



Aggregation behaviors of alkyl ether carboxylate surfactants in water



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ARTICLE INFO

Article history:

Received 19 August 2016

Received in revised form 1 December 2016

Accepted 1 December 2016

Available online 08 December 2016

Keywords:

Fatty alcohol polyoxyethylene ether carboxylate

Phase behavior

Micelle

Lyotropic liquid crystalline

ABSTRACT

Two fatty alcohol polyoxyethylene ether carboxylate surfactants (NEX-*n*) with different oxyethylene units have been employed to investigate the effect of headgroup on their aggregation behaviors in water. Surface tension and electrical conductivity measurements were conducted to characterize the surface activities and micelle formation in NEX-*n*/water systems. Different from nonionic surfactant systems, the critical micelle concentration of NEX-7 surfactant with more oxyethylene units is a little lower than that of NEX-4. The thermodynamic parameters obtained on surface tension measurements suggest a stronger hydrophobic interaction in NEX-7 aqueous solution, and disclose the driving forces for micelle formation. In addition, the liquid crystalline (LC) phase behaviors have been studied by polarized optical microscopy and small angle X-ray scattering techniques. With increasing NEX-4 concentration, the hexagonal, lamellar, sponge, and reverse cubic phases have been observed to appear in sequence, whereas only hexagonal and lamellar are formed in NEX-7/H₂O system. Comparison with sodium myristate and C₁₂E₄ systems further reveals that the electrostatic interaction combining with the hydrogen bonding should be the main driving forces for the LC phase formation.

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1. Introduction

Traditional surfactant molecules are generally composed of both one hydrophilic head unit and one hydrophobic moiety in a single molecule [1]. Mixtures of different surfactants or with other additives are widely used in the fields of oil recovery, cosmetics, drug delivery, materials synthesis, and printing etc. [2–5]. In the last decades, some new types of surfactants such as gemini, bola surfactants etc. have attracted a lot of research attention due to their special structures possessing several hydrophobic and hydrophilic groups in a single molecule [6–8]. Among them, fatty alcohol polyoxyethylene ether – anionic surfactants contain two hydrophilic groups (oxyethylene chain and anionic headgroup) and one hydrophobic tail, exhibiting the characteristics of both nonionic and anionic surfactants, such as higher surface activity, excellent emulsifying property, and good foaming capacity, which make them have many potential applications in the enhanced oil recovery and cosmetics formulations [8–11].

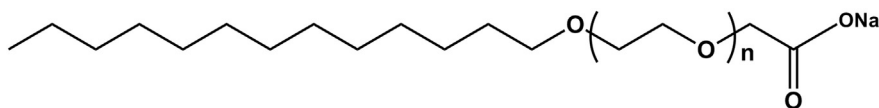
Lin et al. have synthesized several anionic-nonionic surfactants, which contain polyoxyethylene chains and sodium phosphonate groups as hydrophilic moieties [9]. Their surface activities are superior to those of traditional surfactants containing only one nonpolar or hydrophobic moiety and one polar head unit. Wang and Yang found that the

introduction of polyoxyethylene (EO) unites in the anionic surfactants make them present excellent surface activities especially in adsorption efficiency and spreading behavior [12]. Yu et al. have synthesized several polyoxyethylene alkyl ether carboxylic surfactants with different hydrophobic structures, and explored the relationship between surfactant structures and physicochemical properties [13,14]. They demonstrated that longer hydrophobic group leads to low dynamic surface activity and low foam volume. In addition, the surfactants with branched-alkyl chain show high dynamic surface activities and high foam volume. While, for straight chain surfactants, the results of surface dilational rheological measurements demonstrate that the longer hydrophobic chain surfactants show higher dilational modulus and better form stability. Thanks to the presence of poly(ethylene oxide) linker, the surface activity of these surfactants could be tuned by changing the length of polyoxyethylene chain or the structure of ionic hydrophilic group. Chen and coworkers have prepared a series of polyoxyethylene carboxylated modified Gemini surfactants with different polyoxyethylene chain length, which possess multiple hydrophilic groups [15]. These surfactants all exhibit excellent surface activities. And an increase of polyoxyethylene chain length results in higher surface tension values of solutions at critical micelle concentration (CMC).

Various phases like the micelle, gel and emulsion were also characterized in these binary aqueous systems. Li and Penfold have reported that the sodium dodecyl trioxyethylene sulfate surfactants could form wormlike micelles with high viscoelasticity with the presence of different inorganic salts [16,17]. Typical aqueous dilutions of polyoxyethylene

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Scheme 1. Chemical structures of employed fatty alcohol polyoxyethylene ether carboxylate surfactants, $n = 4$ and 7 .

alkyl ether carboxylic surfactants have substantial gel regions [11]. However, to the best of our knowledge, systematic studies on the self-assembly of polyoxyethylene ether – anionic surfactants in aqueous solution, especially studies on the driving force on the formation of micelle and lyotropic liquid crystal (LLC) were rarely reported.

Based on this motivation, two fatty alcohol polyoxyethylene ether carboxylate surfactants with their chemical structures given in Scheme 1 were employed in this work. Their phase behaviors in water at room temperature were characterized by surface tension measurement, polarizing optical microscopy (POM), and small-angle X-ray scattering (SAXS). As the differences in surface activities and phase behaviors have been reported to closely connect with the EO chain length, the obtained results should lead us to a better understanding of the relationship between molecular structure and physicochemical properties.

2. Material and methods

2.1. Materials

The fatty alcohol polyoxyethylene ether carboxylate surfactants (NEX- n , where n is the number of oxyethylene units, $n = 4$ and 7), namely, sodium tetraethylene glycol monotridecyl ether carboxylate, NEX-4 and sodium heptaethylene glycol monotridecyl ether carboxylate, NEX-7 were kindly supplied by Nikko Chemicals Shanghai Co., LTD. The reagents were used without further purification. Triply distilled water was used throughout the experiments.

2.2. Methods

2.2.1. Surface tension measurements

Surface tension measurements were performed on a QBYZ-2 automatic surface tensiometer automatic tensiometer (Shanghai Fangrui Instrument Co. Ltd., accuracy ± 0.01 mN/m) with the Wilhelmy plate method. The uncertainty of the surface tension measurements is ± 0.2 mN m^{-1} . Temperatures were controlled by a super constant temperature trough with an accuracy of ± 0.1 °C. All measurements were repeated at least twice until the values were reproducible.

2.2.2. Electrical conductivity measurements

To calculate the degree of counterion dissociation (α) of micelles, the electrical conductivities were determined by DDS-11A conductivity analyzer (Shanghai Shengci Instrument Co. Ltd., accuracy $\pm 1\%$). Temperatures were controlled by a super constant temperature trough with an accuracy of ± 0.1 °C.

2.2.3. Dynamic light scattering (DLS) measurements

The size of micelles in ILs was measured by DLS using a Malvern Zetasizer Nano (UK). The viscosity (η) value of 0.8872 cP and refractive index (n) value of 1.330 for water at 25 °C, which are necessary for DLS measurements, were adopted in this work.

2.2.4. Polarized optical microscopy (POM) measurement

The texture types of the formed lyotropic liquid crystalline phases were taken by a Nikon POM with a CCD camera (Nikon eclipse LV100ND POL/DS).

2.2.5. Small-angle X-ray scattering (SAXS) measurement

The structural characterization of LLC phases was performed using small angle X-ray scattering (SAXSess Anton-Paar, Austria) with a Cu K α radiation (0.154 nm) operating at 50 kV and 40 mA. The distance from samples to detector was 261 mm. Excepted as noted, the temperature was kept at 25.0 ± 0.1 °C.

3. Results and discussion

The aggregation behaviors of NEX- n in water vary with their concentration. The observed phase behaviors are analyzed and discussed based on micelle and lyotropic liquid crystalline regions.

3.1. Surface activities and micelle regions of NEX- n surfactants

The surface tension (γ) profiles with NEX- n concentration respectively in water were measured to explore their aggregation behaviors at 25 °C. As shown in Fig. 1, the γ values of both NEX- n /H $_2$ O systems decrease with increasing the surfactant concentration. At higher concentration, the surface tension becomes more or less constant. The concentration corresponding to the flex point on the surface tension curve is assigned to the CMC of NEX- n . Such an abrupt change of γ suggests the formation of micelles both in water, which phenomenon is similar to the conventional nonionic or anionic surfactant aqueous solutions [1]. As we known, the nonionic surfactants with longer polyoxyethylene chain have the higher CMC values [1]. While, the CMC of NEX-7 surfactant with more oxyethylene units ($\sim 2.91 \times 10^{-4}$ mol/L) is a little lower than that of NEX-4 ($\sim 3.12 \times 10^{-4}$ mol/L). Moreover, it can also be found that the oxyethylene groups make NEX- n surfactants have much lower CMC than that of sodium myristate in water ($\sim 4.0 \times 10^{-3}$ mol/L) [18]. Hence, we speculate that the increasing oxyethylene chain could result in the aggregation of NEX- n to micelle easier in water. This phenomenon also appear in sodium polyethylene glycol monoalkyl ether sulfate (SLES) aqueous solutions [19], but quite different from most nonionic surfactants systems [20,21]. It can be speculated that the presence of oxyethylene chain could reduce the intramicellar headgroup electrostatic repulsion, which is supported by other related researches on

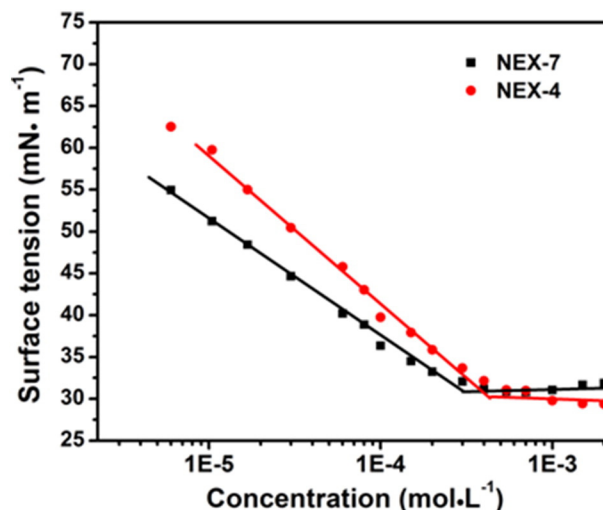


Fig. 1. Surface tension profiles for NEX- n aqueous solutions at 25.0 °C.

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