A Novel Bio-based Sulfonic Zwitterionic Surfactant Derived from Transgenic Soybean Oil and its Performance in Surface and Interfacial Activities

Wenjie Xu [1], Pengcheng Bian [1], Hongze Gang[1], Jinfeng Liu[1],Bozhong Mu [1,2], and Shizhong Yang [1]*

[1]State Key Laboratory of Bioreactor Engineering and Institute of Applied Chemistry, East China University of Science and Technology, Shanghai 200237, China

[2]Shanghai Collaborative Innovation Center for Biomanufacturing Technology, Shanghai 200237, China

ABSTRACT

Bio-based surfactants have attracted increasing attention due to their renewable resources and excellent surface properties. In this study, a novel bio-based sulfonic zwitterionic surfactant (BSZS) derived from transgenic soybean oil was prepared using a simple reaction route with two steps of the amidation and quaterisation. The bio-based sulfonic zwitterionic surfactant showed a critical micelle concentration (CMC) as low as 33.34 mg/L with a surface tension of 28.50 mN/m. In addition, it also showed good performance in foamability, emulsibility, and wettability. The excellent performances indicated the great potential applications of the bio-based sulfonic surfactant from vegetable oils in both daily life and industrial fields.

Keywords: Bio-based Surfactant, Zwitterionic Surfactant, Transgenic Soybean Oil

INTRODUCTION

Surfactants have been widely used as detergents in daily life and industrial fields such as daily washing products [1], enhanced oil recovery (EOR) [2-3], and oil spill disposal processing (OSDP) [4-5]. Compared with the traditional surfactants which are generally petroleum-based, bio-based surfactants have received increasing attention because of its renewable resource, outstanding physicochemical property, low costs [6]. Biomass has been used as the raw materials of bio-based surfactants such as proteins [7], carbohydrates [8], alcohols [9-10], vegetable oils, and fatty acids [11-13]. Non-edible vegetable oil is one of the most common biomass and has received a great interest as platform chemicals for surfactants, biodiesel, biopolymers etc. due to their universal availability, inherent biodegradability, and low costs [14-17].

Non-edible vegetable oil has been applied to producing bio-based surfactants such as sodium N-fatty acyl amino acid [16], N-phenyl fatty amidopropyl-N, N dimethyl carboxyl betaine [18], UC18DAB [19], which have shown good surface and interfacial properties. However, the synthetic methods of bio-based surfactant are still defective and could be improvable.

Alkaline hydrolysis, alkylation, and alkaline hydrolysis were commonly used in the synthetic route of bio-based surfactant derived from nonedible vegetable oil, which made the reaction complex with high

*Corresponding author

Shizhong Yang

Email: meor@ecust.edu.cn

Tel: +86 21 6425 2063

Fax: +86 21 6425 2063

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A Novel Bio-based Sulfonic Zwitterionic Surfactant Derived from Transgenic ...

**Journal of Petroleum
Science and Technology**

energy consumption and emission of pollutants. For example, after the alkaline hydrolysis, a large amount of acid was consumed to neutralize the alkaline, and a great deal of salt was produced, which increased the burden to the environment. Meanwhile, the complexity of the reaction process greatly increased the energy consumption. On the other hand, SO_2 and HCl would be produced in the acyl-chlorination, because of the use of thionyl chloride. It is neither economic nor environmentally friendly.

In the present study, a novel bio-based sulfonic zwitterionic surfactant was synthesized using renewable transgenic soybean oil as the starting material by a strategy of a facile two-step route, amidation, and quaterisation, which was simpler, was more energy saving, and had lower pollutants. The fatty acid amine obtained from amidation was detected by GC-MS. The novel bio-based sulfonic zwitterionic surfactant (BSZS) was determined by ESI-MS, and its surface behavior; moreover, foamability, emulsibility, and wettability were evaluated in this paper.

EXPERIMENTAL PROCEDURES
Materials

N, N-Dimethyl-1, 3-propane diamine (AR, Aladdin, Shanghai, China), sodium 3-chloro-2-hydroxy propane sulfate (95%, Aladdin, Shanghai, China), KOH (AR, Shanghai Lingfeng Chemical Reagent Co. Ltd., Shanghai, China), acetic ether (AR, Shanghai Lingfeng Chemical Reagent Co. Ltd., Shanghai, China), sulfuric acid (AR, Shanghai Lingfeng Chemical Reagent Co. Ltd., Shanghai, China), methanol (AR, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China), anhydrous sodium sulfate (AR, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China), 1,

4-dioxane (AR, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China), and isopropanol (AR, Shanghai Lingfeng Chemical Reagent Co. Ltd., Shanghai, China) were used without further purification. Transgenic soybean oil was purchased from supermarkets, and its saponification value was determined to be 194.93 mg KOH/g.

Synthesis Methods

BSZS was synthesized from transgenic soybean oil through two processes, namely amidation, and quaterisation.

Amidation

(1) Direct Amidation

A certain amount of transgenic in which the content of main fatty acids were listed in Table 1, N, N-Dimethyl-1, 3-propane diamine, and KOH were added into a flask and were then refluxed at temperatures of 120, 130, and 140°C for several hours.

(2) Transesterification-amidation

8.97 grams (1.03×10^{-2} mol) transgenic soybean oil, 0.18 grams (3.26×10^{-3} mol) KOH, and 12.0 mL methyl alcohol were added into a flask, and refluxed at 65 °C for 2 hours. The resulted mixtures were then remained quiescently for a while until layering. The supernate was a mixture of the methyl alcohol, KOH (potassium hydroxide), and fatty acids methyl ester produced in the reaction and glycerol ester which were not react completely, and the lower layer was glycerol. The supernate was then transferred to another flask and refluxed at 110°C to recycle methyl alcohol for 1 hour; then, the process was followed by the addition of 8.97 grams (8.61×10^{-2} mol) N, N-Dimethyl-1, 3-propane diamine, and 0.19 grams KOH into the flask, and refluxing at 140°C for 8 hours.

After the amidation reaction, the remained N,

N-Dimethyl-1, and 3-propane diamine were recycled by being evaporated under reduced pressure. 5 mL of a 15 (wt.%) NaCl solution was added into the reaction mixture to separate glycerol and KOH. Then 15 mL ethyl acetate was used to extract the organic phase for 3 times. The fatty acid amides were obtained from the organic layer.

Quaterisation

1.00 grams fatty acid amide and 0.68 grams sodium 3-chloro-2-hydroxy propane sulfate were added into a flask along with 0.034 grams NaOH as the catalyst and isopropanol/water mixture as solvent. Under the condition of a reaction time equal to 4 hrs and variable temperature, $V_{isopropanol}/V_{water}$, and amount of solvent, the optimum condition was obtained by the method of orthogonal experiments. After the reaction, the solvent was evaporated under reduced pressure, and then extracted in ethyl alcohol to filtrate and remove the insoluble sodium 3-chloro-2-hydroxy propane sulfate and NaCl. After that, the ethyl alcohol was evaporated under reduced pressure to obtain the crude BSZS, and then the crude BSZS was weighed. Finally, the crude BSZS was extracted in ethyl acetate to remove the soluble fatty acid amine, and obtain the insoluble BSZS. The removed soluble fatty acid amine was washed by water for three times and dried to obtain the unreacted fatty acid amine.

Characterization

Gas chromatography mass spectrometry (GC-MS) was recorded on Agilent 6890N Network GC system and 5978 inter Mass Selective Detector. Electrospray ionization high resolution mass spectrometry (ESI HRMS) was recorded on the Waters LCT Premier XE Mass Spectrometers [17].

Measurements of Surface Tensions

BSZS aqueous solutions of different concentrations ranging from 1.7×10^{-6} mol/L to 5.9×10^{-3} mol/L were prepared by using double distilled water. The surface tensions (SFT) of these solutions were measured by the plate method using a DCAT 21 tensiometer (Dataphysics, Germany) at 25.0 ± 0.1°C [20] for three times, and the average value was obtained. The surface tension between air and double distilled water was 71.9 mN/m at 25 °C. Surface excess at CMC (Γ_{max}) was derived from the Gibbs adsorption isotherm equation[21].

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

where, C is the concentration of the surfactant in aqueous solution, and R is equal to 8.314 J/mol/K; T was set at 298.15 K; SFT is expressed in mN/m, and η was set to 1 for zwitterionic surfactants [22]. The area occupied per surfactant molecule (A_{min}) at CMC on air/water interface is related to the surface excess Γ_{CMC} as follows [21].

$$A_{min} = (N_A \Gamma_{max})^{-1} \times 10^{16} \tag{2}$$

where, N_A is the Avogadro's constant.

Measurements of Interfacial Tensions

Solutions of BSZS were prepared at different concentrations ranging from 0.005 g/L to 0.500 g/L in Daqing oil field simulated formation water; the concentrations of main ions were shown in Table 2.

Table 1: The content of main fatty acids in transgenic soybean oil.

	Palmitic Acid C16: 0	Stearic Acid C18: 0	Oleic Acid C18: 1	Linoleic Acid C18: 2	Linolenic Acid C18: 3
%.wt	10.68	4.99	25.96	50.72	7.65

Table 2: The concentrations of main ions in formation water of Daqing oil field.

Salinity	Cl^-	SO_4^{-2}	HCO_3^-	CH_3COO^-	Na^+	Ca^{+2}	Mg^{+2}
5318	1068	12	2307	216	1665	41	0.45

A Novel Bio-based Sulfonic Zwitterionic Surfactant Derived from Transgenic ...

**Journal of Petroleum
Science and Technology**

Interfacial tensions (IFT) between Daqing crude oil and these solutions were measured by the spinning-drop method at 50 ± 0.1 °C (the average stratum temperature of Daqing oilfield, China) using a SVT 20 tensiometer (Dataphysics, Germany) [23]. The interfacial tension between Daqing crude oil and the simulated formation water was 9.40 mN/m at 50 °C.

Measurement of Contact Angle

The contact angles of 0.500 g/L BSZS solution were measured by sessile drop technique at 25 °C [24] for 5 times for each sample and the average value was figured out. Double distilled water showed an average contact angle of 92.04° on the hydrophobic acrylic substrate at 25 °C [24].

Measurement of Foaming Property

The foaming property of 0.500 g/L BSZS solution was obtained according to Ross-Miles test [25] at 40 °C [7]. The foam heights at the beginning and after 10 min were recorded (hr./mm). The experiments were repeated for 3 times.

Measurement of Emulsifying Property

10 mL BSZS aqueous solution of 0.50 g/L concentration

and 10 mL liquid paraffin were added into 20 mL graduated test tube at room temperature. The tube was shaken violently for 2 min, and was then left quietly for 1 min. The time was recorded when the volume of the separated water was 3 mL (15% volume of the emulsion) and 5 mL (25% volume of the emulsion) [17].

Measurement of Krafft Point

5 mL of a 1% (m/m) BSZS aqueous solution was added into the test tube, which was placed in a thermostat water bath at 50 °C. Then, water temperature was reduced slowly until solid appeared in the aqueous solution.

RESULTS AND DISCUSSION
The Structural Characterization and Yields of Amidation

The GC spectrogram of the product from amidation reaction is shown in Figure 1, in which peaks with the retention time of 12.25, 13.86, 13.92, 14.05, and 14.35 min represent the different fatty acid amides, corresponding to the fatty acid amides with hydrophobic carbon chains of C16:0, C18:2, C18:1, C18:3, C18:0 respectively.
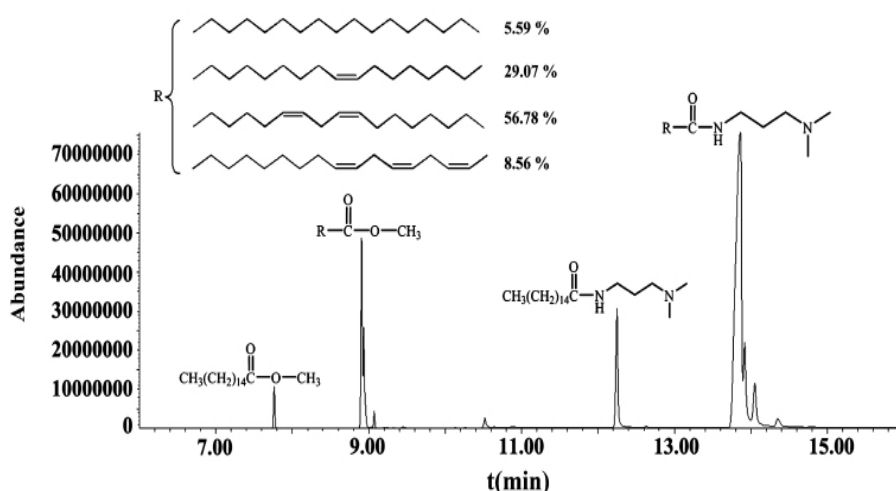

Figure 1: The GC spectrogram of the product from amidation reaction.

Moreover, peaks with retention time of 7.77, 8.90, 8.93, and 9.07 min represented the different fatty acid methyl esters respectively. Furthermore, the molecular weights of each fatty acid amide with hydrophobic carbon chain of C16:0, C18:2, C18:1, C18:3, and C18:0 were detected by the mass spectrum shown in Figure 2.
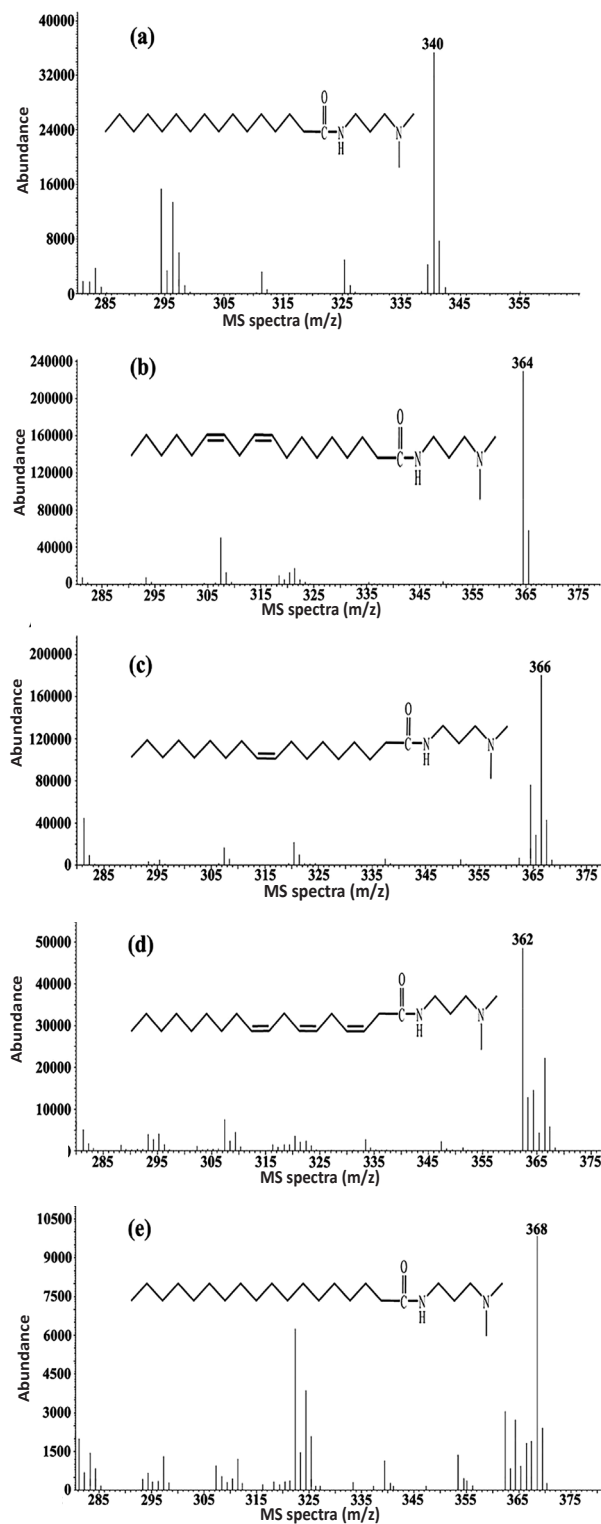

Figure 2: The MS spectrogram of the fatty acid amides.

A Novel Bio-based Sulfonic Zwitterionic Surfactant Derived from Transgenic ...

Journal of Petroleum Science and Technology

The condition and yields of amidation orthogonal experiment are shown in Table 3. Under the condition of number of transgenic soybean oil to the number of N, N-Dimethyl-1, 3-propane diamine equal to 1:3, the variables were temperature, reaction time, and the amount of KOH. In addition, the optimum condition was obtained by the method of orthogonal experiment. *A*, *B*, and C in Table 3 represent the temperature, reaction time, the mole ratio of KOH to transgenic soybean oil respectively.

Table 3: The yields of amidation in different conditions.

	A T (°C)	*B* t (hr.)	*C* KOH /transgenic soybean oil (n/n)	*K* Yield (%)
1	120	2	6	1.67
2	120	3	3	9.35
3	120	4	1.5	10.40
4	130	2	3	3.36
5	130	3	1.5	7.66
6	130	4	6	11.72
7	140	2	1.5	10.98
8	140	3	6	3.25
9	140	4	3	26.96
*K*1	7.14	5.34	9.68	-
*K*2	7.58	6.75	13.23	-
*K*3	13.73	16.36	5.55	-
R	6.59	11.02	7.68	-

K corresponds to the yield under different conditions, and R is the range of yield in different conditions. The results show that the higher the temperature is, the higher the yield is. Also, a higher yield was obtained at longer times. Moreover, when the mole ratio of KOH to transgenic soybean oil was 3, the yield was the highest. In addition, $R_B > R_C > R_A$, which means that the reaction time was the most influential factor; moreover, the mole ratio of KOH to transgenic soybean oil took the second place. Additionally, temperature was the least influential factor and had a little effect on the yield.

The yield of amidation was very low, and KOH was not distributed well in the reactants in the absence of solvent. To promote the yield, 3 different solvents at different concentrations were used to optimize the reaction condition listed in Table 4.

Table 4: The yields of amidation using different solvents.

Solvent	Volume	Yield (%)
Dioxane	4 mL (0.0469 mol)	32.21
methanol	4 mL (0.0988 mol)	32.13
N, N-Dimethyl-1, 3-propane diamine	3.8 mL (0.0304 mol)	74.11

It is clear that the yields were obviously increased differently when different solvents were used. When both of the dioxane and methanol were used as the solvents, the yield was very low. KOH could not be dissolved in dioxane in the reaction system, and it may hinder the smooth progress of the reaction. On the other hand, KOH may be dissolved in methanol. However, since the low boiling point of methanol was 64.7 °C, the reaction temperature could not reach 140 °C when the reaction refluxed. As a result, the yield was still low. When N, N-dimethyl-1, and 3-propane diamine was used as the solvent, it acted as a reactant too. Meanwhile, KOH could be dissolved in excess N, N-dimethyl-1, 3-propane diamine, which ensured the smooth progress of the mass transfer. Consequently, the

yield at the mole ratio of transgenic soybean oil to N, N-dimethyl-1, and 3-propane diamine to KOH equal to 1:15:3, at a temperature of 140 °C, and for a reflux time of 8 hours reached 74.11%, which was much higher than that obtained in the other conditions.

For the amidation reaction in two steps of transesterification-amidation, the yield was 83.14% which was higher than that of the direct amidation in one step. When methyl alcohol was added into the flask, the transesterification of transgenic soybean oil was first happened through the catalysis of KOH; fatty acid methyl ester was then produced, which reacted with N, N-dimethyl-1, 3-propane diamine through amidation. Compared with transgenic soybean oil, fatty acid methyl ester more easily reacted with N, N-dimethyl-1, 3-propane diamine. However, transesterification-amidation needed complicated operation and more energy consumption; for example, glycerol and methanol needed to be removed respectively. As a result, the direct amidation was more practical and economical. In addition, in comparison with the method reported for the synthesis of nonedible fatty acid amide [16], the direct amidation is simpler, is more environmentally friendly, and has lower pollutant emission since the glycerol produced in the reaction could be used as an industrial raw material; this is significant for its application to industrial production.

The Yields of Quaterisation and Structural Characterization

Table 5 lists yields (K) at different temperatures (A), volume ratios of isopropanol to water (B), and volumes of solvent (C) in quaterisation reaction optimized by the orthogonal experiment.

Table 5: The yields of quaterisation in different conditions.

	A T (°C)	B Isopropanol /Water (v/v)	C $V_{solvent}$ (mL)	K Yield/%
1	70	2: 1	10	87.14
2	70	1: 1	7	85.05
3	70	1: 2	5	86.57
4	80	2: 1	7	92.59
5	80	1: 1	5	89.25
6	80	1: 2	10	84.37
7	90	2: 1	5	85.92
8	90	1: 1	7	92.93
9	90	1: 2	10	91.38
$K1$	86.25	88.55	87.63	-
$K2$	88.74	89.08	90.19	-
$K3$	90.08	87.44	87.25	-
R	4.55	1.64	2.94	-

It is suggested that the higher the temperature should be, the higher the yield should be. Also, when isopropanol to water ratio (v/v) was 1:1, the yield was the highest. $V_{solvent}$ = 7 mL per 1 gram of fatty acid amine was the best. $R_A > R_C > R_B$ indicated that temperature was the most significant factor, and $V_{solvent}$ took the second place, while isopropanol to water ratio (v/v) was the least influential factor. As a result, the optimum reaction condition for quaterisation was a temperature of 90 °C, an isopropanol to water ratio (v/v) of 1: 1, and a $V_{solvent}$ of 7 mL/g, which lead to a yield of 92.93 %.

The molecular weight of the BSZS was determined by ESI-MS, and the ionization way of ESI-MS was positive ion mode with Na⁺, as shown in Figure 3.
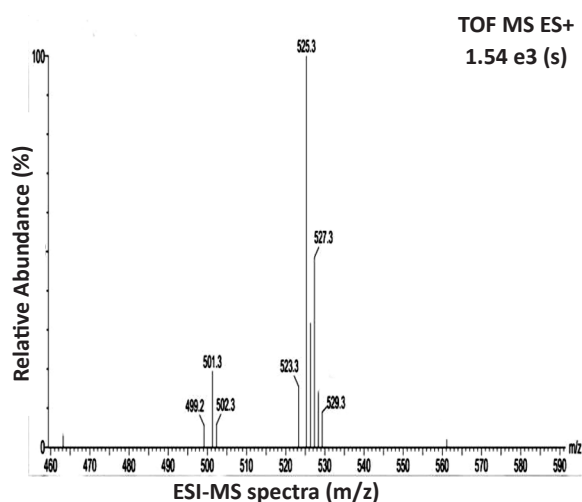
A Novel Bio-based Sulfonic Zwitterionic Surfactant Derived from Transgenic ...

**Journal of Petroleum
Science and Technology**

Figure 3: The ESI-MS spectrogram of BSZS.

The mass to charge ratios (*m/z*) of main peaks were 499.2 501.3, 523.3, 525.3, 527.3, and 529.3, which respectively correspond to BSZS with C16:0, C18:3, C18:3, C18:2, C18:1, C18:0. The *m/z* ratios of BSZS with different fatty acid alkyl chains are listed in Table 6.

Table 6: The *m/z* of BSZS with different fatty acid alkyl chains.

Type of fatty acid alkyl chain	Molecular formula of BSZS	M	M+H$^+$	M+Na$^+$	M+K$^+$
C16: 0	$C_{24}H_{48}N_2O_5S$	476.3284	477.3362	499.3182	515.2921
C18: 0	$C_{26}H_{54}N_2O_5S$	506.3753	507.3832	529.3651	545.3391
C18: 1	$C_{26}H_{52}N_2O_5S$	504.3597	505.3675	527.3495	543.3234
C18: 2	$C_{26}H_{50}N_2O_6S$	502.3441	503.3518	525.3339	541.3077
C18: 3	$C_{26}H_{48}N_2O_6S$	500.3285	501.3361	523.3183	539.292

Surface Properties

Equilibrium surface tension as a function of BSZS concentrations at 25.0 °C is illustrated in Figure 4.
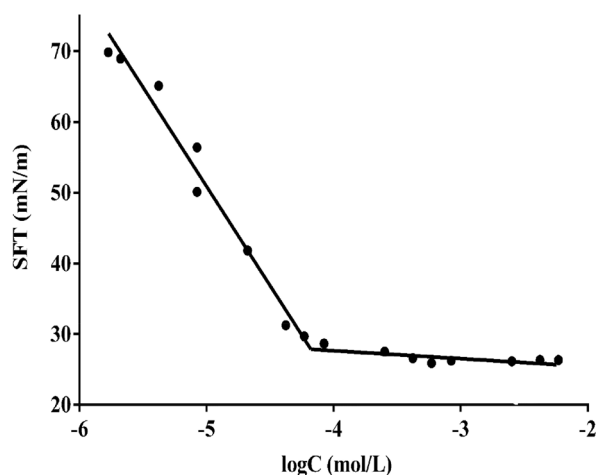

Figure 4: The surface tensions versus the concentration of BSZS at 25.0 °C.

The critical micelle concentration (CMC) and surface tension at CMC (SFT_{CMC}) were estimated from the breakpoints of the plots. The CMC of BSZS was as low as 6.92×10^{-5} mol/L with a SFT_{CMC} of 28.50 mN/m. Moreover, the calculated surface excess (Γ_{max}) and the area occupied per surfactant molecule (A_{min}) at CMC on air/water interface were 4.90 µmol/m^2 and 0.339 nm^2/molecule respectively.

An exceptive phenomenon shown in Figure 4 depicts that the surface tension kept decreasing by raising the BSZS concentration above the CMC point. This may be related to the double bond in the major hydrophobic chain of BSZS (as shown in Scheme 1).

a   **Amidation**

b   **Quaterisation**
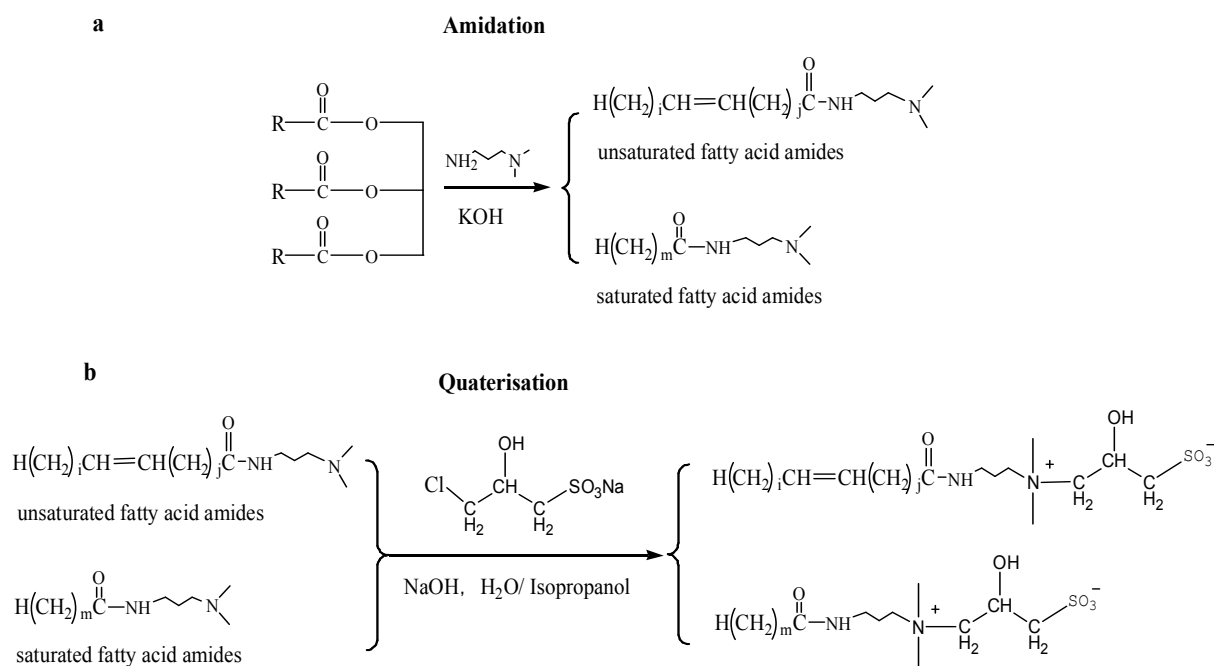
Scheme 1: The synthetic method of BSZS from transgenic soybean oil.

Double bonds are mostly cis-formed; moreover, the hydrophobic chain with a double bond has compressibility; as a result, the arrangement of surfactants molecules is incompact. When reaching the CMC of BSZS, the arrangement of the surfactant molecules on the surface is relatively incompact. When the surfactant concentration was increased, the air–water surface could accommodate more surfactant molecules. Hydrophobic chains with double bonds could also be compressed to decrease space. Surfactant molecule arrangement was more compact, and the surface tension of the solution was lower [18]. A similar phenomenon of anionic surfactants with a double bond hydrophobic chain had been reported elsewhere [26].

Interfacial Properties

Dynamic interfacial tensions (DIFT) between Daqing crude oil and the simulated formation water at the different concentrations of BSZS solutions and at a temperature of 50.0 °C are displayed in Figure 5(a).
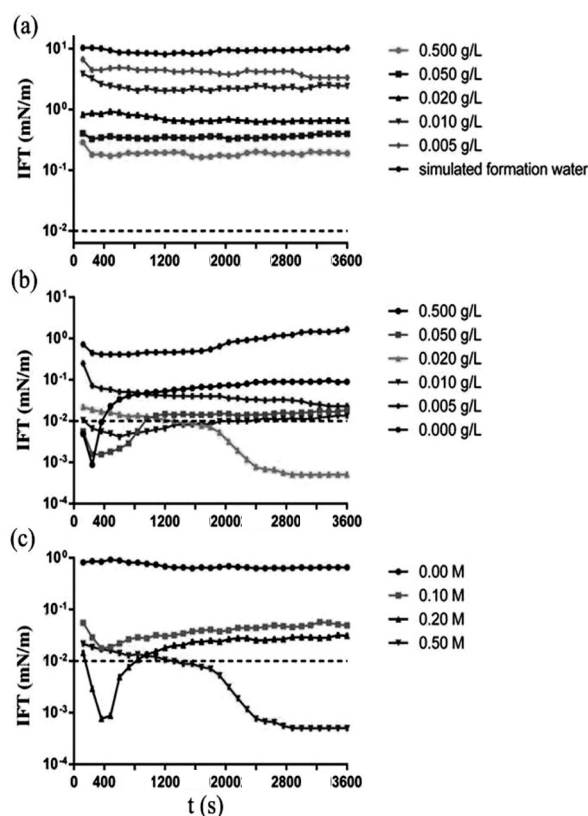

Figure 5: Dynamic interfacial tensions between Daqing crude oil and different concentrations of BSZS in the simulated formation water at 50.0 °C; (a) without Na_2CO_3, (b) with 0.5 M Na_2CO_3 added, (c) dynamic interfacial tensions between Daqing crude oil and 0.02 g/L BSZS in the simulated formation water having different concentrations of Na_2CO_3 at 50.0 °C.

It shows that DIFT is remained unchanged by changing time, but it is decreased by an increase in concentrations. The interfacial tension between crude oil and the simulated formation water solutions decreased to 7.91 mN/m at a BSZS concentration of 0.500 g/L.

When Na_2CO_3 was added into the simulated formation water, DIFT was decreased significantly, and the interfacial properties were improved obviously, as shown in Figure 5(b). A stable ultra-low IFT between crude oil and the simulated formation water was obtained with the system containing 0.010 g/L BSZS and 0.500 M Na_2CO_3 in solutions. Traditional petroleum-based surfactants such as petroleum sulfonates [27] and alkyl benzene sulfonates [28] along alkali (NaOH or Na_2CO_3) are widely used in oil recovery. The acidic components (petroleum acids) in crude oil can react with alkaline in solution to produce in situ surfactant, which can interact with petroleum-based surfactants and reduce the IFT between crude oil and water remarkably [29-32]. Meanwhile, it can be seen in Figure 5(c) that the interfacial properties could be further reduced by an increase in the concentration of Na_2CO_3. The minimum DIFT is in 10^{-3} mN/m orders of magnitude at 0.02 g/L BSZS, which is critically required for the effective displacement of residual crude oil from the pores and capillaries of petroleum reservoirs [33].

Foaming and Emulsification Properties

The Ross–Miles test revealed the initial foam height of 86 mm at a 0.500 g/L BSZS solution; after 5, 10, and 30 min, the foam height was 86, 82, and 80 mm respectively, indicating a little change after 30 minutes. This implied that BSZS inherited very strong foaming ability and stability.

The average time for separating 3 mL (15 vol.% of the emulsion) and 5 mL (25 vol.% of the emulsion) water was 283.6 and 504.4 s respectively, which confirmed that BSZS had a strong emulsification property. Moreover, the emulsion produced by BSZS and liquid paraffin was pretty stable because the emulsion layer still existed after 30 min.

Contact Angle and Krafft Point

The average contact angle of air/water/solid was reduced from 92.04 to 44.1° at a BSZS concentration of 0.500 g/L, which showed an excellent wetting property. The Krafft point of 1% surfactant solution was below 0 °C. 1% BSZS in an aqueous solution was clear and transparent at different temperatures greater than 0 °C. The Krafft point is the temperature below which the solubility of surfactant is quite low and insufficient for micellization; moreover, the solubility changes evidently at this point [34]. The Krafft point of $C_{16}H_{33}SO_3Na$ and $C_{18}H_{37}SO_3Na$ were 55.3 and 64.8 °C respectively in a previous research [34]. The Krafft point blew 0 °C indicates that BSZS has better solubility than normal alkyl benzene sulfonates.

CONCLUSIONS

A novel bio-based sulfonic zwitterionic surfactant derived from renewable transgenic soybean oil was successfully synthesized using the strategy of the two-step route of amidation and quaterisation. The novel bio-based sulfonic zwitterionic surfactant showed a CMC as low as 33.34 mg/L with a surface tension of 28.50 mN/m and a higher interfacial activity in aqueous solutions containing Na_2CO_3. The interfacial tension between crude oil and the simulated formation water was greatly reduced to an ultra-low order ($\leq 10^{-2}$ mN/m) at 10 mg/L BSZS in

solutions. The novel bio-based sulfonic zwitterionic surfactant also exhibited strong emulsifying (504.4 s for 25 vol.% of the emulsion), foaming ability (a foam height 80 mm after 30 min), and good wetting performance (44.1°), which suggested that the novel bio-based sulfonic zwitterionic surfactant should be a very competitive candidate for surfactant flooding in oil recovery, for oil spill treatment, and for many other industrial applications.

NOMENCLATURES

BSZS	: Bio-based Sulfonic Zwitterionic Surfactant
C	: The Concentration of the Surfactant (mol/L)
CMC	: Critical Micelle Concentration (mol/L)
DIFT	: Dynamic Interfacial Tensions
EOR	: Enhanced Oil Recovery
IFT	: Interfacial Tensions (mN/m)
KOH	: Potassium Hydroxide
OSDP	: Oil Spill Disposal Processing
SFT	: Surface Tensions (mN/m)

ACKNOWLEDGMENTS

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