## Article

## Synthesis and Micellar Behaviors of an Anionic Polymerizable Surfactant

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A novel anionic polymerizable surfactant sodium (5-acryloyl-2-(dodecyloxy)phenyl) methane sulfonate has been synthesized from phenol, acrylic acid and bromododecane by esterification, Frise rearrangement, sulfomethylation reaction and Williamson etherification. The parameters of the micellar behaviors are as follows: The CMC was 150 ppm at 40 °C; The surface absorption amounts  $\Gamma_m$  was  $3.208 \times 10^{-6}$  mol m<sup>-2</sup>; The molecular areas  $A_m$  was  $0.550 \times 10^{-18}$ m<sup>2</sup> at the interface of air–water respectively; The aggregation number (N<sub>agg</sub>) at C = CMC of this surfactant was 12.

Keywords: Synthesis; Polymerizable surfactant.

### INTRODUCTION

Polymerizable surfactants have been widely used in industry and daily life. The precursors of surfactants are called surface-active monomer(abbreviated as surfmer), which contain hydrophobic tail, hydrophilic head group and polymerizable vinyl double bonds.<sup>1</sup> Due to wide applications in scientific research and industry, surfmer has been attracted more and more attention, such as in biological simulation, functional polymer microspheres and novel water-soluble hydrophobically associating polymers.<sup>2-7</sup> Especially, surfmer plays a very important role in the synthesis of hydrophobically associating polyacrylamide (HPAM), which contains a small proportion of hydrophobic groups, usually in the form of pendant side chains or terminal groups. Intermolecular hydrophobic interactions cause the formation of a transitory three-dimensional network of polymer chains in aqueous solution at certain polymer concentration. Thereby, because of the reversible dissociation process of the physical links occurring under shear, these polymers exhibit particular rheological properties in solution. For instance, HPAM can show interesting behavior as a function of shear rate or shear time, such as shear thinning or thixotropy. The rheological behavior of these compounds have led to great technological interest, especially for tertiary oil recovery.<sup>8-9</sup>

Surfmers were discovered by Freedman et al. in 1958 and much effort had been directed toward the synthesis and application of them. Most of the studies focused on the micellar behavior and the ability of polymerization of surfmers. Many satisfactory results have been acquired, but these surfmers are ester or amide, which were hydrolyzed in acidic or alkalic condition. So the surface tension increases sharply and the surfmers can not be used.<sup>10</sup> Phenyl ether is a kind of useful surfactant and no hydrolyzation is observed in acidic or alkalic condition. Based on this, a novel anionic surface-active monomer sodium (5-acryloyl-2-(dodecyloxy)phenyl) methane sulfonate has been synthesized. The  $\alpha,\beta$ -unsatuated group and sodium sulfomethyl group were introduced in to the phenyl ether segment by esterification, Fries rearrangement and sulfomethylation reaction respectively. The surfmer, which was synthesized by the above-mentioned methods was phenyl ether, and wasn't hydrolyzed in acidic or alkalic condition.

# **RESULTS AND DISCUSSION**

## The character of the surfactant

Because of having one hydrophilic head group (sulfonic acid group) and two hydrophobic groups (phenol ether chain and  $\alpha,\beta$  unsaturated ketone), the molecule of the surfactant (5a) in the Scheme 1 was obviously amphiphilic. According to the molecular structure character of the surfactant and previous works,<sup>1,3</sup> it could be speculated that the single hydrophilic head group extended into water, the hydrophobic groups got close to each other under the hydrophobic interaction, and finally the micelles were formed. Because there were two hydrophobic groups, and the long hydrophobic phenol ether chain would be bent, the micelles of the surfactant would be looser than some common surfactants, such as sodium dodecyl sulfate (SDS) and nonylphenol ether, which vertically arranged on the waterair surface when forming micelles.

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Scheme 1 Synthesis of sodium (5-acryloyl-2-(dodecyloxy)phenyl)methanesulfonate phenyl acrylate



# Measuring solubility in water and determining Krafft temperature

The solubility of the surfactant (5a) at different temperatures in water was measured by the UV absorptions method.<sup>1</sup> The UV absorbance of the surfactant (5a) solution at 200-500 nm wavelength was showed in Fig. 1 (small figure). The absorption intensity of the surfactant (5a) in different concentration at different temperature at 215 nm wavelength was also measured, and the curves of solubility versus temperature (C~T) was shown in Fig. 1. It could be clearly seen that there was an inflexion point on the curve. The temperature corresponding to the inflexion point was namely the Krafft temperature. For ionic surfactants, Krafft temperatures were micellar critical temperatures, above which the solubility increased rapidly due to the large numbers of micelles in the solution. Here the Krafft temperature was about 35 °C.



Fig. 1. UV-absorption spectra and solubility curves of the surfactant (5a).

### Determining critical micellar concentration and surface activity

For the surfactant (5a), the aqueous solutions with a series of concentrations were prepared. The surface tensions of these solutions were measured at a given temperature, and the curves of surface tensions versus concentrations ( $\gamma$ ~C) were plotted. Their CMC were determined from the inflection points, and at the same time the surface tensions corresponding to CMC,  $\gamma_{CMC}$ , was also obtained on the curves of  $\gamma$ -C. Fig. 2 displayed the measuring results at 40 °C, and the CMC was 150 ppm for the surfactant. The driving force of forming micelles of the surfactant was hydrophobic interaction of phenyl ether chain and  $\alpha$   $\beta$  unsaturated ketone. The stronger the hydrophobic interaction was, the smaller the CMC was. The CMC of the surfactant (5a) was smaller, compared with the CMC of SDS, which was 2700 ppm at 40 °C.<sup>1</sup> This could be attributed to the srtonger hydrophobic interaction between phenyl ether chain and  $\alpha$   $\beta$  unsaturated ketone in the molecule 5a. It was similar to those common surfactants in a homologous series.<sup>1</sup> The longer hydrocarbon chain was, the smaller the CMC was.

# Measuring surface excess and area occupied by a surfactant molecule at water-air interface

The surface excess concentrations  $\Gamma_m$  (mol m<sup>-2</sup>) at CMC were calculated from the Gibbs adsorption isotherm equation,<sup>11</sup>

$$\Gamma_m = -\frac{C}{2.303RT} \left(\frac{\partial \gamma}{\partial C}\right)_{\max,T} \tag{1}$$



Fig. 2. Curve of surface tension vs. concentration of three kinds of surfactants at 40 °C.

where  $\gamma$  (mN m<sup>-1</sup>) was the equilibrium surface tension at the surfactant concentration, C (mol L<sup>-1</sup>), T was the absolute temperature, and R = 8.314 J mol<sup>-1</sup> K<sup>-1</sup>. In order to extract the minimum surface area occupied by a surfactant molecule, A<sub>m</sub> (m<sup>2</sup>), at water–air interfaced, at surface saturation, the following equation was used,<sup>11</sup> where N<sub>A</sub> was Avogadro's constant.

$$A_m = \frac{10^{14}}{N_A \Gamma_m} \tag{2}$$

The adsorption at water—air interface of the surfactant (5a) was derived from the results in Fig. 2 and obtained by using the Gibbs adsorption isotherm equation.

$$\Gamma_m = 3.028 \times 10^{-6} \text{ mol m}^{-2}$$
  
 $A_m = 0.55 \times 10^{-18} \text{ m}^2$ 

From the above data it could be seen that  $\Gamma_m$  of the surfactant was smaller than that of SDS,  $^1$  whose  $\Gamma_m$  was 3.6  $\times$  10<sup>-6</sup>, whereas the  $A_m$  (m<sup>2</sup>) was greater than that of SDS, whose was  $0.46 \times 10^{-18}$  m<sup>2</sup>. The hydrophobic groups of the surfactant was bigger than that of SDS, and this conformation would make the molecule area  $A_m$  of surfactants at water–air interface greater, so smaller  $\Gamma_m$  was resulted in.

#### Determining micellar aggregation number

The micelle aggregation numbers of micelles,  $N_{agg}$ , for the surfactant (5a) was determined by the steady-state fluorescence quenching technique (SSFQ).<sup>12</sup> This method was based on quenching of pyrene fluorescence by a hydrophobic quencher. Benzophenone was used as the quencher. Excitation of the probe was at 340 nm and the emission was monitored at 475 nm. By changing the quencher concentration  $C_q$  (0–0.045 mmol L<sup>-1</sup>), a linear relationship between  $ln \frac{I_0}{I}$  and  $C_q$  was obtained, the corresponding equation is as follows:

$$\ln \frac{I_0}{I} = \frac{N_{agg}}{C - C_{CMC}} \times C_q \tag{3}$$

where  $I_0$  was the fluorescence intensity of the probe in the micellar solutions as in the absence of the quencher, and I was the fluorescence intensity of the probe in the presence of the quencher.  $C_{CMC}$  and C were the critical micellar concentration and the total concentration of the surfactant, respectively. According to the Eq. (3), the straight lines of logarithm of the intensity ratio versus the quencher concent

tration  $C_q$  were plotted, and the aggregation numbers ( $N_{agg}$ ) of the surfactant (5a) at a given concentration was obtained. The curves of  $N_{agg}$  versus C were plotted, and the  $N_{agg}$  at CMC were gained for the surfactant (5a) by extrapolation.

The solution of the sufactant at 8CMC, the fluorescence spectra of pyrene at different concentrations of benzophenone were shown in Fig. 3, and the line of  $\ln(I_0/I)$  versus  $C_q/(C-C_{cmc})$  was plotted in Fig. 4, and the  $N_{agg}$  of the surfactant at this concentration was gained. By the same method, the  $N_{agg}$  of the surfactant at other concentrations



Fig. 3. Emission spectrum of pyrene probe at diffent Concentrations of quencher for sodium (5-acryloyl-2-(dodecyloxy)phenyl) methanesulfonate system. The concentration was: 8 CMC; concentration of quencher:  $C_7 (0.045 \text{ mmol } \text{L}^{-1})$ >  $C_1(0)$ ; temperature: 40 °C.





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were obtained, and the line of  $N_{agg}$  versus C was regressed. Fig. 5 showed linear feature of  $N_{agg}$  versus C for the surfactant. The  $N_{agg}$  at C = CMC were driven from extrapolating the straight line, and the  $N_{agg}$  was 12.

From Fig. 4 it could be seen that the micellar aggregation number for the surfactant increased with concentration enhancing, and there were fine linear relationship between  $N_{agg}$  and concentration in the concentration range of 3–8 CMC. The  $N_{agg}$  of the surfactant was much smaller than that of SDS, namely, 50.<sup>1</sup> It was possible that the hydrophobic tail of the surfmer was bigger than that of SDS, and this was disadvantageous to the association of the hydrocarbon chains, which made the micelles looser, so very smaller  $N_{agg}$  was resulted in.

#### **EXPERIMENTAL**

**Material:** Analytical grade solvents were used without purification. Phenol, thionyl chloride, acrylic acid, aluminum trichloride, carbon disulfide, formaldehyde and sodium sulfite, bromododecane and dimethylformamide were purchased from Kelong Inc. (Chengdu, Sichuan, China).

**Equipment:** <sup>1</sup>H NMR spectra was recorded by Bruker-400 MHz spectrometers, and the mass spectrometry was recorded by Agilent 6224. UV-vis absorbance spectra was obtained by using a SHIMADZU UV-1800 spectrometer and synthesized surfactant were individually characterized by WQF-520 Infrared spectroscopy (Beijing Beifen-Ruili Analytical Instrument Co). The solution surface tensions were measured by using a TX500C spinning drop tensiometer (BOWING INDUSTRY CO.), and the fluorescence emission spectra of probe pyrene in different media were



Fig. 5. Relationship between N<sub>agg</sub> and C for sodium (5acryloyl-2-(dodecyloxy)phenyl)methanesulfonate.

determined by a 970CRT fluo-rescence spectrophotometer (Shanghai Jingke).

Synthesis and characterizing of sodium (5-acryloyl-2-(dodecyloxy)phenyl)methanesulfonate: Sodium (5-acryloyl-2-(dodecyloxy)phenyl)methane sulfonate was synthesized from phenol, thionyl chloride, acrylic acid, aluminum trichloride, carbon disulfide, formaldehyde, sodium sulfite, bromododecane and dimethylformamide as Scheme 1 and IR spectrum of the surfactant (2a~5a) were shown in Fig. 6. Phenyl acrylate (2a): Phenol (20.00 g, 0.21 mol) and (16.00 g, 0.22 mol) acrylic acid were placed in a 100 mL three-necked flask, fitted with a reflux condenser and the condenser was connected to a gas absorption trap. Thionyl chloride (24.00 g, 0.21 mol) were slowly added to the above mixture. The mixture was heated on a water bath, cautiously at first, until hydrogen chloride and sulphur dioxide ceasesd to be evolved (about 1 hour). Then the apparatus was placed on a ceramic-centred wire gauze and heated until the contents were brought just to the reflux temperature in order to complete the reaction (about 20 min). The reaction product was distilled and 24.00 g (80%) of colorless oil was obtained. <sup>1</sup>H-NMR has signals at (CDCl<sub>3</sub>, TMS)  $\delta = 5.96-6.17$  (m, 2H, CH<sub>2</sub>=CH-C(O)-O-Ph), 6.30-6.37 (m, 1H, CH<sub>2</sub>=CH-C(O)-O-Ph). 7.10-7.12 (m, 2H, aromatic), 7.14-7.25 (m, 3H, aromatic) ppm. HRMS (ESI) calcd for C<sub>9</sub>H<sub>8</sub>O<sub>2</sub> (M<sup>+</sup>1) 149.0524, found 149.0602. The benzene C-H stretching vibrations were observed at 3056 cm<sup>-1</sup>, the C-H stretch vibration of C=C-H group was found at 3407 cm<sup>-1</sup>, at 1741, 1602, 1494 and 1403 cm<sup>-1</sup> were the C=C stretching vibrations of the ring carbons, at 1717 cm<sup>-1</sup> was the C=O stretching vibrations, at 1373 and 1066 cm<sup>-1</sup> were the C-O stretching vibrations. 1-(4-hydroxyphenyl)prop-2-en-1-one (3a): 18.70 g (0.14 mol) anhydrous aluminium chloride and 20 mL of carbon



Fig. 6. IR spectrum of the surfactant (2a~5a).

disulphide were placed in a 100 mL three-necked flask, which was equipped with a dropping funnel, a sturdy mechanical stirrer and a reflux condenser. The reflux condenser was attached a gas absorption trap to the top of the condenser. 18.50 g (0.13 mol)phenyl acrylate was slowly added in the flask, stirred. Much hydrogen chloride was evolved and absorbed by the trap. When all the phenyl acrylate was introduced, the reaction mixture was gently refluxed on a water bath for 2 hours. After the solvent was distilled off, the result mixture was maintained at 80-100 °C by heating for 3 hours. Then the reaction mixture was cooled and the aluminium chloride complex was decomposed by slowly adding 100 mL 3N HCl. After cooling, the 1-(4-hydroxyphenyl)prop-2en-1-one was collected on the surface. Most of the product in the upper layer had solidified by setting aside overnight and then was filtered off by the pump. The product was rinsed thoroughly with water, and dried at 70 °C. Final 12.00 g 65% dark solid was acquired. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS) has signals at  $\delta$  4.57-4.60 (m, H, CH<sub>2</sub>=CH-C(O)-Ph-O-H), 5.98 (d, J = 10.04 Hz, H, H-CH=CH-C(O)-Ph-OH), 6.11-6.15 (m, H, H-CH=CH-C(O)-Ph-OH), 6.92-6.94 (m, 2H, aromatic), 7.19 (d, J = 4.20 Hz, H, H-CH=CH-C(O)-Ph-OH), 7.51-7.73 (m, 2H, aromatic) ppm. HRMS (ESI) calcd for C<sub>9</sub>H<sub>8</sub>O<sub>2</sub> (M<sup>+</sup>1) 149.0524, found 149.0602. A new absorption peak was the O-H stretching vibrations of phenol at 3444 cm<sup>-1</sup>. 735 cm<sup>-1</sup> was the C-H stretching vibrations of ortho phenol. Sodium (5-acryloyl-2-(dodecyloxy)phenyl)methanesulfonate (4a): 5.00 g (0.07 mol) of 40% formaldehyde, 2 g NaOH, 13 g (0.10 mol) sodium sulfite, 50 mL of water, 10.00 g (0.068 mol) of 1-(4-hydroxyphenyl)prop-2-en-1-one were added into a flask equipped with a stirrer and a reflux condenser. The mixture was heated with steam for 6 hours. After cooling, the supernatant liquid was decanted from the undissolved sodium sulfite. This reaction solution was neutralized with dilute sulfuric acid and evaporated to dryness over steam. The residue was extracted with portions of boiling 95% ethanol (200 mL), rotary evaporation to give 9.80 g (61%) brownish yellow solid. <sup>1</sup>H-NMR (D<sub>2</sub>O, TMS) has signals at  $\delta$  4.70 (s, 2H, H-CH=CH-C(O)-PhONa-CH<sub>2</sub>-SO<sub>3</sub><sup>-</sup>), 6.48-6.50 (m, H, H-CH=CH-C(O)-PhONa-CH2-SO3-), 6.51 (d, J = 2.00 Hz, H, H-CH=CH-C(O)-PhONa-CH<sub>2</sub>-SO<sub>3</sub>-), 6.59 (s, H, aromatic), 7.18-7.74 (m, H, H-CH=CH-C(O)-PhONa-CH<sub>2</sub>-SO<sub>3</sub>-), 7.77-7.79 (m, H, aromatic), 7.93-7.95 (m, H, aromatic) ppm. HRMS (ESI) calcd for  $C_{10}H_8O_5S$  (M<sup>-1</sup>) 240.2325, found 240.0092. 1186, 1049 cm<sup>-1</sup> were stretch vibrations for sulfonic acid group, and 626 cm<sup>-1</sup>, 522 cm<sup>-1</sup> were in-plane bending vibration. Sodium (5-acryloyl-2-(dodecyloxy)phenyl)methane sulfonate (5a): 5.00 g of the product of the previous step, 4.25 g (0.017 mol) of biomedicine and 20 mL dimethyl sulfoxide were

placed in a 100 mL round-bottomed flask fitted with a reflux condenser and sealed stirrer unit. The flask was boiled on a oil bath, stirred for 8 hours. The solvent was removed with a rotary evaporator and the result mixture was mixed into 100 mL of water. 5.80 g (68%) of sodium (5-acryloyl-2-(dodecyloxy)phenyl)methane sulfonate was obtained by filtering the solid off by the pump. <sup>1</sup>H-NMR (DMSO, TMS) has signals at  $\delta$  0.79 (s, 2H, H-CH=CH-C(O)-PhOCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>-SO<sub>3</sub><sup>-</sup>), 1.12 (s, 16H, H-CH=CH-C(O)-PhOCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>-SO<sub>3</sub>), 2.71 (s, 2H, H-CH=CH-C(O)-PhOCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>-SO<sub>3</sub>, 2.87 (s, 2H, H-CH=CH-C(O)-PhOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>-SO3<sup>-</sup>), 4.05 (s, 2H, H-CH=CH-C(O)-PhOCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>-CH2-SO3<sup>-</sup>), 4.12 (s, 2H, H-CH=CH-C(O)-PhOCH2CH2(CH2)8 CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>-SO<sub>3</sub>), 4.17 (s, 1H, H-CH=CH-C(O)-PhOCH<sub>2</sub>CH<sub>2</sub> (CH<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>-SO<sub>3</sub>), 4.70 (s, H, H-CH=CH-C(O)-PhOCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>-SO<sub>3</sub>-), 7.19 (s, H, aromatic), 7.78 (s, H, H-CH=CH-C(O)-PhOCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>-SO3-), 8.30 (s, 2H, aromatic) ppm. HRMS (ESI) calcd for C<sub>22</sub>H<sub>33</sub>O<sub>5</sub>S (M<sup>+</sup>-1) 409.2049, found 409.2052. 2960 cm<sup>-1</sup>, 2854 cm<sup>-1</sup> were C-H stretching vibrations of methyl group and 2923 cm<sup>-1</sup> was C-H stretching vibrations of methylene.

#### CONCLUSIONS

A novel anionic surface-active monomer sodium (5acryloyl-2-(dodecyloxy)phenyl) methane sulfonate has been synthesized, which was phenyl ether and wasn't hydrolyzed in acidic or alkalic condition. The structure was confirmed by <sup>1</sup>H NMR spectra, mass spectrometry and IR spectrum. The micellar behaviors showed that the CMC was 150 ppm at 40 °C, the surface absorption amounts  $\Gamma_m$ was  $3.208 \times 10^{-6}$ mol m<sup>-2</sup> and the molecular areas  $A_m$  was  $0.550 \times 10^{-18}$ m<sup>2</sup> at the interface of air–water respectively. The aggregation number (N<sub>agg</sub>) at C = CMC of this surfactant was 12 by steady-state fluorescence probe method. This study was aimed at supplying basic theory references for synthesis hydrophobically associating polyacrylamide (HPAM), which could be used in both acidic and alkalic condition for tertiary oil recovery.

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