listed above were AR grade and used directly without further purification. The alkaline catalyst was provided by China Research Institute of Daily Chemical Industry (Taiyuan, China). The deionized water with a resistivity of $18.25 \text{ M}\Omega \cdot \text{cm}$ was used from a UPD-II ultrapure water purifier.

FT-IR for $i\text{-OE}_3\text{S}$ was detected from the product absolute ethanol solution smearing onto KBr prisms with a Bruker Vertex-70 spectrometer. ^1H NMR spectra was determined in CDCl_3 using a Varian INOVA-400 MHz spectrometer.

2.2. Synthesis

The product, $i\text{-OE}_3\text{S}$, was synthesized via a three-step reaction according to Scheme 1.

2.2.1. Synthesis of isooctyl polyoxyethylene ether alcohol ($i\text{-OE}_3$)

Isooctyl alcohol (130.23 g) mixed with catalyst (0.79 g) was placed in an autoclave and heated to 140°C after the air in the autoclave was

replaced by N_2 three times. Then, EO (5 g) was added into the autoclave to induce the reaction. When the mixture was reheated to 160°C , EO (127.15 g) was continuous to be inputted into the reactor under a pressure of 0.35 MPa gradually. Finally, the system was aged to keep the pressure constant, pumped vacuum to remove the free EO at temperature below 80°C , and filled with N_2 for discharge. The product, with an average of about 3 EO, was obtained after removing catalyst by filtration.

2.2.2. Synthesis of $i\text{-OE}_3\text{S}$

- 1) Preparation of liquid SO_3 : Fuming sulfuric acid (45 mL) was added into a 250 mL round-bottom flask equipped with an air-cooled condenser and heated to 90°C . Liquid SO_3 was collected through the condensation of SO_3 vapor evaporating from the fuming sulfuric acid and stored in a constant-temperature funnel at 36°C .
- 2) Synthesis of $i\text{-OE}_3\text{S}$: The sulfation took place in a set-up assembled by research group as shown in Fig. 1. Liquid SO_3 (21.5 mL) was added drop wise into the leftmost flask within half an hour and the droplet was evaporated at 140°C . The SO_3 vapor was diluted with nitrogen which has a constant velocity of $0.14 \text{ m}^3/\text{h}$. Then, the mixed well gas in the middle flask was passed bubble by bubble into the $i\text{-OE}_3$ (131.12 g) placed in a three-necked 500 mL round-bottom flask at $(40 \pm 1)^\circ\text{C}$. The esterified product was neutralized by 30 wt.% aqueous sodium hydroxide to $\text{pH} = 8$ gradually in an ice-water bath.

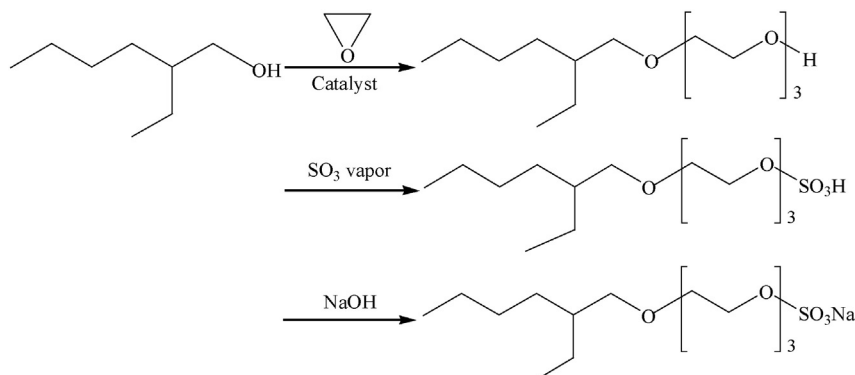
The raw product was dried under vacuum at 55°C after extracting the unreacted $i\text{-OE}_3$ with petroleum ether and filtered out inorganic salts in absolute ethanol. Because of the multiple distributions of EO units, the product cannot crystallize [22]. After removing the solvent by reduced pressure distillation, $i\text{-OE}_3\text{S}$ presenting a viscous but pourable light yellow liquid was obtained at 55°C , then becoming wax-like solid at room temperature.

2.3. Krafft point

The technique for studying the Krafft point of surfactant was referred to literature [23]. One percent solution of the surfactant was whisked to dissolution extremely, then the solution was cooled to cloudy and reheated slowly to clear at a rate of $1^\circ\text{C} \cdot \text{min}^{-1}$. The temperature at which the solution became one homogeneous phase was recorded as the Krafft point.

2.4. Static surface tension

Static surface tension measurements were performed using a processor tension meter K122 (Krüss Company, Germany, accuracy $\pm 0.01 \text{ mN} \cdot \text{m}^{-1}$) by the plate technique at $(25 \pm 0.1)^\circ\text{C}$. Ultrapure water with a surface tension of $(72.1 \pm 0.2) \text{ mN} \cdot \text{m}^{-1}$ was used for



Scheme 1. The Synthetic route of $i\text{-OE}_3\text{S}$.

Download English Version:

<https://daneshyari.com/en/article/5410566>

Download Persian Version:

<https://daneshyari.com/article/5410566>

[Daneshyari.com](https://daneshyari.com)