



# Properties of branched alcohol polyoxyethylene ether carboxylates

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## ABSTRACT

A novel anionic surfactant alcohol polyoxyethylene ether carboxylates with three branched chains ( $A_{13}EC_5\text{-Na}$ ,  $A_{13}EC_7\text{-Na}$ ) were studied in the paper. Their surface properties were investigated by surface tension and dynamic surface tension. It was found that branched surfactants showed lower surface tension, which can decrease the surface tension of water to around 27 mN/m. The critical micelle concentration (CMC) of  $A_{13}EC_5\text{-Na}$  is lower than that of  $A_{13}EC_7\text{-Na}$ . What's more,  $A_{13}EC_5\text{-Na}$  molecules can adsorb to the surface faster than  $A_{13}EC_7\text{-Na}$ . The wetting abilities, emulsifying capacities, foam ability and detergency of branched surfactant aqueous solutions were studied in contrast to that of linear surfactants. The wetting ability of  $A_{13}EC_5\text{-Na}$  is better than that of  $A_{13}EC_7\text{-Na}$ . Compared with linear alcohol polyoxyethylene ether carboxylates ( $A_{12}EC_5\text{-Na}$ ,  $A_{12}EC_7\text{-Na}$ ), branched surfactants exhibit preferable wetting ability. Broadly speaking, the emulsifying capacities of branched surfactants for liquid paraffin and soybean oil are relatively good than that of linear surfactants. When the hydrophobic chains are the same, the emulsifying capacities of surfactants with smaller oxyethene (EO) number for liquid paraffin and soybean oil perform better. The foam ability and foam stability of  $A_{12}EC_5\text{-Na}$  are the best. The foam ability of  $A_{13}EC_7\text{-Na}$  is better, but the foam stability is poor. In short, the foam stability of branched surfactants is inferior to that of linear surfactants. The detergency performance of linear and branched surfactants to sebum cloth performs the best compared with protein stain and carbon black cloth. The detergency effect of  $A_{12}EC_7\text{-Na}$  for sebum cloth is the best,  $A_{13}EC_7\text{-Na}$  takes second place and  $A_{13}EC_5\text{-Na}$  is the worst. Branched surfactants are expected to become a promising product for their outstanding wetting abilities and emulsifying capacities and their better foam ability and detergency.

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## 1. Introduction

The adsorption and micellization of surfactants at the water-air interface play an important role in the properties of water. The adsorption of surfactants can decrease the surface tension of water, which provides the possibility for a series of applications of surfactants [3,7,9,13,18,31]. Studying the physicochemical properties (like surface tension, dynamic surface tension, contact angle of the synthesized surfactants is of great importance to explore the adsorption behavior of surfactants. The self-assembly of surfactant molecules on liquid-liquid or solid-liquid surface has promoted the application of surfactants in emulsions, foaming, detergent formulations and enhanced oil recovery. There are other researchers [19–21,26] studying the adsorption behavior of anionic surfactants at air-water and polymer-water interface.

As is known to us all, surfactants include generally nonionic, anionic, cationic and zwitterionic surfactants, of which anionic surfactants show a wide use in industry [6]. After all, traditional surfactant molecules consist of generally one hydrophilic head group and one hydrophobic

moiety in a single molecule [36]. Fatty alcohol polyoxyethylene ether carboxylate (AEC) and sulfonate (AES) have been popular with people due to their excellent performances in surface activity, wetting ability, emulsifying property and the capacity to decrease the interfacial tension (IFT) between oil and water [1,2,23,28,29,32]. AEC can be considered to be a derivative of nonionic surfactants fatty alcohol polyoxyethylene ether (AEO), whose structure contains two hydrophilic groups ( $-\text{CH}_2\text{CH}_2\text{O}-$  and  $-\text{CH}_2\text{COO}-$ ), thus AEC could possess good water solubility, biodegradability, salt tolerance and resistance to hard water, furthermore extending the application in cosmetics formulations and the enhanced oil recovery [12,16,17,22]. The surface adsorption and aggregation behavior of AEC may be regulated by changing the number of -EO- and the length of hydrophobic chain [5].

Wang and Yang [27] concluded that the introduction of oxyethene (EO) into anionic surfactants would contribute to their preferable surface activities, wetting abilities and adsorption efficiency. Song et al. [24] elucidate the relationship between foaming properties and surfactant structures of polyoxyethylene alkyl ether carboxylic salts aqueous solutions by dynamic surface tension, foaming properties and surface dilatational properties. They proposed that dynamic surface tension was closely related to the decision of foamability: The longer the hydrophobic group length, the lower the dynamic surface activity and the higher

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the foam volume; surfactants with branched chain had higher dynamic surface activity and higher foam volume. Zhang et al. [33] also studied the dynamic dilational viscoelastic properties of polyoxyethylene alkyl ether carboxylic salts at the air-water interface and foam stability. Their results showed straight-chain surfactants with the highest dilational modulus exhibited the best foam stability. However, they cannot explain the foam stability of branched chain surfactants by film elasticity alone.

In our research, we chose branched alcohol polyoxyethylene ether carboxylates with different EO number ( $A_{13}EC_5\text{-Na}$ ,  $A_{13}EC_7\text{-Na}$ ) to study their physicochemical properties and adsorption rate by surface tension and dynamic surface tension measurement. The wetting ability, emulsifying ability, foaming properties and detergency of branched alcohol polyoxyethylene ether carboxylates ( $A_{13}EC_5\text{-Na}$ ,  $A_{13}EC_7\text{-Na}$ ) and straight chain alcohol polyoxyethylene ether carboxylates ( $A_{12}EC_5\text{-Na}$  and  $A_{12}EC_7\text{-Na}$ ) were investigated by a series of methods in national standard, of which straight chain surfactants were seen as contrast. Furthermore, we attempted to correlate the relationship between the application performance and surface tension and dynamic surface properties of surfactant aqueous solutions.

## 2. Experimental section

### 2.1. Materials

Branched and linear chain alcohol polyoxyethylene ether carboxylates ( $A_{13}EC_5\text{-Na}$ ,  $A_{13}EC_7\text{-Na}$ ,  $A_{12}EC_5\text{-Na}$  and  $A_{12}EC_7\text{-Na}$ ) were obtained from China Research Institute of Daily Chemical Industry.  $A_{12}EC_5\text{-Na}$  and  $A_{12}EC_7\text{-Na}$  were used to make comparison. Their structures were showed in Scheme 1. Liquid paraffin was purchased from Tianjin University Chemical Reagents Co. Ltd. Soybean oil marked with Arawana was purchased by Qinhuangdao, Hebei province.

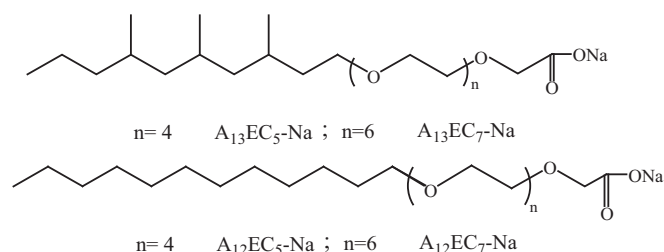
### 2.2. Properties

#### 2.2.1. Surface tension

The measurements of surface tension of samples were carried out by a Krüss K12 Processor Tension meter with Wilhelmy plate method. We must prepare surfactant solutions in advance using double-distilled water to stand for one day. And originally the surface tension of double-distilled water was measured to adjust the instrument, which was deemed to be  $72.0 \pm 0.5$  mN/m. The experimental temperature was controlled to  $25 \pm 0.1$  °C and every sample solution was repeated three times to reduce the error. The error of the surface tension is controlled in  $\pm 0.2$  mN/m.

#### 2.2.2. Dynamic surface tension

The dynamic surface tension of surfactant aqueous solutions was performed at  $25 \pm 0.1$  °C by a Krüss bubble pressure tensionmeter BP100 method, which was used to measure the maximum pressure by blowing a bubble in a liquid from the tip of a capillary. Effective surface ages of the measurements range from 0.01 s to 250 s. The error of dynamic surface tension is  $\pm 0.2$  mN/m.



Scheme 1. Chemical structures of AEC.

### 2.2.3. Wetting ability

The wetting abilities of samples were measured by canvas sedimentation [11]. Different concentration of surfactant solutions was prepared in advance into 1000 mL beaker. A canvas was immersed to the surfactant solution at room temperature, after some time, the canvas was permeated by surfactant solutions and began to sink. We generally record the period from immersion to sinking to evaluate the wetting ability. The above operation was repeated 5 times. The average value is wetting time of surfactant solutions. The accuracy of wetting time is within  $\pm 1$  s.

### 2.2.4. Emulsifying ability

The emulsifying abilities of samples were measured in the mixing cylinder with stopper of 100 mL. About 40 mL surfactant solutions and 40 mL liquid paraffin or soybean oil were added into the 100 mL cylinder together and shaken up and down five times vigorously each minute [34]. Record the time of separating 10 mL water from the emulsion. The above operation was repeated five times to obtain average value. The emulsifying capacity was judged by the time of separating water. The longer the time, the better the emulsifying ability of the surfactant. The error of emulsifying time is within  $\pm 2\%$ .

### 2.2.5. Foaming properties

We measured the foaming properties of samples by modified Ross-Miles method at the temperature of 50 °C [10]. Surfactant solutions (1.5 g/L) were prepared to stand for one night. Before the experiment, sample solutions and water circulation system were preheated to 50 °C. Then pour 500 mL solutions to the top of the flask from the height of 450 mm. record the foam volume at 30 s, 3 min and 5 min. We generally evaluate the foaming power by the foam volume of 30 s. And we evaluate the foaming stability by the ratio of the foam volume at 5 min and 30 s. The reproducibility in foaming volume is found to be  $\leq 15$  mL.

### 2.2.6. Detergency

The detergency of  $A_{13}EC_5\text{-Na}$ ,  $A_{13}EC_7\text{-Na}$ ,  $A_{12}EC_5\text{-Na}$  and  $A_{12}EC_7\text{-Na}$  surfactants was investigated by a RIDCI RHLQ washing machine. The concentration of studied surfactants was set at 1 g/L (active content) which was confected by using 250 ppm hard water. The detergency test was operated with a wash cycle of 20 min at the agitation speed of 120 rpm and the temperature of 30 °C. We selected protein stain, sebum cloth and carbon black cloth to do the experiment and they were dried at room temperature. The values of whiteness before and after washing were measured by a Kangguang WSD-3C whiteness meter. The detergency abilities were evaluated by the difference value of whiteness after and before washing. The error of whiteness value is  $< \pm 2\%$ .

## 3. Results and discussion

### 3.1. Static surface tension

The measurement of surface tension is indispensable, by which we can know the critical micelle concentration (CMC) and surface tension at this concentration ( $\gamma_{cmc}$ ) of surfactant solutions. The static surface tensions of  $A_{13}EC_5\text{-Na}$  and  $A_{13}EC_7\text{-Na}$  aqueous solutions were measured to explore their surface abilities. Surface tension of the surfactant solutions with different concentrations were carried out at 298 K. As is shown in Fig. 1, we can observe that the surface tension curve of  $A_{13}EC_5\text{-Na}$  solution is different from that of  $A_{13}EC_7\text{-Na}$  solutions. For  $A_{13}EC_5\text{-Na}$ , surface tension decreases firstly and then keeps stable. However, surface tension of  $A_{13}EC_7\text{-Na}$  decreases firstly with the increase of the concentration, and it has two breaks which were deemed to have vesicle to micelle transition [35]. The CMC can be obtained by calculating the surface tension as a function of the concentration. Other parameters like the maximum surface excess concentration ( $\Gamma_m$ ) and the

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