### Accepted Manuscript

Asymmetric sodium benzenesulfonate Gemini surfactant: Synthesis, properties and application

Bin Lyu, Yajin Yu, Dangge Gao, Yuefeng Wang, Jianzhong Ma

PII:	80167-7322(18)36102-6
DOI:	https://doi.org/10.1016/j.molliq.2019.04.109
Reference:	MOLLIQ 10832
To appear in:	Journal of Molecular Liquids
Received date:	22 November 2018
Revised date:	6 April 2019
Accepted date:	21 April 2019

Please cite this article as: B. Lyu, Y. Yu, D. Gao, et al., Asymmetric sodium benzenesulfonate Gemini surfactant: Synthesis, properties and application, Journal of Molecular Liquids, https://doi.org/10.1016/j.molliq.2019.04.109

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



### Asymmetric sodium benzenesulfonate Gemini surfactant: synthesis, properties and application

Bin Lyu<sup>\*a, b</sup>, Yajin Yu<sup>a, b</sup>, Dangge Gao<sup>a, b</sup>, Yuefeng Wang<sup>a, b</sup>, Jianzhong Ma<sup>a, b</sup> a College of Bioresources Chemical and Materials Engineering, Shannxi University of Science & Technology, Xi'an 710021;

b National Demonstration Center for Experimental Light Chemistry Engineering Education (Shaanxi University of Science & Technology), Xi'an 710021, China

<sup>\*</sup> Corresponding author. Tel.: 13991372196. E-mail address: xianyanglvbin@163.com.

**ABSTRACT:** An asymmetric sodium benzenesulfonate Gemini surfactant (ASBGS) designed and prepared by esterification and sulfonation reaction using 4- (dodecyl amide) phenol (4-DAP), dodecanol maleic acid monoester (DMM) and NaHSO<sub>3</sub>. The structure of the ASBGS characterized by FT-IR and <sup>1</sup>H NMR. The surface tension, emulsifying force and aggregation property of the ASBGS tested. The results showed that the critical micelle concentration and  $\gamma_{CMC}$  of ASBGS were  $0.8 \times 10^{-4}$  mol/L and 25.1 mN/m, respectively. Thermodynamic parameters results showed that the micellization of this surfactant was a spontaneous process. DLS and TEM results showed that the concentration of 10 CMC surfactant solution aggregated into vesicles, and the average particle size was 85 nm. Then ASBGS was used to emulsify rapeseed oil for lubricating collagen fiber. The emulsifying ability. In addition, we prepared collagen fiber lubricating materials (CFLMs) by blending different dosages of the ASBGS with rapeseed oil collagen fiber lubricating material (ROCLM), its emulsifying ability increased from 47.37% to 87.37% in cold water.

**Key word:** sodium benzenesulfonate, gemini surfactant, collagen fiber lubricating material, emulsifying ability

### **1** Introduction

A surfactant is composed of a non-polar lipophilic group and a polar hydrophilic group, allows the surfactant molecules to have both hydrophilic and lipophilic properties <sup>[1-2]</sup>. Liquid surface tension can significantly reduce when the surfactant concentration is very low <sup>[3-4]</sup>. It was known as a classic of the latest "industrial monosodium glutamate", used in various industrial production areas <sup>[5-7]</sup>. The conventional surfactants have the disadvantages of low surface activity, poor

solubility in cold water, poor solubilization, poor synergistic effect, and difficulty in forming micelles, which cannot meet the higher demands of current industrial applications <sup>[8]</sup>. Therefore, some new surfactants with special structures and functions have been developed successively <sup>[9]</sup>. Gemini surfactant is a special new surfactant, which contains two hydrophilic groups and two hydrophobic groups. Compared with conventional surfactants, Gemini surfactant has many excellent properties, including higher surface activity, lower critical micelle concentration (CMC) and better compatibility with other surfactants, better water solubility, wettability and emulsifiability <sup>[10-11]</sup>. Consequently, a large number of Gemini surfactants have been prepared to reveal the relationship between structure and properties <sup>[12-14]</sup>.

Among them, alkyl benzene sulfonate Gemini surfactant is a very important anionic Gemini surfactant, which has high surface activity, good water solubility, wettability, dispersibility. Good performances make alkyl benzene sulfonate Gemini surfactant become a research hotspot <sup>[15-18]</sup>. Du et al. <sup>[19]</sup> synthesized an alkylbenzene sulfonate Gemini surfactant with flexible methylene as a connecting group. Its CMC was about two orders of magnitude lower than that of conventional alkylbenzene sulfonate, and its surface activity was good. Wang et al. <sup>[20]</sup> synthesized anionic sulfonate Gemini surfactants 8-s-8 (SO<sub>3</sub>)<sub>2</sub> and 12-s-12 (SO<sub>3</sub>)<sub>2</sub> (s = 3~6). Its CMC of 8-s-8 (SO<sub>3</sub>)<sub>2</sub> was two orders of magnitude larger than the 12-s-12 (SO<sub>3</sub>)<sub>2</sub>, while the influence of the spacer length on the CMC was relatively small. Li et al. <sup>[21]</sup> synthesized a new sulfonate Gemini surfactant (3C<sub>10</sub>-DS) and investigated the interfacial activity and emulsifying properties of 3C<sub>10</sub>-DS and different surfactants

with different mass ratios. The results showed that the interfacial tension of OP-10, PS and HABS can be significantly reduced by adding  $3C_{10}$ -DS, and the interfacial tension of the composite system [m ( $3C_{10}$ -DS: m (PS)=2:8] was  $2.8 \times 10^{-3}$  mN/m, and the emulsification rate was 90%. Therefore, compared with traditional surfactants, the alkylbenzene sulfonate Gemini surfactants are more widely used due to their excellent properties, such as emulsifiers, foam stabilizers, thickeners, and other additives.

Gemini surfactants can be structurally classified into symmetric Gemini surfactants and asymmetric Gemini surfactants. Among them, the asymmetric Gemini surfactant structure is a novel surfactant, which contains different polar groups, different hydrophobic segments, and various linking groups <sup>[22]</sup>. Due to its structurally rich and controllable factors, asymmetric Gemini surfactants have superior performance, for example, better surface activity, better water solubility, higher hydrophilicity, lower critical micelle concentration, good foaming, etc. Wang <sup>[7]</sup> prepared three asymmetric sulfosuccinate diester Gemini surfactants and all three surfactants can significantly reduce the surface tension and have a good emulsifying ability, good permeability, and certain foaming ability.

Rapeseed oil is one of the world's largest vegetable oils and is one of the first vegetable oils used to lubricate collagen fiber materials. However, natural rapeseed oil is easily oxidized due to a large amount of unsaturated double bonds, which limited the application of rapeseed oil in collagen fiber lubricating materials <sup>[23]</sup>. Therefore, it was usually necessary to chemically modify the rapeseed oil to prepare rapeseed oil collagen fiber lubricating material (ROCLM). However, the traditional ROCLM

needed to be emulsified by hot water before lubricating collagen fiber, which was complex and time-consuming. Therefore, in order to emulsify the traditional ROCLM in cold water and simplify the operation steps, we proposed a strategy to introduce Gemini surfactant as an emulsifier into the ROCLM to obtain a new collagen fiber lubricating material (CFLM). And the obtained CFLM may have better water solubility and better emulsifying ability in cold water.

Based on the above background, an asymmetric sodium benzenesulfonate Gemini surfactant (ASBGS) was synthesized and its structure as showed in Figure 1a. Two sulfonic acid groups (-SO<sub>3</sub>Na) made it emulsifying properties better. The basic performances of ASBGS were measured. Due to the similar hydrophilic group in structure and commonly used surfactant, sodium dodecylbenzene sulfonate (SDBS) was used as a control sample. Then different dosages of surfactants (ASBGS and SDBS) were introduced into the traditional ROCLM to obtain CFLMs, and their emulsifying ability in cold water was investigated by R-value.



Figure 1 Structural formula of ASBGS (a) and SDBS (b)

Note:  $R_1$  is an alkyl long chain of dodecanoic acid and  $R_2$  is an alkyl long chain of dodecanol.

### 2 Experimental

### 2.1 Materials

Dodecanoic acid, Guangdong Chemical Reagent Engineering Technology Research and Development Center ( $\geq$ 98.5%); p-aminophenol, Shanghai Shanpu Chemical Co., Ltd ( $\geq$ 99%); dodecanol, Tianjin Fuchen Chemical Reagent Factory ( $\geq$ 99%); maleic anhydride (MAH), Hedong District, Tianjin Hongyan reagent plant ( $\geq$ 99.5%); dimethylsulfoxide (DMSO) ( $\geq$ 99.5%), anhydrous sodium acetate ( $\geq$ 99.0%), ethyl acetate ( $\geq$ 99.5%), Tianjin Tianli Chemical Reagent Co., Ltd. All the materials are analytical pure.

### 2.2 Synthesis of asymmetric sodium benzenesulfonate Gemini surfactant

#### 2.2.1 Synthesis of 4- (dodecyl amide) phenol

With dodecanoic acid and p-aminophenol as raw materials, ethyl acetate as catalyst (the dosage was 0.5% of dodecanoic acid quality), the mixture of sodium bisulfate and sodium borohydride as antioxidant (the dosage of dodecanoic acid 0.4%, wherein m (sodium bisulfate): m (sodium borohydride) = 3:2) for reaction. The reaction formula was shown in Scheme 1. The reactants were weighed according to the ratio of n (dodecanoic acid): n (p-aminophenol) = 1:1.05. The p-aminophenol was dissolved with DMSO. All reactants were added into the 250 mL hydrothermal reactor (Xi'an Zhiyan Instrument Equipment Co., Ltd.) and put it into the oven for a reaction. The reaction temperature was 160  $^{\circ}$ C and the reaction time was 5 h. The crude product 4-DAP was obtained. The product was extracted with ethyl acetate and distilled water, then washed with distilled water for 3 to 4 times to remove the solvent DMSO; the ethyl acetate phase was rotary evaporated and then vacuum drying for several hours; the dried product was recrystallized to obtain the purified product.

FT-IR: 3311 cm<sup>-1</sup> (phenolic hydroxyl), 1653 cm<sup>-1</sup> (amide linkage), 1548 cm<sup>-1</sup> (secondary amine), 1247 cm<sup>-1</sup> (cyano), 1515 cm<sup>-1</sup> and 1467 cm<sup>-1</sup> (aromatic hydrocarbons), and 832 cm<sup>-1</sup> (benzene ring). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta 0.854$  (3H,

CH<sub>3</sub>), δ1.057 (18H, CH<sub>3</sub> (CH<sub>2</sub>)<sub>9</sub>), δ1.240 (2H, CH<sub>2</sub>-C=O), δ4.388 (1H, Ar-OH), δ6.653 (1H, -NH-), δ7.343 (2H, Ar-H).



Scheme 1 Reaction formula of 4-DAP

Note: R<sub>1</sub> is an alkyl long chain of dodecanoic acid and R<sub>2</sub> is an alkyl long chain of dodecanol.

### 2.2.2 Synthesis of dodecanol maleic acid monoester

In a 250 mL four-necked flask equipped with condensate, agitator and temperature control device, then passed into N<sub>2</sub>, the reaction was carried out with MAH and dodecanol as raw materials and anhydrous sodium acetate as the catalyst (accounting for 0.1% of the mass fraction of the system). The reaction formula was shown in Scheme 2. The reactants were weighed according to the ratio of n (MAH): n (dodecanol) = 1:1. The reaction temperature was 85 °C and the reaction time was 4 h. The crude product DMM was obtained. Finally, the product was recrystallized to obtain the purified product.

FT-IR: 1716 cm<sup>-1</sup> (ester carbonyl), 1646 cm<sup>-1</sup> (carbon-carbon double bond), 1292 cm<sup>-1</sup> and 1166 cm<sup>-1</sup> (ether bond). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ0.901 (3H, CH<sub>3</sub>), δ1.283 (18H, CH<sub>3</sub> (CH<sub>2</sub>)<sub>9</sub>), δ1.725 (2H, CH<sub>2</sub>-C=O), δ4.310 (2H, CH<sub>2</sub>-O), δ6.411 (2H, -CH=CH-), δ7.264 (1H, -COOH).



Scheme 2 Reaction formula of DMM

Note:  $R_1$  and  $R_2$  are the same as scheme 1.

#### 2.2.3 Synthesis of 4- (dodecyl amide) phenyl maleic acid diester

The reaction was carried out with the purified 4-DAP and DMM as raw materials, and zinc oxide as the catalyst (accounting for 0.2% of the mass fraction of the system). The reaction formula was shown in Scheme 3. The reactants were weighed according to the ratio of n (4-DAP): n (DMM) = 1:1. The reactions were added into the 250 mL hydrothermal reactor and put it into the oven for a reaction. The reaction temperature was 140  $^{\circ}$ C and the reaction time was 5 h. The crude product 4- (dodecyl amide) phenyl maleic acid diester (4-DAPMD) was obtained. It was extracted with ethyl acetate and then the ethyl acetate phase was rotary evaporated to obtain the purified product.

FT-IR: 1729 cm<sup>-1</sup> (ester carbonyl), 1645 cm<sup>-1</sup> (amide linkage), 1162 cm<sup>-1</sup> (ether bond), 1548 cm<sup>-1</sup> (secondary amine), 1216 cm<sup>-1</sup> (cyano), 1457 cm<sup>-1</sup> (aromatic hydrocarbons), and 832 cm<sup>-1</sup> (benzene ring). <sup>1</sup>H NMR (DMSO, ppm): δ0.857 (6H, CH<sub>3</sub>), δ1.081 (36H, CH<sub>3</sub> (CH<sub>2</sub>)<sub>9</sub>), δ1.243 (2H, CH<sub>2</sub>-C=O), δ4.347 (2H, CH<sub>2</sub>-O), δ6.361 (2H, -CH=CH-), δ6.689 (1H, -NH-), δ7.354 (2H, Ar-H).



Note:  $R_1$  and  $R_2$  are the same as scheme 1.

#### 2.2.4 Synthesis of sodium benzenesulfonate Gemini surfactant

The pH value of the diester product system was adjusted to 7 by the sodium hydroxide solution with a mass fraction of 30%. Phase transfer catalyst was dodecanol maleate monoester salt, which was synthesized by DMM and sodium hydroxide (n (DMM): n (sodium hydroxide) = 1:1). Next, the catalyst was added to the diester product system and stirred uniform. Then, 30% of sodium bisulfate

solution was slowly added to carry out sulfonation of the reaction system. Wherein the quality of sodium bisulfate was weighed by the ratio of n (4-DAPMD): n (sodium bisulfate) = 1:2.2). The reaction formula was shown in Scheme 4. The reaction temperature was 150  $^{\circ}$ C and the time was 6 h. The crude product ASBGS was obtained, which was extracted with distilled water and heated in a water bath at 80  $^{\circ}$ C for 30 min. The insoluble matter was removed by filtration, and the filtrate was collected. The filtrate was evaporated to crystallize, and crystals were collected and washed three times with absolute ethanol to remove excess phase transfer catalyst. Finally, the product obtained was a purified product.

FT-IR: 3472 cm<sup>-1</sup> (phenolic hydroxyl), 1716 cm<sup>-1</sup> (ester carbonyl), 1603 cm<sup>-1</sup> (amide linkage), 1409 cm<sup>-1</sup> and 1133 cm<sup>-1</sup> (ether bond), 1047 cm<sup>-1</sup> and 624 cm<sup>-1</sup> (sulfonate group). <sup>1</sup>H NMR (D<sub>2</sub>O, ppm):  $\delta 0.791$  (6H, CH<sub>3</sub>),  $\delta 1.189$  (36H, CH<sub>3</sub> (CH<sub>2</sub>)<sub>9</sub>),  $\delta 2.030$  (2H, CH<sub>2</sub>-C=O),  $\delta 2.770$  (1H, -CH-),  $\delta 3.807$  (2H, -CH<sub>2</sub>-O),  $\delta 6.841$  (1H, -NH-),  $\delta 7.208$  (2H, Ar-H).



Scheme 4 Reaction formula of ASBGS

Note:  $R_1$  and  $R_2$  are the same as scheme 1.

#### 2.2.5 Preparation of collagen fiber lubricating materials

The CFLMs were prepared by the surfactants (ASBGS, SDBS) and ROCLM. The amount of surfactant showed in Table 1. The reaction vessel was a three-necked flask equipped with a stirrer, a condensing and a temperature control device. The reaction needed to be stirred at 85 C for 1 h. The specific experimental scheme showed in Table 1.

CFLMs types	1	2	3	4	5
Mass fraction (%)	0	0.5	1	2	4

Table 1 Experimental scheme for preparation of CFLMs

Note: 1 represents the original CFLMs which was not added with surfactants (ASBGS, SDBS); 2 to 5 respectively represent the mass fraction of surfactants (ASBGS, SDBS) in the CFLMs of 0.5%, 1%, 2%, 4%.

#### 2.3 Surface tension measurement

With reference to QB/T1323-1991, the surface tension measurement was conducted using a ring-pull liquid film method on XJZ-200 automatic surface tension meter (Chengde Jinjian Testing Instrument Co., Ltd) at 298.15  $\pm$  0.3 K. The surface tension meter calibrated by measuring the surface tension of pure water of known concentration. The prepared Gemini surfactant could be dissolved at room temperature (25 °C) by more than 90%, and the higher temperature (~ 40 °C) can completely dissolve it in water. Therefore, a series of different concentrations of aqueous surfactant solutions prepared at a certain temperature (~ 40 °C) and their surface tensions were measured separately. And the surface tension values measured three times and the recorded values taken from the average of these values. Then drew the curve that the surface tension followed the concentration changed ( $\gamma$ -c curve). Critical micelle concentration (CMC) determined by the inflection point of the  $\gamma$ -c curve. At this time, the concentration was the critical micelle concentration, and the corresponding surface tension was the surface tension corresponding to the critical micelle concentration (CMC).

The surface activity at C<sub>20</sub>, the surfactant concentration required to reduce the

surface tension of water by 20 mN/m <sup>[16]</sup>, as well the surface tension at CMC ( $\gamma_{CMC}$ ) also determined by the same curve.

### 2.4 Conductivity measurement

The conductivity of the surfactant solution measured by a conductivity meter DDJS-308A (Shanghai Instrument and Electric Scientific Instrument Co., Ltd., an accuracy of 1%). The conductivity meter calibrated by measuring the conductivity of the solution with a known concentration of potassium chloride. The electrode of the conductivity meter washed with distilled water to remove impurities adsorbed on the surface, and finally immersed in the calibration solution. After the calibration, the conductivity of the surfactant solutions at a temperature of 298.15 $\pm$ 0.3, 308.15 $\pm$ 0.3 K measured <sup>[24]</sup>.

#### 2.5 Emulsification measurement

A certain volume of the surfactant solution thoroughly mixed with the liquid paraffin wax to form an emulsion. The emulsification performance of the surfactant evaluated according to the time required to separate 10 mL of water <sup>[25]</sup>. In this study, another major objective was to improve the emulsifying property in cold water for CFLMs by combining Gemini surfactant with the ROCLM. Therefore, when we examined the emulsifying property of the surfactant, the ROCLM selected instead of the liquid paraffin wax, thereby detecting the emulsifying effect of the surfactant on the grease. The specific operation was as follows:

Firstly, a surfactant solution with a mass fraction of 0.1% prepared with ultrapure water. Then, adding 40 mL of the surfactant solution and 40 mL of the ROCLM to

100 mL graduated cylinder with stopper. Putting it into a 40  $^{\circ}$ C water bath constant temperature 5 min. Turning the cylinder up and down five times, then standing for another minute, repeated the same operation five times, and recorded the results with a stopwatch. At this point, the water and oil phase gradually separated. The water phase appeared slowly, and until the height of the water phase reached to 10 mL. Finally, recording the time required for separation.

#### 2.6 Dynamic Light Scattering (DLS)

The DLS measurement was recorded using a Zetasizer Nano-ZS90 (Malvern Instrument Ltd., Malvern, UK) at a 90° scattering angle. The concentration of the surfactant solution configured was 10 CMC. The solution ultrasonically dispersed uniformly and then measured, and the temperature controlled at  $25.0\pm0.1$  °C. Each sample repeatedly measured 3 times and the average value was taken.

#### 2.7 Transmission Electron Microscope (TEM)

TEM images obtained by a negative-staining method using a Tecnai G2 F20 S-TWIN transmission electron microscope (FEI Company, US). Phospho-tungstic acid solution (1 wt %) used as a dyeing agent. The copper mesh placed on one drop of the sample solution for 5 minutes, and the excess surfactant solution wiped off with filter paper to form a thin liquid film on the copper mesh. Afterward, a small drop of phospho-tungstic acid solution added to the surface of the thin liquid film and the excess solution was wiped off, and then the samples dried in the air. After drying, the aggregated morphologies of the samples observed using the TEM.

#### 2.8 Emulsifying property in cold water

As the oil density is smaller than the water, so the emulsified oil will float on the upper emulsion. The emulsified CFLMs and water evenly distributed in the lower layer of the test tube. The height of the lower layer emulsion can express as the emulsification capability of the CFLMs in cold water. The higher the height indicates the better the emulsification capability of the CFLMs in cold water. Therefore, in this study, different types of CFLMs were used. The CFLMs were diluted 4 times with normal temperature water and mixed well. Then standing for 4 h, the oil film observed. After the end of standing, the h-value and the H-value measured. Finally, the R-value calculated according to the formula (1):

$$R = \frac{h}{H} \tag{1}$$

Where R is the emulsion stability [%], h is the emulsified emulsion height [cm], and H is the total emulsion height [cm].

### **3 Results and discussion**

#### 3.1 Surface tension



Figure 2 Plot of surface tension versus molar concentration of ASBGS aqueous

solution.

The CMC refers to the concentration that the surfactant solution begins to form a

large number of micelles, which is also an important measure of the activity of the surfactant active parameters. When CMC reached, the nature of the solution will change significantly. The smaller the CMC is, the higher the efficiency of the surfactant is <sup>[26]</sup>. The CMC usually determined by the turning point of the surface tension-concentration curve ( $\gamma$ -c curve). The surface tension at the CMC ( $\gamma_{CMC}$ ) is one of the measures of the decrease in surface tension, which means the maximum extent that the surface tension can reduce. It can use as one of the indicators of measuring surfactant activity advantages and disadvantages at the gas/liquid interface <sup>[16]</sup>. C<sub>20</sub> refers to the surfactant concentration at which the surface tension of pure solvent reduced by 20 mN/m <sup>[27]</sup>. The  $\gamma_{CMC}$  and C<sub>20</sub> also determined from the same  $\gamma$ -c curve. The  $\gamma$ -c curve of the synthesized ASBGS showed in Figure 2. The surface tension decreased as the concentration of ASBGS increased. At the CMC, micelles formed and the surface tension reached a platform.

The values of the CMC,  $\gamma_{CMC}$ , and  $C_{20}$  of the ASBGS and data corresponding to the conventional analog SDBS <sup>[16]</sup> summarized in Table 2. It was obvious that the surface tension of ASBGS at the CMC ( $\gamma_{CMC} = 25.1 \text{ mN/m}$ ) was lower compared with the SDBS ( $\gamma_{CMC} = 39.0 \text{ mN/m}$ ), indicating that the ASBGS adsorbed strongly at the air/water interface and demonstrated effective surface activities <sup>[14]</sup>. The value of  $C_{20}$ ( $C_{20} = 0.4 \times 10^{-4} \text{ mol/L}$ ) indicated that the efficiency of ASBGS in reducing the surface tension of water increased by three orders of magnitude compared with SDBS ( $C_{20} = 26.0 \times 10^{-4} \text{ mol/L}$ ).

Surfactants	CMC (10 <sup>-4</sup> mol/L)	$\gamma_{CMC} (mN/m)$	$C_{20}(10^{-4} \text{ mol/L})$	CMC/C <sub>20</sub>
ASBGS	0.8	25.1	0.4	2.0
SDBS [16]	16.3	39.0	26.0	0.6

Table 2 Surface active parameters of ASBGS and SDBS

In addition, the CMC/C<sub>20</sub> ratio indicates whether the surfactant has a better affinity for micellization or adsorption at the air/water interface <sup>[28]</sup>. The value of CMC/C<sub>20</sub> (CMC/C<sub>20</sub> = 2.0) indicated the relationship that the micellization and surface adsorption of ASBGS was one order of magnitude higher than the value of SDBS (CMC/C<sub>20</sub> = 0.6). That was to say, the ASBGS adsorbed more easily at the air/water interface compared with SDBS. In summary, the ASBGS offered high efficiency in reducing the surface tension of water and showed high surface activity <sup>[29]</sup>

#### 3.2 Thermodynamic parameters

In order to obtain the thermodynamic parameters of the micellization of ASBGS aqueous solution, the micellization behavior of the aqueous surfactant solution was determined by conductivity at different temperatures. The electrical conductivity (k) versus concentration (c) plots for the aqueous solutions of the surfactant showed in Figure 3. The corresponding thermodynamics parameters of micellization and CMC values at different temperatures listed in Table 3. Obviously, the CMC obtained from surface tension and conductivity measurement was consistent for the surfactant.

In each diagram, two straight lines with different slopes obtained and intersected at CMC points. It was observed that the CMC values of ASBGS increased with the increase of temperature (Figure 3). Generally speaking, the influence of temperature

on ionic surfactant CMC mainly includes two aspects. A higher temperature reduces the hydration degree of the hydrophilic cephalic base, which is conducive to the formation of micelles and the reduction of CMC <sup>[24, 30]</sup>. On the contrary, the ordered structure of water molecules around hydrocarbon chains may be destroyed, which may promote the dissolution of surfactant monomers and hinder the micellization of surfactant monomers <sup>[31]</sup>. For ASBGS, the latter factor dominated the micellization in the studied temperature range.



Figure 3 Conductivity versus concentration plot of ASBGS aqueous solutions at

### different temperatures.

According to the phase separation model, the thermodynamic parameters of micellization calculated. The standard Gibbs free energy ( $\Delta G^{0}_{mic}$ ), entropy ( $\Delta H^{0}_{mic}$ ) and enthalpy ( $\Delta S^{0}_{mic}$ ) of micellization of the synthesized ASBGS could obtain from the following Eqs <sup>[30, 32]</sup>.

$$\Delta G_{mic}^{0} = RT \ln X_{cmc}^{0} \tag{2}$$

$$\Delta H_{mic}^{0} = -RT^{2} \frac{\partial \ln X_{cmc}^{0}}{\partial \Delta T}$$
(3)

$$\Delta S_{mic}^{0} = \frac{\Delta H_{mic}^{0} - \Delta G_{mic}^{0}}{T}$$
(4)

Where R is the gas constant [8.314 J/(mol·k)]; T is the absolute temperature [K];  $X_{cmc}$  is the CMC expressed as mole fraction,  $X_{cmc} = CMC/55.4$ , 55.4 is the number of moles of 1L water at 298.15 K. All the calculated parameters were listed in Table 3.

T(K)	CMC (×10 <sup>-3</sup> mol/L)	$\Delta G^{0}_{mic}$ (kJ/mol)	$\Delta H^0_{mic}$ (kJ/mol)	$-T\Delta S^{0}_{mic}(\mathrm{kJ/mol})$
298.15	0.084	-33.22	-1.74	-31.48
308.15	0.086	-34.27	-1.39	-32.88
318.15	0.087	-35.35	-0.97	-34.38
328.15	0.088	-36.43	-1.03	-35.40

Table 3 Micellar thermodynamic parameters of ASBGS at different temperatures

In the range of 298.15~328.15K, the values of  $\Delta G^{0}_{mic}$  found to be negative for the ASBGS system, indicating that the micellization process of the surfactant in aqueous solution was spontaneous (Table 3). The micellar solution formed was a thermodynamically stable system <sup>[33]</sup>. At the same time, it could see from the table that the  $\Delta G^{0}_{mic}$  values decreased with increasing temperature, indicating that the increase of temperature not conducive to the formation of micelles <sup>[34-35]</sup>. In other words, value of  $|\Delta G^{0}_{mic}|$  increased gradually with the increase of temperature. Due to the increase of temperature destroyed the hydrogen bond between the surfactant and water molecule, which makes the stability of micelles higher <sup>[36]</sup>. The  $\Delta H^{0}_{mic}$  was also negative, indicating that micellization was an exothermic process. And within the temperature range studied, the  $\Delta H^{0}_{mic}$  of ABSGS did not change much, indicating that there was no significant change in the environment around the hydrophobic chain of ABSGS molecules during the temperature changed. Obviously, the main contribution to  $\Delta G^{0}_{mic}$  during micelle formation came from  $\Delta S^{0}_{mic}$ . Therefore, the micellization process of ABSGS was an entropy-driven process over the temperature range studied

<sup>[37]</sup>. However, positive  $\Delta S^0_{mic}$  value indicated that the process of forming micelles would increase the degree of disorder of the system. The main reason for this might be when a small amount of surfactant dissolved in an aqueous solution, parts of the hydrogen bonding structures between the water molecules rearranged and a new structure (different from water structure) formed around the hydrophobic hydrocarbon chains. That is, the so-called "iceberg structure" <sup>[38]</sup>. When the concentration of surfactant reached to the critical micelle concentration, the hydrophobic hydrocarbon chains moved closer and associated with each other, which led to the destruction of the water molecules around the hydrophobic carbon chains, thus strengthen the chaos of surfactant solution <sup>[39]</sup>. As seen from Table 3,  $|-T\Delta S^0_{mic}|$  value increased with temperature increasing, indicating that the increase of temperature increased the molecular motion of surfactant. In other words, the increase in temperature strengthened the chaos of the system.

#### **3.3 Emulsification**

Emulsification means that under certain conditions, the two immiscible liquids can be formed with certain stability of the role of a liquid-liquid dispersion system. Only after the addition of an emulsifier to emulsify, thereby obtain a stable emulsion. The emulsifier is mostly surfactant <sup>[40]</sup>. The emulsion is a heterogeneous dispersion system formed by dispersing a liquid in another immiscible liquid. The surfactant is added as an emulsifier to reduce the interfacial tension and adsorbs at the interface to form an interfacial film that can prevent or delay the aggregation and condensation caused by the mutual collision of the dispersion liquid beads. The stronger the effect of surfactant adsorption at the interface, the stronger the interfacial film formed, and the more stable the emulsion was.

We investigated the emulsifying ability of ASBGS for ROCLM (Table 4), which

qualitatively evaluated according to the time required to separate 10 mL of the water phase. The longer separation time of the water phase was, and the higher emulsion power was. The ASBGS had the separation time of 283 s for ROCLM. The results showed that the ASBGS had a better emulsifying ability for ROCLM than SDBS. In other words, the ASBGS has a good emulsifying effect on grease. The main reason is that Gemini surfactants have two hydrophobic chains in their molecules, which are closely linked by linkers and increase the hydrophobic interaction. Thus, Gemini surfactants are more likely to encapsulate oil-soluble groups than conventional surfactants containing only one hydrophobic group, so which emulsifying properties are greater than conventional surfactants. And Gemini surfactants have good affinity for hydrophobic substances (oils, solids, etc.), which can greatly reduce the surface tension between water and oil and therefore have good emulsifying properties <sup>[41]</sup>. That is, the ASBGS emulsified the ROCLM better than SDBS.

Table 4 Results of the emulsification force testing

Surfactants	emulsification capacity (s)		
ASBGS	283		
SDBS	176		

**3.4 Aggregation property** 



Figure 4 Apparent particle size distributions of the ASBGS and SDBS

The aggregate size distributions of the ASBGS and SDBS studied at the concentration of 10 CMC by DLS and TEM measurements at 25 °C, separately. Figure 4 showed the size distribution of the ASBGS and SDBS in solution as observed at the concentration of 10 CMC by DLS. It could be seen from Figure 4 that there was both only one peak in DLS, the average peak diameter of the ASBGS was 80 nm and the SDBS was 200 nm. This indicated that the concentration of 10 CMC of ASBGS and SDBS aggregated in aqueous solution may be the vesicles. And the vesicle was a mono-dispersed system, which indicated that its particle size distribution was more uniform.



Figure 5 TEM images of negatively-stained aggregates formed in the ASBGS (a) and SDBS (b) solution at a concentration of 10 CMC.

To further elucidate the conclusion of DLS, the aggregation morphologies of the ASBGS and SDBS at the concentration of 10 CMC tested by TEM measurement. Figure 5 showed the presence of micelle and vesicle. Figure 5a was the TEM image of the ASBGS. As could see from Figure 5a, it could observe that the size of the vesicles formed by the ASBGS in aqueous solution (the concentration of 10 CMC) was about 80-90 nm. The size of vesicles provided by TEM was consistent with the result of DLS. The majority shapes of the emulsion were spherical or spherical-like. In the

ASBGS studied, the aromatic rings in the head may participate in the  $\pi$ - $\pi$  interaction between molecules, thereby affecting the formation of vesicles, as observed by Wang <sup>[42]</sup>. And Figure 5b was the TEM image of the SDBS. As could be seen from Figure 5b, the size of the vesicles formed by the SDBS in aqueous solution (the concentration of 10 CMC) was about 200± nm. The size of vesicles provided by TEM was not consistent very well with the result of DLS.

#### 3.5 Emulsifying property in cold water

The emulsifying ability of CFLMs in cold water could qualitatively characterize by measuring its R-value. The higher the R-value, the better the emulsifying property. The experimental results showed that with the increase of the ASBGS, the emulsifying property of the CFLMs increased gradually (Table 5). Since the prepared surfactant is a dark brown solid powder, the addition of too much amount will affect the color and viscosity of the CFLMs, so the amount of the surfactant added was only 4%. Although only 4% was added, the emulsifying capacity of the CFLMs was still improved from 47.37% to 87.37%. The R-value of CFLMs prepared by introducing SDBS ranged from 47.37% to 54.24%. Although the R-value increased, the growth rate was small, indicating that SBDS contributed little to the emulsification ability of CFLMs in cold water.

In other words, the addition of ASBGS could improve the emulsification of CFLM. And its emulsifying ability in cold water increased from 47.37% to 87.37% (Table 5). The experimental results further proved that Gemini surfactants have excellent emulsification and compounding properties.

dosage of surfactants	0	0.5%	1%	2%	4%
R (ASBGS) (%)	47.37	63.16	75.79	78.95	87.37
R (SDBS) (%)		48.14	49.61	51.16	54.26

Table 5 Results of the emulsifying ability of CFLMs in cold water

#### **4** Conclusions

An asymmetric sodium benzenesulfonate Gemini surfactant was synthesized. The resulting Gemini surfactant was more effective at reducing surface tension than SDBS. The CMC of the Gemini surfactant determined from surface tension and conductivity measurements was at least two orders of magnitude lower than the CMC of the SDBS. And the micellization of this Gemini surfactant was a spontaneous process. In most cases, 10 CMC Gemini surfactant in aqueous solution presented an aggregate having an apparent hydrodynamic diameter of about 80 nm. The Gemini surfactant has excellent emulsifying ability, and can significantly improve the emulsification ability of the rapeseed oil collagen fiber lubricating materials in cold water. The application of the Gemini surfactant in collagen fiber lubricating materials not only simplifies the operation procedure but also saves energy. The Gemini surfactant with excellent emulsifying ability in cold water has a certain application prospect in the fields of the leather industry and tertiary oil recovery.

### Acknowledgements

This work was supported by the key research project of Shaanxi Province [2017GY-187]; the National Natural Science Foundation Project [21878182].

#### References

 Ruiz A, Pinazo A, Pérez L, et al. Green Catanionic Gemini Surfactant-Lichenysin Mixture: Improved Surface, Antimicrobial and Physiological Properties, ACS Appl. Mater. Interfaces, 2017, 9(27). https://doi.org/10.1021/acsami.7b03348.

- [2] Zeng X C, Xiao-Rui L I. Study on the synthesis and properties of gemini quaternary ammonium surfactant, Applied Chemical Industry, 2017, 46(2): 221-225.
- [3] Zhang L, Huang L X, Shun-Qin L I, et al. Preparation and Properties of Sulfonate Fluorosilicone Surfactant, Fine Chemicals, 2017, 34(1): 45-51. https://doi.org/10.13550/j.jxhg.2017.01.008
- [4] Ma J Z, Yun C, Liu L. Application of surfactants in leather making with nano-tech, J. Soc. Leather Technol. Chem., 2005, 89(2): 80-82.
- [5] Liao X, Gao Z, Xia Y, et al. Correction to "Rational Design and Synthesis of Carboxylate Gemini Surfactants with an Excellent Aggregate Behavior for Nano-La<sub>2</sub>O<sub>3</sub> Morphology- Controllable Preparation", Langmuir, 2017, 33(30): 7588.

https://doi.org/10.1021/acs.langmuir.7b02112.

- [6] Ma J Z, Gao J J, Wang H D, et al. Dissymmetry Gemini sulfosuccinate surfactant from vegetable oil: a kind of environmentally fatliquoring agent in leather industry, ACS Sustainable Chem. Eng., 2017, 5(11). https://doi.org/10.1021/acssuschemeng.7b02662.
- [7] Wang H D. Synthesis, Properties and Application of Dissymmetry Gemini Sulfossuccinate Surfactant, Shaanxi University of Science & Technology, 2016.
- [8] Wei Z H. The present situation and development trend of surfactants at home and abroad, Economic Analysis of China Petroleum and Chemical Industry, 2014(9): 46-50.

- [9] Wang M, Qiang X X, Wang P, et al. Research Progress of New Surfactants, Liaoning Chem. Ind., 2017(3): 256-258.
- [10]Sadeghi-Kiakhani M, Tehrani-Bagha A R. Cationic ester-containing gemini surfactants as retarders in acrylic dyeing, Colloids Surf., A, 2015, 479: 52-59.
   https://doi.org/10.1016/j.colsurfa.2015.03.030
- [11]Zhou M, Chen Y, Zou J, et al. Recent Advances in the Synthesis of Sulfonate Gemini Surfactants, J. Surfactants Deterg., 2018, 21(4): 443-453.

https://doi.org/10.1002/jsde.12046

- [12]Niu R, Wang C, Sun Z, et al. A Novel Alkyl Sulphobetaine Gemini Surfactant Based on S-triazine: Synthesis and Properties, J. Surfactants Deterg., 2017(1): 1-8. https://doi.org/10.1007/s11743-017-1996-y
- [13]Niu R, Wang C, Song H, et al. Synthesis and Surface/Interfacial Properties of Novel Dialkyl Disulfonate Gemini Surfactants Derived from 1,3,5-triazine, Tenside Surfactants Deterg., 2016, 53(6): 595-600.

https://doi.org/10.3139/113.110466

- [14]Zhou Y, Su P, Han F, et al. Synthesis and Characterization of Saturated Cardanol Sulfonate Salt Gemini Surfactant, Tenside Surfactants Deterg., 2017, 54(4): 322-326. https://doi.org/10.3139/113.110504
- [15]Du X G, Wang C W, Niu R Q, et al. Study on Foam Properties of Alkylbenzene Sulfonate Gemini Surfactants, Adv. Mater. Res., 2011, 418-420: 528-531. https://doi.org/10.4028/www.scientific.net/AMR.418-420.528

- [16]Hordyjewicz-Baran Z, Woch J, Kuliszewska E, et al. Aggregation behavior of anionic sulfonate gemini surfactants with dodecylphenyl tails, Colloids Surf., A, 2015, 484: 336-344. https://doi.org/10.1016/j.colsurfa.2015.08.012
- [17]Li J, Zhu R, Liu Y, et al. Synthesis and Performance of Novel Sulfonate GeminiSurfactant with Trialkyl Chains, J. Dispersion Sci. Technol., 2016, 37(3):374-379.

https://doi.org/10.1080/01932691.2015.1028069

- [18]Xu H, Hui G, Peng K, et al. Synthesis and Properties of a Novel Linear Alkylated
   Diphenylmethane Sulfonate Gemini Surfactant, J. Surfactants Deterg., 2013, 16(1): 57-61. https://doi.org/10.1007/s11743-012-1407-3
- [19]Du X, Lu Y, Li L, et al. Synthesis and unusual properties of novel alkylbenzene sulfonate gemini surfactants, Colloids Surf., A, 2006, 290(1-3): 132-137. https://doi.org/10.1016/j.colsurfa.2006.05.013
- [20] Wang R, Yan H, Hu W, et al. Micellization of Anionic Sulfonate Gemini Surfactants and Their Interactions with Anionic Polyacrylamide, J. Surfactants Deterg., 2018, 21(1): 81-90. https://doi.org/10.1002/jsde.12003
- [21]Li J, Xie Y C, Li Z F, et al. Synthesis and emulsifying properties of the sulfonate gemini surfactant, Sci. Technol. Chem. Ind., 2017, 25(6): 12-16.
- [22] Mafalda A B, Lidia P, Celia F. Amino acid-based cationic gemini surfactant-protein interactions, Colloids Surf., A, 2015, 480: 105-112. https://doi.org/10.1016/j.colsurfa.2014.12.022

- [23]Lyu B, Gao J, Gao D, et al. Research Progress of Modified Rapeseed Oil and Application in Leather Fatliquor, China Leather, 2012(21):48-50.
- [24]Bao Y, Guo J, Ma J, et al. Cationic silicon-based gemini surfactants: effect of hydrophobic chains on surface activity, physic-chemical properties and aggregation behaviors, J. Ind. Eng. Chem., 2017, 53: 51-61. https://doi.org/10.1016/j.jiec.2017.03.045
- [25]Huang D, Zhu W F, Jiang X, et al. Synthesis and Properties of Nonionic-anionic Gemini Surfactant, Fine Chemicals, 2009, 26(6): 533-520.
- [26]Zhu S, Liu L, Cheng F. Influence of Spacer Nature on the Aggregation Properties of Anionic Gemini Surfactants in Aqueous Solutions, J. Surfactants Deterg., 2011, 14(2): 221-225. https://doi.org/10.1007/s11743-010-1226-3
- [27] Ao M, Xu G, Zhu Y, et al. Synthesis and properties of ionic liquid-type Gemini imidazolium surfactants, J. Colloid Interface Sci., 2008, 326(2): 490-5. https://doi.org/10.1016/j.jcis.2008.06.048
- [28]Tsubone K. The interaction of an anionic gemini surfactant with conventional anionic surfactants, J. Colloid Interface Sci., 2003, 261(2): 524. https://doi.org/10.1016/S0021-9797(03)00088-2
- [29] Rosen M J, Murphy D S. Effect of the nonaqueous phase on interfacial properties of surfactants. 2. Individual and mixed nonionic surfactants in hydrocarbon/water systems, Langmuir, 1991, 7(11): 2630-2635.https://doi.org/10.1021/la00059a039

[30]Wang X, Liu J, Yu L, et al. Surface adsorption and micelle formation of imidazolium-based zwitterionic surface active ionic liquids in aqueous solution, J. Colloid Interface Sci., 2013, 391(1): 103.

https://doi.org/10.1016/j.jcis.2012.09.073

- [31]Wang L, Zhang Y, Ding L, et al. Synthesis and physiochemical properties of novel gemini surfactants with phenyl-1,4-bis(carbamoylmethyl) spacer, RSC Adv., 2015, 5(91): 74764-74773. https://doi.org/10.1039/c5ra13616d
- [32]Saxena N, Pal N, Ojha K, et al. Synthesis, characterization, physical and thermodynamic properties of a novel anionic surfactant derived from Sapindus laurifolius, RSC Adv., 2018, 8(43): 24485-24499.

https://doi.org/10.1039/c8ra03888k

- [33]Kumar D, Rub M A. Effect of anionic surfactant and temperature on micellization behavior of promethazine hydrochloride drug in absence and presence of urea, J. Mol. Liq., 2017, 238:389-396. https://doi.org/10.1016/j.molliq.2017.05.027
- [34] Azum N, Rub M A, Asiri A M. Bile salt-bile salt interaction in mixed monolayer and mixed micelle formation, J. Chem. Thermodyn., 2019, 128: 406-414. https://doi.org/10.1016/j.jct.2018.08.030
- [35]Rub M A, Azum N, Khan F, et al. Aggregation of sodium salt of ibuprofen and sodium taurocholate mixture in different media: A tensiometry and fluorometry study, J. Chem. Thermodyn., 2018, 121: 199-210.

https://doi.org/10.1016/j.jct.2018.02.019

- [36]D'Andrea M G, Domingues C C, Malheiros S V P, et al. Thermodynamic and Structural Characterization of Zwitterionic Micelles of the Membrane Protein Solubilizing Amidosulfobetaine Surfactants ASB-14 and ASB-16, Langmuir, 2011, 27(13): 8248-56. https://doi.org/10.1021/la1037525
- [37] Jiao J, Dong B, Zhang H, et al. Aggregation Behaviors of Dodecyl Sulfate-Based Anionic Surface Active Ionic Liquids in Water, J. Phys. Chem. B, 2012, 116(3): 958-965. https://doi.org/10.1021/jp209276c
- [38]Stodghill S P, Smith A E, O'Haver J H. Thermodynamics of micellization and adsorption of three alkyltrimethylammonium bromides using isothermal titration calorimetry, Langmuir, 2004, 20(26): 11387-92. https://doi.org/10.1021/la047954d

- [39] Wei T. Study on the Micellization and Interfacial Activity of Cationic Surfactants, Zhejiang University, 2012.
- [40]Kim H J, Decker E A, Mcclements D J. Preparation of multiple emulsions based on thermodynamic incompatibility of heat-denatured whey protein and pectin solutions, Food Hydrocolloids, 2006, 20(5): 586-595. https://doi.org/10.1016/j.foodhyd.2005.06.007
- [41]D. Muller, M. Malmsten, B. Bergenstahl, et al. Competitive Adsorption of Gelatin and Sodium Dodecylbenzenesulfonate at Hydrophobic Surfaces, Langmuir, 1998, 14 (11): 3107-3114. https://doi.org/10.1021/la971040s

[42]Wang Y, Han Y, Huang X, et al. Aggregation behavior of a series of anionic sulfonate gemini surfactants and their corresponding monomeric surfactant, J. Colloid Interface Sci., 2008, 319 (2): 534.

https://doi.org/10.1016/j.jcis.2007.11.021

Stranger MANSON

### Highlights:

- 1. An asymmetric sodium benzenesulfonate Gemini surfactant was designed.
- 2. The surfactant could emulsify rapeseed oil for lubricating collagen fiber.
- 3. The surfactant could improve emulsifying ability of the ROCLM in cold water.

Joseph Marines