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Synthesis and properties of two surfactants containing polyoxypropylene block and short branched alkyl chain

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ABSTRACT

Short branched alkyl polyoxypropylene sulfates, sodium isohexyl polyoxypropylene sulfate (i-HPS) and sodium isooctyl polyoxypropylene sulfate (i-OPS) were synthetized via propoxylation, sulfation, and neutralization three-step reactions, and characterized by FT-IR and ^{1}H NMR. Their Krafft points were measured and the results were all below freezing point. Their critical micelle concentrations (cmc) and minimum surface tension (γ_{cmc}) determined by equilibrium surface tension were 54.74 mmol L^{-1} and 32.12 mN m^{-1} for i-HPS, 15.57 mmol L^{-1} and 33.33 mN m^{-1} for i-OPS, respectively. The measurement of dynamic surface tension indicated that both the equilibrium values of surface tension and the time required for reaching the equilibrium decreased with the increasing concentration of surfactant solutions. The spreading ability on paraffin film researched through dynamic contact angle revealed that the droplet of i-HPS solution presented a minimum contact angle of 58.9° at a concentration of 150 mmol L^{-1}, while the equilibrium contact angle of i-OPS droplet was 52.8° under the same condition. Their salt tolerance measurement showed that 1.0 wt% i-HPS solution and 1.0 wt% i-OPS solution could endure 183.1 g L^{-1}, 143.9 g L^{-1} NaCl, 206.3 g L^{-1}, 198.4 g L^{-1} $MgCl_2$, and 229.7 g L^{-1}, 217.9 g L^{-1} $CaCl_2$, respectively.

1. Introduction

Alkyl polyoxypropylene sulfates (APS), one kind of extended surfactants, consist of hydrophobic alkyl chain, hydrophilic sulfate group, and poly(propylene oxide) linker as intermediate polarity group to provide a smooth transition between the hydrophobic and hydrophilic parts [1,2]. The insertion of propylene oxide (PO) into hydrophilic head and hydrocarbon tail contributes to the surfactant not only extending its tail length without sacrificing its own water solubility but also acting as one component of the middle phase microemulsions which possess superior solubilization capacity and ultralow interfacial tension (IFT) [2–4]. The APS with such unique surfactant molecular structure have been widely studied due to their extensive applications in soil and aquifer remediation, enhanced oil recovery, pharmaceutical formulations, nanoparticle preparations and froth flotation [5–7].

Phan T.T. et al. [8] researched the effect of structure of APS, which involves the number of PO units and the branching of hydrophobic chain, on the microemulsion formation and IFT values. They found that both the optimum salinity and minimum IFT values decreased with the increase of the inserted PO units or the degree of branching of the hydrocarbon tail. Angelika K. et al. [2] studied the effects of a series of anions and cations on the cloud point of a long hydrophobic chain extended surfactant through phase behavior observation and micelle structure investigation. Their experiments showed that the changes of the surfactant solubility caused by the addition of salts followed the same order as Hofmeister series. Zeng J.X. et al. [9] synthetized a series of APS with different PO adduct numbers through Williamson reaction, sulfating with chlorosulfonic acid and neutralizing with sodium hydroxide. They determined the structure of synthesized compounds and found out that APS could decrease the IFT between aqueous solution and model oil to a low value.

The APS reported in the literatures above have shown excellent performances in microemulsion, IFT, and salt tolerance. However, the sulfating agents used in the synthesis of APS cause a massive amount of waste acid and other pollutants during the sulfonation reaction, which lead to an increase in energy consumption further. Therefore, it is of great importance to develop an environmental friendly and economical sulfating method occupying vapor SO_3. However, to the best of our knowledge, the related research has not yet been reported. In addition, the performances of APS were focused on their functions combined with other components, while the physical and chemical properties of single APS aqueous solution have not been investigated systematically. Hence, an economical and practical sulfating method for synthetizing APS is a pioneer of APS industrialization. The APS fundamental research can expand its application to various fields such as coating technology, mineral flotation and other surface science technology.

In this article, two APS with branching hydrophobic chain, sodium isohexyl polyoxypropylene sulfate (i-HPS) and sodium isooctyl

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polyoxypropylene sulfate (i-OPS) were synthesized through sulfating with vapor SO_3. Their structures were confirmed by FT-IR and ^1H NMR. Sodium isooctyl polyoxyethylene sulfate (i-OES) and sodium hexyl polyoxypropylene sulfate (HPS) were also synthesized through the same method for comparing with i-OPS and i-HPS to show how the differences between ethylene oxide (EO) groups and PO units, branched chain and straight tail would impact on the Krafft point, minimum surface tension (γ_{cmc}), and critical micelle concentration (cmc). Moreover, dynamic surface tension, dynamic contact angle and salt tolerance of i-HPS and i-OPS aqueous solutions were measured by bubble pressure method, sessile drop technique, and ultraviolet-visible detector, respectively.

2. Experimental methods

2.1. Materials

Isooctyl alcohol (99%), *n*-octanol (98%), *n*-hexyl alcohol (98%), absolute ethanol (99.7%), cyclohexane (98%), sodium chloride (NaCl 99.6%), magnesium chloride ($MgCl_2$ 98%), and calcium chloride ($CaCl_2$ 96%) were supplied by Tianjin Kermel Chemical reagent Co., Ltd. (China) and used without further purification. Acetone (98%), sodium hydroxide (96%), and fuming sulfuric acid (65% concentration) were purchased from Tianjin Shentai Chemical reagent Co., Ltd. (China). Isohexyl alcohol (98%) was provided by TCI Development Co., Ltd. (Shanghai). PO (99.5%) was offered by Sinopharm Chemical reagent Co., Led. (China). The catalyst was prepared by our workgroup in advance. The deionized water with a resistivity of 18.25 MΩ·cm prepared by a UPD-II ultrapure water purifier was used in the preparation of all solutions.

2.2. Synthesis and characterization

2.2.1. Synthesis of i-HPS and i-OPS

Two surfactants, i-HPS and i-OPS were synthesized by a three-step reaction as shown in Scheme 1.

The autoclave charged with isohexyl alcohol (102.17 g) or isooctyl alcohol (130.23 g) and catalyst (0.70 g) was pumped and filled with nitrogen three times to remove oxygen under stirring and heating. Then, PO (6 g) was put into the reactor to induce the reaction at a temperature of 150 °C. When the system was heated to 165 °C by the energy of chemical reaction, a required amount of PO (169 g) was gradually added into the reactor under a stable pressure of 0.30 MPa. Finally, the mixture was separated using filtration after aging and cooling. Thus, the intermediate product with an average of 3 PO units, isohexyl polyoxypropylene ether alcohol (i-HP) or isooctyl polyoxypropylene ether alcohol (i-OP), was obtained.

The target products, i-HPS and i-OPS, were sulfated, neutralized and purified by the method described in our previous article [10]. The dried surfactants, a light yellow wax-like solid at room temperature, cannot crystallize owing to the polydispersity of the PO units [1].

2.2.2. Structural characterization

The intermediate products (i-HP, i-OP) and target products (i-HPS, i-OPS) were dissolved in respective absolute ethanol and each of the solutions was smearing onto KBr prisms. Then, FT-IR for the products was recorded via a Bruker Vertex-70 spectrometer, respectively. ^1H NMR spectra for the target product $CDCl_3$ solutions was detected on a Varian INOVA-400 Hz spectrometer, respectively.

2.3. Krafft point

The method for determining the Krafft points of experimental products and control products was described in literatures [10,11]. The solutions with a concentration of 1.0 wt% were cooled to cloudy after the process of using ultrasonic technique to form a homogeneous continuous phase. Then, the heterogeneous solutions were heated gradually to clear again under a heating rate of 0.5 °C min^{-1}. The temperature at which the system became clear was the Krafft point of surfactant. For each measurement, the reported Krafft point was the average value of three replications.

2.4. Equilibrium surface tension

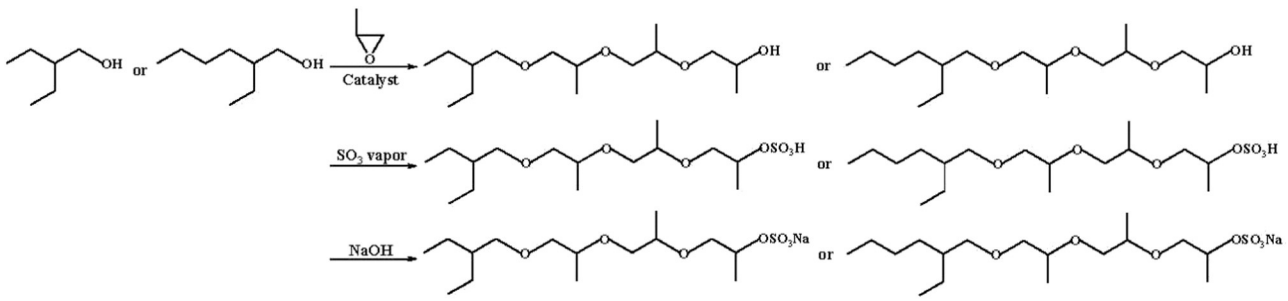
The surface tension (γ) was obtained by a Krüss K12 Processor Tensiometer (Krüss Company, Germany, accuracy ± 0.01 mN m^{-1}) via the Wilhelmy plate method at 25 ± 0.1 °C. The recorded value of each concentration was the mean value determined from the three repeated measurements with an interval of 30 s. The γ of ultrapure water (72.0 ± 0.3 mN m^{-1}) was carried out before the measurement to make sure that the silica dish had no impurity.

2.5. Dynamic surface tension

Dynamic surface tension was conducted on a Krüss BP-100 bubble pressure tensiometer (Krüss Company, Germany, accuracy ± 0.01 mN m^{-1}) with a range of effective surface ages from 10 to 200,000 ms at 25 ± 0.1 °C. Ultrapure water was used for calculating the internal diameter of capillary in advance.

2.6. Dynamic contact angle

Dynamic contact angle was measured using a drop shape analyzer DSA-25 (Krüss Company, Germany, accuracy ±0.1°) to judge the spreading property of the target product aqueous solution on paraffin film at 25 ± 0.1 °C. The ultrapure water drop with a contact angle of (106 ± 2)° on paraffin substrate [12] was performed before measuring to ensure the system was clean. The final value of each sample was the average data from three droplets recorded at an air humidity of (55 ± 5)%.



Scheme 1. Synthetic routes of i-HPS and i-OPS.