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



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# A R T I C L E I N F O

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## 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) leaded 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

# ABSTRACT

A branched alkyl polyoxyethylene ether alcohol sulfate, sodium isooctyl polyoxyethylene ether sulfate (i-OE<sub>3</sub>S), was synthesized and its physic-chemical properties were investigated systematically. The experiment on Krafft point gave a result that the Krafft temperature of i-OE<sub>3</sub>S was below 0 °C. The measurement of static surface tension showed that the critical micelle concentration (cmc) and surface tension at cmc ( $\gamma_{cmc}$ ) of i-OE<sub>3</sub>S were 21.67 mmol·L<sup>-1</sup> and 27.4 mN·m<sup>-1</sup>, respectively. From the results of dynamic surface tension (DST) measurements, we could obtain that the adsorption of i-OE<sub>3</sub>S 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-OE<sub>3</sub>S aqueous solution on paraffin film was investigated by dynamic contact angle and the results demonstrated that i-OE<sub>3</sub>S possessed an excellent spreading ability.

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that the introduction of EO units in the anionic surfactants might enhance the  $Ca^{2+}$ -tolerance of original surfactants through molecular dynamics simulation.

Compared to straight chain surfactants, the branched tail surfactants possess excellent properties, including lower  $\gamma_{cmc}$  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 (SO<sub>3</sub>) 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.

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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<sub>3</sub> 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-OE<sub>3</sub>S) was synthesized using bubbling SO<sub>3</sub> 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-OE<sub>3</sub>S were investigated systemically by various measurements. Sodium octyl ethoxy sulfate (OE<sub>3</sub>S) and sodium isooctyl sulfate (i-OS) were also synthesized for comparing with i-OE<sub>3</sub>S on Krafft point, static surface tension, and dynamic contact angle. Moreover, DST and aggregation behavior of aqueous solution of i-OE<sub>3</sub>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 M $\Omega$ ·cm was used from a UPD-II ultrapure water purifier.

FT-IR for i-OE<sub>3</sub>S was detected from the product absolute ethanol solution smearing onto KBr prisms with a Bruker Vertex-70 spectrometer. <sup>1</sup>H NMR spectra was determined in CDCl<sub>3</sub> using a Varian INOVA-400 MHz spectrometer.

## 2.2. Synthesis

The product, i-OE<sub>3</sub>S, was synthesized via a three-step reaction according to Scheme 1.

#### 2.2.1. Synthesis of isooctyl polyoxyethylene ether alcohol ( $i-OE_3$ )

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<sub>2</sub> 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<sub>2</sub> for discharge. The product, with an average of about 3 EO, was obtained after removing catalyst by filtration.

### 2.2.2. Synthesis of i-OE<sub>3</sub>S

- 1) Preparation of liquid SO<sub>3</sub>: 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<sub>3</sub> was collected through the condensation of SO<sub>3</sub> vapor evaporating from the fuming sulfuric acid and stored in a constant-temperature funnel at  $36^{\circ}$ C.
- 2) Synthesis of i-OE<sub>3</sub>S: The sulfation took place in a set-up assembled by research group as shown in Fig. 1. Liquid SO<sub>3</sub> (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<sub>3</sub> vapor was diluted with nitrogen which has a constant velocity of 0.14 m<sup>3</sup>/h. Then, the mixed well gas in the middle flask was passed bubble by bubble into the i-OE<sub>3</sub> (131.12 g) placed in a three-necked 500 mL roundbottom flask at (40  $\pm$  1) °C. The esterified product was neutralized by 30 wt.% aqueous sodium hydroxide to pH = 8 gradually in an ice–water bath.

The raw product was dried under vacuum at 55 °C after extracting the unreacted i-OE<sub>3</sub> 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-OE<sub>3</sub>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) °C. Ultrapure water with a surface tension of (72.1  $\pm$  0.2) mN·m<sup>-1</sup> was used for



Scheme 1. The Synthetic route of i-OE<sub>3</sub>S.



Fig. 1. The simplified diagram of sulfation reactor.

calibration before measuring to prove that the system was thoroughly clean.

# 2.5. DST

DST was investigated by a Krüss BP100 bubble-pressure tensiometer (Krüss Company, Germany, accuracy  $\pm 0.01 \text{ mN} \cdot \text{m}^{-1}$ ) at 25 °C. Ultrapure water was performed for determining the internal diameter of capillary before measuring. The parameter of effective surface ages was set ranging from 10 to 50,000 ms.

# 2.6. TEM

The microstructures of i-OE<sub>3</sub>S aggregates in solution were observed through a JEM-1011 transmission electron microscopy (JEOL Co, Japan) by negative staining at an acceleration voltage of 100 kV. A carbon-coated grid was used as the substrate to load a thin sample film by adding i-OE<sub>3</sub>S solution and then staining reagent (2 wt.% phosphotung-stic acid). In the process of film preparation, the first and second solutions all need to equilibrate for at least 3 min and blot the excess liquid with a filter paper at room temperature.

#### 2.7. Dynamic contact angle

The spreading ability of surfactants at the air/liquid/solid interface was measured by the contact angle of droplet on hydrophobic substrate using a drop shape analyzer DAS-100 (Krüss Company, Germany, accuracy  $\pm 0.1^{\circ}$ ). Paraffin film for water with a contact angle of  $(106 \pm 2)^{\circ}$  was chosen as the solid substrate [24]. Each experiment was repeated at least three times at an environmental humidity of  $(50 \pm 5)$ %.

# 3. Results and discussion

# 3.1. Structure characterization

The FT-IR spectra of  $i-OE_3$  and  $i-OE_3S$  are shown in Fig. 2. From Fig. 2(A), we can see that the major characteristic peak (-OH) of  $i-OE_3$  (B) at 3400 cm<sup>-1</sup> disappears basically while the strong peaks assigning to the C–O–SO<sub>3</sub> group for  $i-OE_3S$  (A) at 1245 cm<sup>-1</sup> and 755 cm<sup>-1</sup> are presenting. The phenomenon announces that  $i-OE_3S$  is synthesized through the insertion of SO<sub>3</sub> into the –OH of  $i-OE_3$ . The presence of the weak hydroxyl peak in Fig. 2(A) is mainly due to the high water absorptivity of  $i-OE_3S$ . Furthermore, since the test sample

was prepared by coating i-OE<sub>3</sub>S ethanol solution on potassium bromide tablet, the residue of ethanol solvent may also contribute to the result.

The <sup>1</sup>H NMR spectrum of i-OE<sub>3</sub>S is illustrated in Fig. 3. In view of the multiple distributions of EO units of the compound, the chemical shifts of hydrogen atoms are piled up, meanwhile, the peaks can just measure the number of hydrogen atoms of characteristic groups through integral quantities and chemical shifts. The assignments of the peaks are as follows:  $\delta$ : 0.873 (6 H, -CH<sub>3</sub>), 1.267 (8 H, -(CH<sub>2</sub>)<sub>4</sub>–), 1.546 (1 H, methylidyne), 3.320 (2 H, -CH<sub>2</sub>–O–), 3.62–3.78 (8 H, -OCH<sub>2</sub>CH<sub>2</sub>O–), 3.921 (2 H, -O–CH<sub>2</sub>–), 4.280 (2 H, -CH<sub>2</sub>OSO<sub>3</sub>–), and 7.260 (CDCl<sub>3</sub>). The analysis of FT-IR and <sup>1</sup>H NMR indicated that i-OE<sub>3</sub>S was successfully obtained.

## 3.2. Krafft point

For micellization of ionic surfactants to occur at a given pressure, there is an equilibrium state at which micelles and monomers are concomitant with solid hydrated surfactant at a particular temperature which is called Krafft point. With further increase of the certain temperature, the solubility of ionic surfactants exceeds its cmc and has a rapid



Fig. 2. FT-IR spectra of i-OE<sub>3</sub>S (A) and i-OE<sub>3</sub> (B).



Fig. 3. <sup>1</sup>H NMR spectrum of i-OE<sub>3</sub>S.

increase so that it enhances its applications in oil recovery and washing industry [15,20]. The system of i-OE<sub>3</sub>S appeared clear solution at  $-4^{\circ}$ C in this study, thus, we believe its Krafft point is below 0 °C. The data for OE<sub>3</sub>S and i-OS was listed in Table 1. It can be seen that i-OE<sub>3</sub>S containing both branched tail and EO units has a lower Krafft point than the surfactants with single branched tail or EO units. The case is caused by two reasons: (1) the intermolecular interaction of solid surfactant is weakened by the introduction of branched tail, and (2) the presence of EO unit makes a contribution to the formation of hydrogen bonds between the polar groups of surfactant and water [20,25]. Because of its structure superiority, the surfactant molecules can separate from its solid state and then combine with water molecules easily so that its solubility has an increase while Krafft point decreases.

# 3.3 Static surface tension

The curves of surface tensions  $(\gamma)$  versus the logarithm of the bulkphase concentration in moles per liter for aqueous solution of surfactants



Fig. 4. Plots of surface tension against log molar concentration of i-OS, OE\_3S, and i-OE\_3S at 25  $^\circ\text{C}.$ 

are shown in Fig. 4. It can be seen that the  $\gamma$  of these surfactants decreased with the variation of concentration which indicated that the surfactant molecules have spread to air/liquid interface. Owing to the multiple distributions of EO units of the compounds, forming the premicellar aggregations, a double inflection point phenomenon is provided in the curves of  $\gamma$  against lgC [26]. The values of cmc and corresponding surface tension  $(\gamma_{cmc})$  are determined by the crossover point of two fitted straight lines of the downward sloping portion and the plateau portion of the plots, and then summarized in Table 1. It can be seen that the values of  $\gamma_{\rm cmc}$ for i-OS, OE<sub>3</sub>S, and i-OE<sub>3</sub>S were 31.5, 28.5, and 27.4 mN $\cdot$ m<sup>-1</sup>, while their cmc were 20.65, 14.11, and 21.67 mmol $\cdot$ L<sup>-1</sup>, respectively. The values for OE<sub>3</sub>S show a basic agreement with those of Li et al. [27]. As a result of the reduction of the effective hydrocarbon chain length by the introduction of branching and the formation of steric hindrance to micellization, the cmc of i-OE<sub>3</sub>S is larger than the value of straight chain surfactant with equal carbon atoms [8]. Since the insertion of EO groups lead to the separation between hydrophobic chain and hydrophilic groups, causing an increase in the area of the polar head groups and a disperse molecular arrangement in solution [28], the cmc of i-OE<sub>3</sub>S should have a decline comparing with that of i-OS. However, the result showed that the cmc of i-OE<sub>3</sub>S was nearly equal to that of i-OS. Barry and Wilson [29] gave an explanation that the effect of the polar group of surfactant molecule on cmc have a limit.

The surface excess concentration ( $\Gamma_{max}$ ) and the minimum area per molecule ( $A_{min}$ ) at the cmc are calculated by the Gibbs adsorption isotherm equations [30] (Eqs. (1) and (2)) and listed in Table 1.

$$\Gamma_{\max} = -\frac{1}{2.303nRT} \left( \frac{\partial \gamma}{\partial \lg C} \right)_T \tag{1}$$

Table 1

Parameters obtained from Krafft point and static surface tension measurements for i-OS, OE<sub>3</sub>S, and i-OE<sub>3</sub>S.

Surfactants	Krafft point °C	$\frac{\text{cmc}}{\text{mmol} \cdot L^{-1}}$	$rac{\gamma_{cmc}}{mN\cdot m^{-1}}$	$\frac{\Gamma_{max}}{mmol \!\cdot\! m^{-2}}$	$\frac{A_{min}}{\mathring{A}^2}$	pC <sub>20</sub>
i-OS	1	20.65	31.5	0.62	268.8	2.5
OE <sub>3</sub> S	6.5	14.11	28.5	0.52	316.5	3.3
i-OE <sub>3</sub> S	<0	21.67	27.4	0.39	422.9	3.5

$$A_{\min} = \frac{10^{16}}{N_A \Gamma_{\max}}$$
(2)  
$$pC_{20} = - lgC_{20}$$
(3)

where *n* is the Gibbs prefactor (for anionic surfactants, n = 2), *R* is the gas constant (8.314 J·mol<sup>-1</sup>·K<sup>-1</sup>), *T* is the absolute temperature, and  $N_4$  is the Avogadro's constant. From Table 1, we can see that the A<sub>min</sub> for i-OE<sub>3</sub>S solution at the air/liquid interface is larger than those of OE<sub>3</sub>S and i-OS, while its  $\Gamma_{max}$  is the lowest. There are three factors that contribute to the result: (1) the increased bulkiness of hydrocarbon chain by the presence of branching, (2) the increased repulsion between the polar groups by the effect of EO groups, (3) the flexible polyoxyethylene chains presenting in curling structure [3,7,8,20]. The adsorption efficiency at the air/liquid interface is indicated by a parameter  $pC_{20}$  proposed by Rosen et al. [31]. It denotes the negative logarithm of the surface active agent concentration (Eq. (3)), at which the surface tension is 20 mN $\cdot$ m<sup>-1</sup> lower than that of pure solvent. With the increase of the  $pC_{20}$  value, the adsorption efficiency of the surfactant increases. The value of pC<sub>20</sub> for i-OE<sub>3</sub>S is 3.5, which is larger than 3.3 and 2.5 for OE<sub>3</sub>S and i-OS, respectively. The reason may be that the curly EO units fill the interval of voluminous branched tails. Then, the close ordered assembly of surfactant molecules at the air/liquid interface can produce a visible increase in the efficiency of surface tension reduction [20].

# 3.4 Dynamic surface tension

The kinetics of surfactant adsorption is frequently studied by DST data measured by the maximum bubble pressure technique at the air/liquid interface [32–35]. The variations of DST data with surface age for i-OE<sub>3</sub>S solutions at different concentration are plotted in Fig. 5. It shows that the concentrated solutions of i-OE<sub>3</sub>S take shorter time than the dilute solutions to reduce the equal surface tension coinciding with Fick's first law.

For the solutions with concentrations below the cmc, the transfer process of surfactant molecules from bulk phase to subsurface can be illustrated by Word–Tordai equation [36]. The diffusion adsorption model is described as Eq. (4).

$$\Gamma_{(t)} = 2C_0 \sqrt{\frac{Dt}{\pi}} - 2\sqrt{\frac{D}{\pi}} \int_0^{\sqrt{t}} C_s d\left(\sqrt{t-\tau}\right)$$
(4)

The parameters  $\Gamma_{(t)}$ , *t*, *C*<sub>0</sub>, *D*, *C*<sub>s</sub>, and  $\tau$  denote the dynamic surface concentration, reference time, bulk concentration, monomer diffusion



Fig. 5. DST for i-OE<sub>3</sub>S aqueous solutions with different concentrations at 25 °C.



Fig. 6. Variation of DST with  $t^{1/2}$  for i-OE<sub>3</sub>S aqueous solutions with different concentrations at 25 °C.

coefficient, subsurface concentration, and dummy time delay variable, respectively. When *t* is approaching zero, so is the value of C<sub>s</sub>. Then, the latter item indicating the surfactant diffusing back from subsurface to bulk phase can be omitted. Finally, we obtain Fig. 6 and Eq. (5) involving a linear relation between  $\gamma_{(t)}$  and  $t^{1/2}$  inferred from Henry's equation for analyzing the short-time adsorption behaviors. When *t* tends to infinite, equilibrium appears between the diffusion from subsurface to bulk and that from bulk to subsurface, which means that C<sub>0</sub> is nearly equal to C<sub>s</sub>. As a simplification, the integral formula is also ignored. In this case, Fig. 7 and Eq. (6) also presenting a linear relation between  $\gamma_{(t)}$  and  $t^{-1/2}$  is developed by Gibbs adsorption equation to process the long-time surface tension data.

Where  $\gamma_{(t)}$  and  $\gamma_{eq}$  refer to the surface tension at time *t* and *t* approaching to infinite respectively,  $\Gamma_{eq}$  is the equilibrium surface excess concentration,  $D_s$  and  $D_l$  indicate the diffusion coefficients for short-time and long-time adsorption processes respectively, *n* is 2 for ionic surfactant [34]. Both of short-time and long-time adsorption models presenting the linear relations can be deduced by fitting linear slopes to calculate the diffusion coefficient D listed in Table 2. For short-time adsorption process,  $D_s$  increases with the increase of solution concentration due to the presence of concentration gradient between subsurface and bulk phase. For long-time adsorption behavior,  $D_l$  decreases with the increase of solution concentration. We believe the



Fig. 7. Variation of DST with  $t^{-1/2}$  for i-OE\_3S aqueous solutions with different concentrations at 25  $^\circ\text{C}$ .

# Table 2

Diffusion coefficients and corresponding coefficient ratios of i-OE<sub>3</sub>S aqueous solutions with different concentrations at 25  $^\circ\text{C}$ .

Concentration (mmol· $L^{-1}$ )	$D_{s}(m^{2} \cdot s^{-1})$	$D_l (m^2 \cdot s^{-1})$	$D_s/D_l$
0.10	$1.76\times10^{-11}$	$\textbf{3.49}\times\textbf{10}^{-13}$	50.43
0.47	$1.92 \times 10^{-11}$	$1.69 \times 10^{-14}$	$1.14  imes 10^3$
0.94	$2.64 \times 10^{-11}$	$5.08 \times 10^{-15}$	$5.20  imes 10^3$
1.88	$2.85 \times 10^{-11}$	$7.54  imes 10^{-16}$	$3.78 imes10^4$
5.13	$5.47  imes 10^{-11}$	$1.00\times10^{-16}$	$5.47  imes 10^5$

main reason is that the free motion among the molecules is limited when the surfactant concentration of subsurface is approaching to that in bulk phase for long-time adsorption. The ratios of  $D_s/D_l$  are also listed in Table 2. The large ratios indicate that the adsorption process of i-OE<sub>3</sub>S is controlled by the mixed diffusion–kinetic adsorption.

$$\gamma_{(t)} = \gamma_0 - 2C_0 nRT \sqrt{\frac{D_s t}{\pi}} \tag{5}$$

$$\gamma_{(t)} = \gamma_{eq} + \frac{nRT}{2C_0} \Gamma_{eq}^2 \sqrt{\frac{\pi}{D_l t}}$$
(6)

# 3.5 Aggregation behavior of i-OE<sub>3</sub>S in aqueous solution

When the concentration of surfactant aqueous solution is above its cmc, surfactant molecules can self-assemble into ordered architecture to minimize the interfacial energy [37]. In order to investigate the morphology and size of the aggregates formed in i-OE<sub>3</sub>S solutions, TEM, an intuitive and reliable technique, was performed to visualize their ultra-structure. The TEM images show that the self-assembled microaggregates of i-OE<sub>3</sub>S present spherical structures with a range of diameters from 263 to 423 nm at a concentration of 100 mmol·L<sup>-1</sup>, and from 273 to 606 nm at 200 mmol·L<sup>-1</sup> in Fig. 8.

Compared to the normal spherical micelles with diameters of less than 100 nm, the aggregates shown in Fig. 8 are larger [38]. Aoudia M. et al. [3] took the view that the micelle size of AES, increasing with the EO units, has no relation with the average micelle aggregation number but with the micelle structure alteration due to the rearrangement of the surfactant molecules in the micelle. For the formation of micelles, a loose structure is needed to accommodate the larger polar head groups due to the introduction of EO units in the surfactant which lies at the periphery of the micelle–water. Moreover, it is widely accepted that the presence of condition near thermodynamic equilibrium and the driven forces such as hydrophobic forces, hydrogen bonding and van der Waals all make some degree of contribution to the formation and isolation of aggregates [32]. In this case, we believe that the amphiphilic aggregates formed in water were mainly driven by the



Fig. 9. Variation of dynamic contact angle of  $i-OE_3S$  aqueous solutions with different concentrations on parafilm surface at 25 °C.

cooperation between the branched hydrocarbon hydrophobic forces and hydrogen bonding on the EO hydrophilic shells.

# 3.6. Dynamic contact angle

The contact angle  $(\theta)$  is used to investigate the air/liquid/solid interfacial properties reflecting a time-dependent adsorption balance of surface active agent [39]. Fig. 9 shows the  $\theta$  of i-OE<sub>3</sub>S aqueous solutions on paraffin film as a function of time with different concentrations. It indicates that the equilibrium value of  $\theta$  decreases with an increase in concentration. The dynamic spreading behaviors of i-OE<sub>3</sub>S, i-OS, and  $OE_3S$  with equal concentration (80 mmol·L<sup>-1</sup>) were studied by the variation of  $\theta$  near the leading edge versus the time on paraffin film in Fig. 10, in which  $\theta$  of i-OE<sub>3</sub>S reaches a lower value (51.51°) in a short time. The spreading behavior can be divided into short-time process and long-time process. The former is called fast spreading controlled by the gradient of surface tension along the air/liquid interface, while the latter is known as slow spreading driven by the transfer of surfactants from bulky phase to the new surface [40]. Varadaraj et al. [18] held the view that the rigid structure and increased A<sub>min</sub> of surfactant with branched tail strengthen the interactions between hydrophobic chains and the lipophilic film with low energy, hence, the branching lower the  $\theta$  of droplet and enhance the water spreading property on paraffin surface. Ruckenstein E. [41] suggested that one structure like bilayer is formed on a low energy substrate to spread water rapidly. The hydrophobic chains of the first layer are absorbed on the solid surface while polar groups extend into water, meanwhile,



Fig. 8. Negative-stained TEM images of aggregates formed in i-OE<sub>3</sub>S solutions: (A) 100 mmol·L<sup>-1</sup> and (B) 200 mmol·L<sup>-1</sup>.



Fig. 10. Dynamic contact angle for i-OE<sub>3</sub>S, i-OS, and OE<sub>3</sub>S on parafilm surface as a function of time at a concentration of 80 mmol $\cdot$ L<sup>-1</sup> at 25 °C.

the layer is covered by another layer with the polar groups of surfactants assembling to the polar groups of the first layer while the hydrophobic chains exposing to air. The structure contributes to the absorption of surfactant molecules at both solid/liquid and air/liquid interfaces and leads to a decrease in interfacial free energy controlling the spreading of solution.

# 4. Conclusions

A branched short-alkyl ethoxy sulfate was synthesized using SO<sub>3</sub> vapor as sulfating agent and characterized by FT-IR and <sup>1</sup>H NMR. The measurements of Krafft point, static surface tension, DST, TEM, and dynamic contact angle gave a wealth of information involving the physicochemical performances and aggregation behaviors of i-OE<sub>3</sub>S aqueous solution. Its Krafft point is lower than those of i-OS and OE<sub>3</sub>S. The cmc and  $\gamma_{cmc}$  of i-OE<sub>3</sub>S solution are 21.67 mmol·L<sup>-1</sup> and 27.4 mN·m<sup>-1</sup> and its adsorption mechanism is mixed diffusion-kinetic controlled adsorption. The spherical aggregates with a range of diameters from 263 to 606 nm are present in the solution with a concentration above its cmc. The contact angle of its droplet can reach a lower value than those of i-OS and OE<sub>3</sub>S in a short time. We believe that the presence of branching and EO groups makes the surfactant present low Krafft point and excellent surface active properties especially in adsorption efficiency and spreading behavior, meanwhile, the combination of high-speed spreading performance on low energy surface, low Krafft point, and formation of spherical assemblies in aqueous solution may contribute to the wonderful applications of i-OE<sub>3</sub>S in agriculture adjuvant and washing industry.

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