

Highly Ca^{2+} -Ion-Tolerant Biobased Zwitterionic Surfactant with High Interfacial Activity

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ABSTRACT: The wide application of surfactants has a harmful effect on the environment, drawing more attention to the development and application of low-toxicity surfactants. A salt-tolerant and low-toxicity biobased zwitterionic surfactant, *N,N*-dimethyl-*N*-[2-hydroxy-3-sulfo-propyl]-*N*-benzyloxyoctadecanoyl-1,3-propanediamine (SPBOPA), was prepared from the oleic acid extracted from waste oils and anise ether extracted from the tarragon. The final surfactant structure was confirmed using gas chromatography–mass spectrometry (GC–MS), liquid chromatography–mass spectrometry (LC–MS), and ^1H nuclear magnetic resonance (NMR) spectroscopy. The SPBOPA surfactant could reduce the interfacial tension between crude oil and formation brine to ultralow (5.2×10^{-4} mN/m) at a low dosage without extra alkali. It still had good interfacial properties in NaCl up to 60 g/L, Ca^{2+} up to 2000 mg/L, and temperature up to 100 °C. Furthermore, SPBOPA had strong antidilution and antiadsorption properties with low toxicity as demonstrated by the high LD_{50} value of >5000 mg/kg-BW. It could also enhance the wetting ability of crude oil surfaces. Meanwhile, it showed a high biodegradability in the environment. All of the results achieved in this work confirmed that the SPBOPA surfactant is a more robust and promising biobased surfactant candidate than traditional surfactants as an eco-friendly surfactant for enhanced oil recovery (EOR).

Non-food plants and wastes



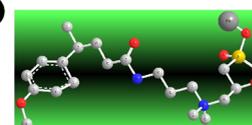
Waste oils



Tarragon

Methyl oleate

Anisole



Bio-based surfactant

INTRODUCTION

Tertiary oil recovery technology is mainly used in the later stage of oil field development, and alkaline–surfactant–polymer (ASP) flooding is one of the most critical methods.¹ Since the subsurface sandstone of oil reservoirs is typically negatively charged, the anionic surfactants are utilized for ASP flooding to reduce the adsorption between sandstone and surfactants.² In ASP flooding, alkalis are often added to avoid the problem that anionic surfactants are challenging to mix with oil–water systems and also to reduce interfacial tension to ultralow value.^{3–5} However, alkalis have several negative consequences, including damage to pipes, strata damage, and pole blocking.⁶ In this challenge, an alkali-free system with improving interfacial activity has gotten a lot of attention.⁷

Ultralow interfacial tension is an essential factor in evaluating surfactants for EOR. In the alkali-free system, the addition of phenyl groups into the hydrophobic chain has been proven to improve the interfacial characteristics of surfactants as well as their performance under high temperatures and salinity conditions.^{8–10} Still, monoaromatic hydrocarbons, polycyclic aromatic hydrocarbons, and phenolic compounds represented by benzene and toluene are being applied, which can contaminate soil and water^{11,12} and cause acute or chronic toxicity.^{13,14} Because of their resistance to degradation, they can accumulate easily in organisms,^{15,16} leading to biological death and human carcinogenesis.¹⁴ Therefore, other compounds such

as cardanol could be used instead of linear alkylbenzene (LAS) to synthesize sulfobetaine-type surfactants, which have lower surface tension than alkylbenzene-type¹⁷ and sulfonated methyl esters of fatty acids with alkyl resins as raw materials to synthesize surfactants as environmentally friendly substitutes for LAS and improved their washing performance.^{18,19} However, there is no potential for application in the petroleum industry.

Recently, the development of surfactants has shifted to more environmentally friendly, less expensive, more readily available raw materials, and more straightforward surfactant-synthesis techniques.¹⁴ Compared to petroleum-based surfactants, the recyclable and sustainable biobased surfactants derived from renewable raw materials could reduce the emissions of carbon dioxide and other hazardous substances,²⁰ and the cost of biobased products is effective compared with that of fossil raw materials.²¹ According to an EU survey, 80% of respondents are enthusiastic about biobased products and 66.6% prefer biobased products to non-biobased ones.²²

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In this paper, we used a facile and an eco-friendly synthetic route to develop a biobased zwitterionic surfactant, *N,N*-dimethyl-*N*-[2-hydroxy-3-sulfo-propyl]-*N*-benzyloxyoctadecanoyl-1,3-propanediamine (SPBOPA), from the oleic acid extracted from waste oil and biomass-derived anise ether. The biobased surfactant SPBOPA demonstrated a high interfacial activity, strong temperature stability, good salt compatibility, and low toxicity, as well as good biodegradability.

MATERIALS AND METHODS

Materials. The following reagents were used, commercial oleic acid, methyl oleate (99%, Nantong Feiyu Biological Technology Co., Ltd.), HND580 (Nanda Synthesis Co., Ltd.), Na₂CO₃ (AR, Sinopharm Chemical Reagent Co., Ltd.), anisole, FeCl₃, sodium 3-chloro-2-hydroxypropanesulfonate (AR, Meryer (Shanghai) Chemical Technology Co., Ltd.), *N,N*-dimethyl-1,3-propanediamine, ethanol, and methanol (99%, Shanghai Macklin Biochemical Co., Ltd.).

Structural Analyses. Alkylation and amidation structural products were determined by gas chromatography–mass spectrometry (GC–MS, SHIMADZU GC–MS-TQ8040 NX) at 120 °C as the initial temperature for 3 min and then at 300 °C at 20 °C/min for 40 min. The quaternization structural product was determined by liquid chromatography–mass spectrometry (LC–MS, SHIMADZU LDMS-8045) at the 0.4 mL/min flow rate with an injection of 10.0 μL and methanol/water as the mobile phase (an initial gradient of 95% methanol for 2 min, and 2–12 min to 100% methanol gradient for 20 min). And finally, it was confirmed using ¹H NMR (Bruker Advance 400 spectrometer (400 MHz)).

Interfacial Tension Measurement. A spinning drop interfacial tensiometer (model TX500, Kruss SDT) was run at 4500 rpm and at 45 °C for 2 h to determine the interfacial tension between the crude oil and SPBOPA surfactant solutions at different conditions.²³ The refined Daqing crude oil had a density of 0.85 g/cm³ and a viscosity of 19.8 mPa·s at 45 °C. The composition of the simulated formation water was as shown in Table 1.

Table 1. Content of Salts in the Formation Water²⁴

salts	concentration (mg/L)
NaCl	1588.3
CaCl ₂	112.2
Na ₂ CO ₃	381.6
MgCl ₂ ·6H ₂ O	91.6
Na ₂ SO ₄	17.1
NaHCO ₃	3176.0

Evaluation of Sand Adsorption. Three grams per liter of the SPBOPA surfactant solution was prepared in the simulated formation water. Then, the surfactant solution was mixed with oil sands in a mass ratio of 9:1. The mixture was oscillated using a constant temperature shaker at 45 °C and 120 rpm for 24 h and centrifuged to obtain the supernatant to test its interfacial tension. Then, the supernatant was mixed with the oil sands at a mass ratio of 9:1, and these procedures were repeated five times until the interfacial tension was above 1.0×10^{-2} mN/m.²⁵ The oil sand was collected from the sixth crude oil production plant of the Daqing oil field in China. Before the experiment, the raw oil sand was extracted three times in petroleum ether and chloroform and then smashed into 80–120 mesh oil sand particles after drying.

Evaluation of Dilution. Three grams per liter of the SPBOPA surfactant solution was prepared in the simulated formation water. Then, the prepared surfactant solution was diluted with the simulated formation water at a ratio of 1:10, 1:20, 1:30, ..., 1:150. Finally, the interfacial tension between the crude oil and each diluted surfactant solution was measured.²⁶

Evaluation of Salt Tolerance and Thermal Stability. Different portions of 0.5 g/L of the SPBOPA surfactant solution were prepared in the simulated formation water, and different extra concentrations of NaCl and Ca²⁺ were added, respectively. The interfacial tensions between the crude oil and each surfactant solution with additional salt contents were measured. Meanwhile, the dynamic interfacial tensions between the crude oil and 0.5 g/L surfactant solution at 45–120 °C were measured to determine SPBOPA's thermal stability.

Evaluation of Wettability. The model of the instrument was JC2000D1. Two identical quartz plates were prepared and evenly covered the crude oil on one of the quartz plates. A 0.5 g/L SPBOPA aqueous solution was prepared and controlled the concentration of Ca²⁺. The solution was dropped onto a plane at 30 °C, and the high-speed camera recorded the shape of droplets. After static equilibrium, the contact angle was calculated by the five-point fitting method, and the average value was obtained by repeating it three times.

Prediction of Toxicity. Toxicity Estimation Software Tool (T.E.S.T) software was used to predict the toxicity of the SPBOPA surfactant using an LD₅₀ toxicity prediction model. The LD₅₀ of the SPBOPA surfactant was also determined according to the HJ/T 154-2004 standard.

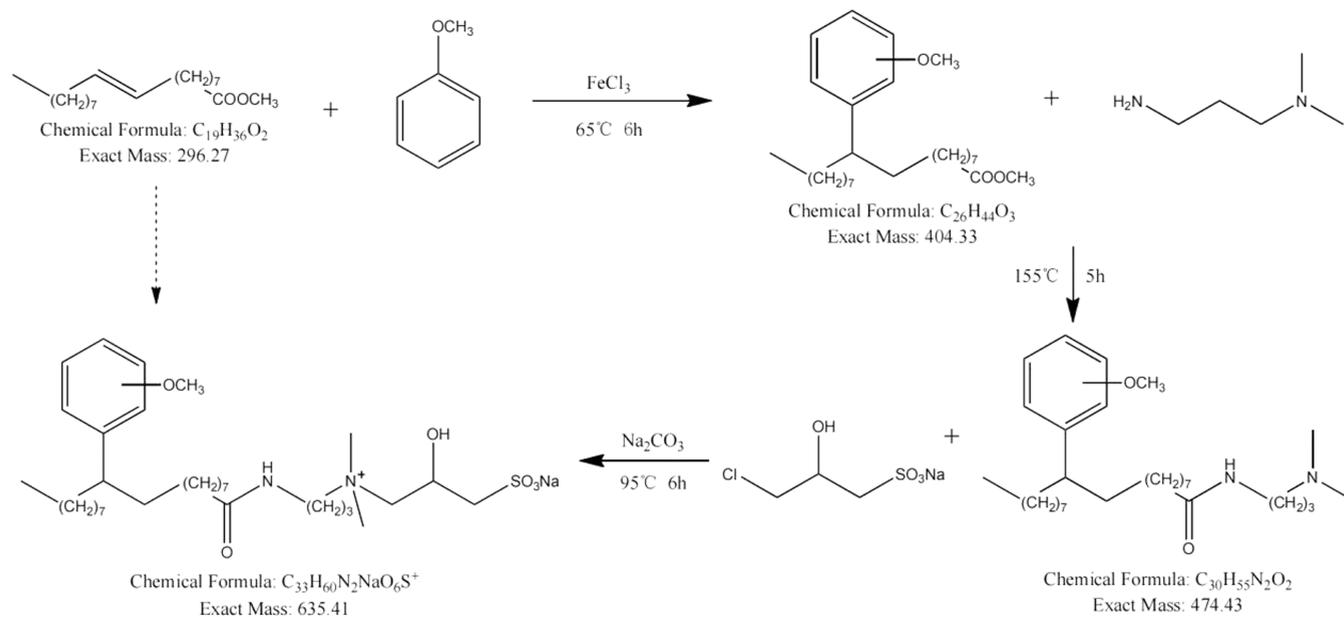
Degradability Prediction. The Estimation Programs Interface (EPI) software provided by the US Environmental Protection Agency was used to evaluate the biodegradability of the SPBOPA surfactant. The AOPWIN module was used to determine the photodegradation characteristics (half-life), and the BIOWIN module was used to determine the detailed biodegradability properties, which included ultimate biodegradation from BIOWIN3 and primary biodegradation using BIOWIN4.²⁷

Synthesis. The synthesis steps included alkylation, amidation, and quaternization (Scheme 1). Methyl oleate, anisole, and FeCl₃ with a molar ratio of 1:8:0.5 were weighed and added in a closed system reactor. Then, the mixture was stirred at 65 °C for 6 h and filtered. The filtrate was evaporated off to obtain an initial methyl benzyloxy octadecanoate (BO) product. Subsequently, BO was amidated using *N,N*-dimethyl-1,3-propanediamine in a molar ratio of 1:3 and was refluxed at 155 °C for 5 h. Then, the mixture was evaporated off to obtain an intermediate *N,N*-dimethyl-*N*-benzyloxyoctadecanoyl-1,3-propanediamine (BOPA) product.²⁸ The BOPA was quaternized using sodium 3-chloro-2-hydroxypropanesulfonate and sodium carbonate in a molar ratio of 1:1.2:1 in a mixed solvent of ethanol–water ($V_{\text{ethanol}}/V_{\text{water}} = 7:3$) and refluxed at 95 °C for 6 h in a closed reaction system.²⁹ After the reaction, the solvent mixture was evaporated, and the concentrated SPBOPA surfactant product mixture was dissolved in methanol and filtered. Finally, the filtrate was evaporated to remove methanol, and the purified SPBOPA surfactant product was obtained.

RESULTS AND DISCUSSION

Structural Analyses. The SPBOPA surfactant was prepared through alkylation, amidation, and quaternization reactions (Scheme 1). The gas chromatograms and mass spectra of alkylation and amidation were obtained. The yields were

Scheme 1. Synthetic Route of *N,N*-Dimethyl-*N*-[2-hydroxy-3-sulfo-propyl]-*N*-benzyloxyoctadecanoyl-1,3-propanediamine (SPBOPA) Biobased Zwitterionic Surfactant



calculated based on integral areas on chromatograms, and the conversion rates of alkylation and amidation were 96.1 and 95.8%, respectively (Figures S1 and S4). The structural products were confirmed according to the mass spectra (Figures S2 and S5). The m/z 's of characteristic fragments of alkylation product were 121.1 and 404.3, and the m/z 's of characteristic fragments of amidation products were 58.1 and 474.4. The LC–MS spectrum of the quaternization product was obtained. The conversion rate of quaternization was found to be 95.6% (Figure S8). The product's structural formation was confirmed according to the mass spectrum (Figure S7). The m/z of hydrogen-ionized or sodium-ionized SPBOPA surfactant products was 613.4 or 635.4, respectively. The calculated SPBOPA surfactant product's purity was 88.0%. The 1H NMR spectrum of SPBOPA was recorded as shown in Figure S10. 1H NMR (400 MHz, methanol- d_4) δ 7.02 (dd, 2H, $-ph-H$), 6.83 (dd, 2H, $-ph-H$), 6.49 (d, 1H, $-CO-NH-$), 3.73 (d, 1H, $-CH_2-CH-OH$), 3.68 (s, 3H, $-ph-OCH_3$), 3.56 (dd, 1H, $-CH_2-CH-OH$), 3.48–3.40 (m, 2H, $-CH_2-SOO$), 3.29–3.21 (m, 2H, $-N(CH_3)_2-CH_2-CH-OH$), 3.05–2.94 (m, 2H, $-CO-NH-CH_2$), 2.87 (dd, 1H, $-ph-CH-$), 2.00 (q, 2H, $-CH_2-N(CH_3)_2$), 1.93 (s, 2H, $-CH_2-CO-$), 1.86 (s, 6H, $(CH_3)_2-N-$), 1.52 (m, 2H, $-CH_2-CH_2-CO$), 1.29–1.09 (m, 28H, $CH_3-CH_2-CH_2$), 0.84 (t, 3H, CH_3-CH_2).

The LC–MS and 1H NMR results indicated that the SPBOPA surfactant product was successfully obtained. The best reaction condition for alkylation was at the ratio of methyl oleate to anisole to ferric chloride of 1:8:0.5 at 65 °C for 6 h to obtain the BO product. The optimum reaction condition for amidation was at the ratio of BO to 3-dimethylaminopropylamine equivalent of 1:3 at 155 °C for 5 h to obtain intermediate BOPA. The best reaction condition for quaternization was at the ratio of BOPA to sodium 3-chloro-2-hydroxypropanesulfonate to sodium carbonate equivalent of 1:1.2:1 at 95 °C for 6 h to obtain the SPBOPA biobased zwitterionic surfactant product. The alkylation catalyst can also be replaced by HND580, which had a conversion rate of 82% after repeating the reaction eight times.³⁰ Excess anisoles and 3-dimethylaminopropylamine

could be distilled off under reduced pressure for its recovery. Excess salt could also be removed by filtration. The synthesis process has a simple operation, a high conversion rate, and recyclable raw materials and is environmentally friendly.

Interfacial Activity. The IFTs between crude oil and solutions of SPBOPA at different concentrations were measured at 45 °C. When the concentrations were 0.010–3.0 g/L, the interfacial tension was lower than 0.010 mN/m. The lowest IFT was 5.2×10^{-4} mN/m at 0.5 g/L (Figure 1). According to other

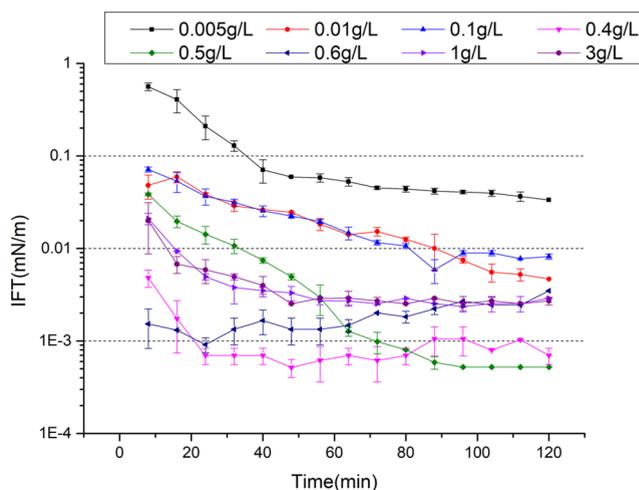


Figure 1. Plot of IFT between the crude oil and the SPBOPA solution at different concentrations at 45 °C.

reports, the IFT of sodium alcohol ether sulfate surfactants AES-205 and 7-58 was measured in the range of 0.001–0.5% at 60 °C, and the IFT of solutions in the range of 0.05–0.5% was lower than 1×10^{-2} mN/m. In addition, the IFT could reach 1.8×10^{-3} mN/m at a concentration of 0.005%.³¹ The IFT of the Guerbet betaine surfactants GC-16 and GC-20 were measured in the range of 0.005–0.3% at 45 °C, and the IFT of solutions in the range of 0.025–0.2% was lower than 1×10^{-2} mN/m.³² In

summary, SPBOPA solutions had a good interfacial performance at the concentration of 0.001% in simulated formation water, and it had a wide range of concentrations at which interfacial tension could reach ultralow levels.

The IFT between the crude oil and the SPBOPA solution (0.5 g/L) was measured at different temperatures. When the temperature was 45–80 °C, the IFT was lower than 0.010 mN/m. However, the interfacial tension gradually increased as the temperature increased further to 100 °C and finally reached above 0.010 mN/m at 110 °C (Figure 2). The temperature

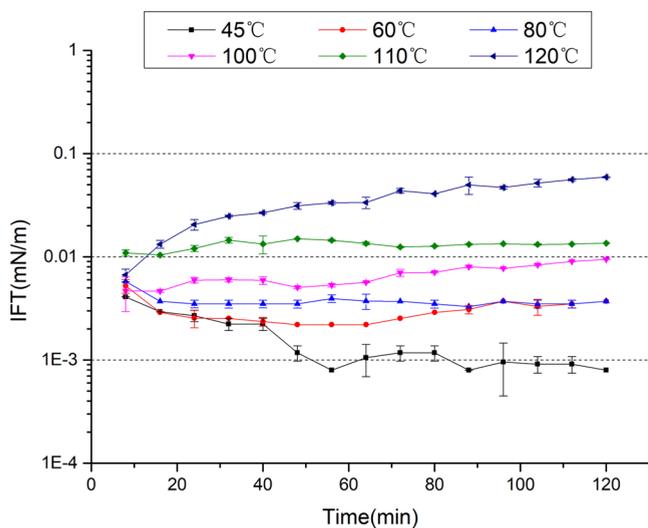


Figure 2. Plot of IFT changes between the crude oil and the 0.5 g/L SPBOPA solution at different temperatures.

resistance experiments showed that SPBOPA had high interfacial activity at a wide temperature of 45–100 °C, the increase in mobility of the surfactant molecules on the liquid–liquid interface because of the temperature increased,³³ and an increase in the number of solvent molecules on the interface,^{5,34} which may reduce the maximum adsorption capacity of surfactants, the higher the temperature, lower the maximum adsorbed.³⁵

To study the performance changes in surfactant solutions under different inorganic salt concentrations, the IFT between the crude oil and the SPBOPA solution (0.5 g/L) was measured at 45 °C with NaCl and Ca²⁺ of different concentrations. Figure 3a shows when the NaCl concentration was between 0 and 50 g/L, the IFT of the system was lower than 0.010 mN/m. The influence of Ca²⁺ electrolyte concentration on IFT was evaluated as shown in Figure 3b. When the concentration was 0–2000 mg/L, the IFT of the system was lower than 0.010 mN/m. Other research showed when that when IFT was lower than 0.010 mN/m, the Ca²⁺ tolerance to phenyl octadecanoic acid sulfobetaine was 500 mg/L,¹⁰ while the petroleum sulfonate was only 80 mg/L.³⁶ The model predictions showed that the IFT increased with the salt concentration since the salt ions and water molecules could form a hydrogen bond cage structure.³⁴ When water molecules contacted the oil–water interface, the hydrogen bonds of the water molecules were destroyed inevitably, the surface adsorption of salt ions on the interface was negative, and the IFT increased at high salt concentration.³⁷ The experiments on salt resistance showed that SPBOPA had good resistance to Ca²⁺ and had the potential to be applied in high-salinity EOR reservoirs.

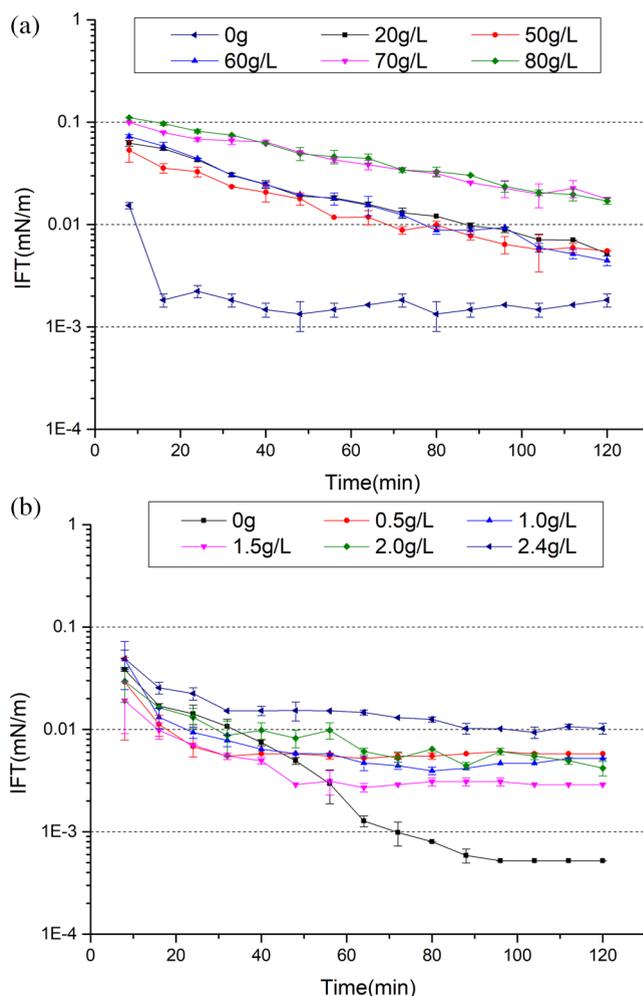


Figure 3. Plot of IFT changes between the crude oil and the 0.5 g/L SPBOPA solution at 45 °C at different concentrations of extra NaCl (a) and extra Ca²⁺ (b).

Sand Adsorption Resistance. The IFT changes of oil sands and 0.5 g/L SPBOPA solution after different times of adsorption were measured at 45 °C. The IFT could still be lower than 0.010 mN/m after being adsorbed by the oil sands four consecutive times (Figure 4).

The influences of electrostatic force, ion exchange, and other factors resulted the surfactant molecules could absorb on the surface of the oil sands to form semi-micelle, causing the concentration of surfactant in solutions to be reduced,³⁸ and the interfacial properties of the solution were decreased with the increase of adsorption times.³⁹ Because the surface of the sandstones was negatively charged, it was more prone to electrostatic interaction with the positive charges of zwitterionic surfactants. Compared with carboxyl betaines, sulfobetaine zwitterionic surfactants had lower adsorption capacity on the surface of Daqing sandstone.⁴⁰ Adsorption experiments showed that SPBOPA showed less loss during oil recovery.

Dilution Resistance. Figure 5 shows the dilution resistance results of SPBOPA solutions. When the dilution ratio reached 120 times, the IFT could still be lower than 0.010 mN/m. In other words, the SPBOPA still had good interfacial properties when the content was 0.0025%. The hydrophilic–lipophilic deviation change with dilution was not necessarily linear nor exhibited the same relative variation with dilution over a wide

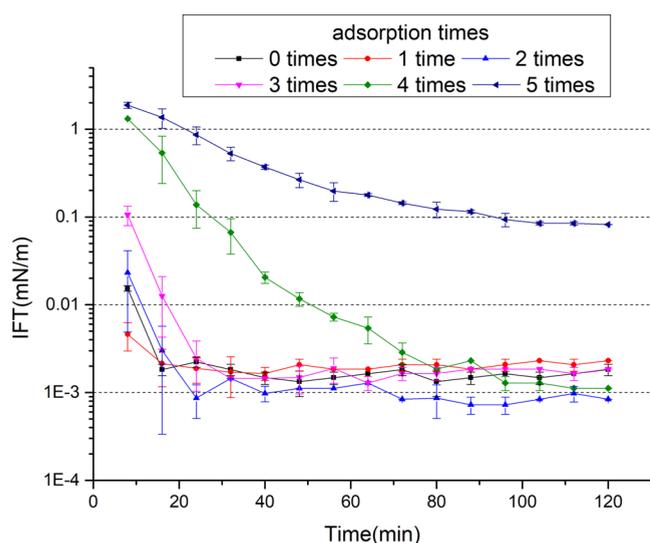


Figure 4. Plot of IFT changes between the crude oil and the 0.5 g/L SPBOPA solution at 45 °C after the sand adsorption.

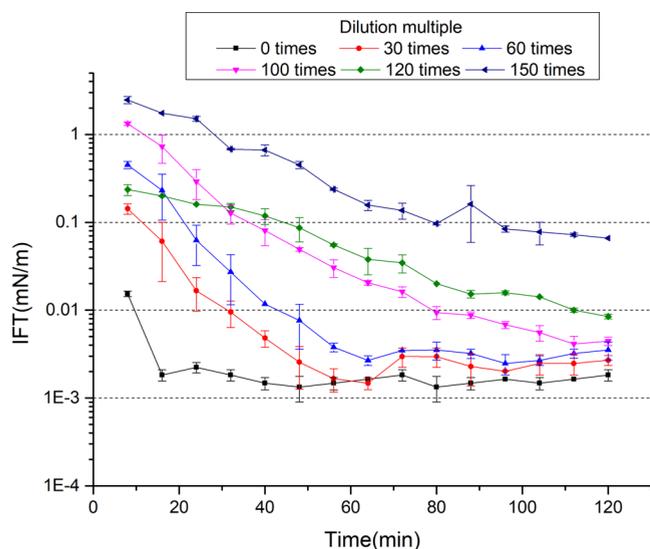


Figure 5. Plot of IFT changes between the crude oil and the 3 g/L SPBOPA solution at 45 °C after dilutions.

range.⁴¹ The dilution experiments showed that SPBOPA had a wide range of applications and good interfacial activity at low dosages.

Flooding Stability. The stability results of SPBOPA were measured as shown in Figure 6. The IFT remained below 0.010 mN/m after 100 days, which indicated that the SPBOPA surfactant had good stability at 45 °C. Thus, it will not decompose or deteriorate basically over the flooding process. The surfactant solutions often stay underground for months or years during the flooding process. Some substances in solutions, such as reactive metals, dissolved oxygen, and free radicals, could degrade the surfactant faster.⁴²

Wettability. The wetting ability of SPBOPA solutions on the quartz and crude oil surface was observed and measured at the different contact angles (Table 2). Compared with pure water, the SPBOPA solution reduced the contact angle of the quartz surface from 83.97 to 71.97° but did not significantly change the wettability of the crude oil surface. However, with the addition of a small amount of Ca²⁺, the contact angle of the crude oil

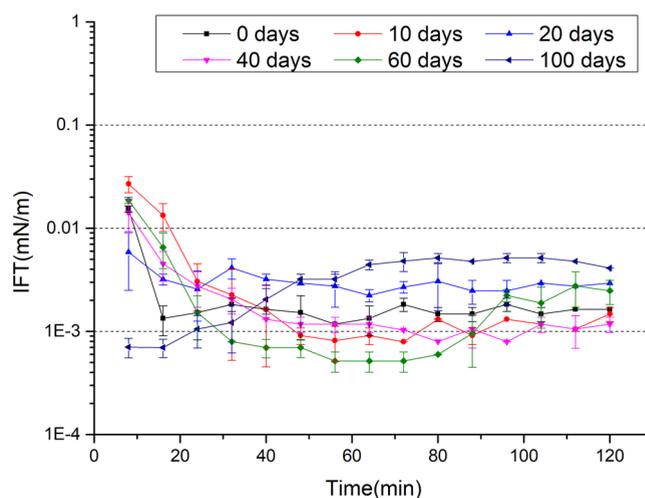


Figure 6. Plot of IFT changes between the crude oil and the 3 g/L SPBOPA solution at 45 °C after different surfactant aging times.

surface was lower than 70°; however, when the Ca²⁺ reached a certain concentration (above 2 g/L), the contact angle increased slightly. The research showed that the change in salt concentration influenced the contact angle, but the linear relationship was not satisfied. With the increase in salt concentration, the contact angle first decreased and then increased after reaching the critical concentration.⁴³ The contact angle and wettability are related as follows: (1) water-wet condition, between 0 and 70°; (2) neutral condition, between 70 and 110°; and (3) oil-wet condition, between 110 and 180°.⁴⁴ It could be seen that the presence of Ca²⁺ could change the wettability of the crude oil surface from neutral to weakly water-wet. Because the surface of the underground sandstone was usually oil-wet, the surfactant solution more easily elutes the crude oil after the wettability had changed. Also, the oil production efficiency had improved.⁴⁵ However, a high concentration of Ca²⁺ could activate the salting-out effect, and the contact angle hardly changed. In addition, with the increased Ca²⁺ concentration, the hydrogen bond formed between the hydrophobic end of the polar group and the water molecule might be destroyed, reducing the solubility of polar substances, and it was not easy to achieve a water-wet condition.⁴⁶

Toxicity. According to the results from the Toxicity Estimation Software Tool (T.E.S.T), the LD₅₀ of SPBOPA belongs to the low toxicity level of 4269 mg/kg. Also, according to the HJ/T 154-2004 classification standard, the acute oral toxicity of SPBOPA in rats is the actual nontoxicity level. Generally, the compounds are classified according to the “Acute Toxicity Classification Standard of Chemicals (WHO)”. A compound with LD₅₀ greater than 2000 mg/kg is considered to have low toxicity, 400–2000 mg/kg is considered to be harmful, 50–200 mg/kg is toxic, and <50 mg/kg is very toxic. Compared with some common surfactants (Table 3), SPBOPA is an environmentally friendly surfactant.

Degradability. The prediction results of photolysis characteristics show that SPBOPA has a half-life of 1.277 h. According to the prediction by software EPI, the primary degradation time was found at the “days level”, and the ultimate biodegradation time was in the “weeks–months” range (Table 4). The degradability time of the compound was estimated according to the standards. The software EPI divided the degradability time of the compound into five categories: 5.0–4.0

Table 2. Contact Angle of the SPBOPA Solution on Quartz and Crude Oil Surfaces

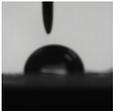
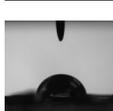
	Contact angle -quartz (°)	Contact angle - crude oil (°)	Oil droplet shape (quartz)	Oil droplet shape (crude oil)
Water	83.97±0.558	78.89±0.330		
SPBOPA	71.97±0.635	77.90±0.733		
SPBOPA (Ca ²⁺ 0.2g/L)	74.91±1.174	67.47±0.740		
SPBOPA (Ca ²⁺ 0.5g/L)	75.64±1.106	65.46±0.134		
SPBOPA (Ca ²⁺ 1.0g/L)	72.99±1.050	69.44±0.129		
SPBOPA (Ca ²⁺ 1.5g/L)	72.47±1.078	67.27±0.220		
SPBOPA (Ca ²⁺ 2.0g/L)	75.78±1.277	72.18±1.817		
SPBOPA (Ca ²⁺ 3.0g/L)	72.99±2.221	72.39±1.211		
SPBOPA (Ca ²⁺ 4.0g/L)	72.55±2.182	72.42±0.101		

Table 3. LD₅₀ Results from Several Surfactants and Raw Materials

	predicted LD ₅₀ (T.E.S.T) (mg/kg·BW)	LD ₅₀ (ChemidPlus) (mg/kg·BW)
benzene	1563.6	930.6
anisole	2109.5	3699
AES	3347.7	1700–5000
MES	2788.29	3000
SDBS	1595.7	2000
SPBOPA	4269.5	>5000 ^a

^aThe result of actual measurement using standard HJ/T 154-2004.

(h), 4.0–3.0 (days), 3.0–2.0 (weeks), 2.0–1.0 (months), and <1.0 (longer).²⁷ The half-life and biodegradation of several surfactants were determined. It showed that LAS is readily degradable in aerobic soil with a half-life of 7–33 days. The half-

Table 4. Half-Life and Biodegradation Prediction Results of Surfactants

	half-life (h)	primary biodegradation	ultimate biodegradation
AEO	0.374	recalcitrant (0.8072)	weeks–months (2.2915)
SDBS	8.588	days–weeks (3.6191)	weeks (2.8744)
POAPMB ²³	2.036	days (3.9159)	weeks–months (2.6395)
SPBOPA	1.277	days (3.7502)	weeks–months (2.3040)

lives of SDS were 6.6–19 days in Antarctic coastal waters.⁴⁷ The times to achieve a 50% primary biodegradation for a series of quaternary ammonium compounds ranged from 3 to 8 days.⁴⁸ The primary degradation of nonylphenol polyethoxylate showed

half-lives of 4 days in water and <10 days in sediments.⁴⁹ The result shows that the degradation time of SPBOPA is moderate, which can meet the needs of tertiary oil recovery.

CONCLUSIONS

The anise esters extracted from tarragon plants and the renewable oleic acids from waste cooking oils were used as raw materials to prepare biobased zwitterionic surfactants with low toxicity and high interfacial performance. A new biobased zwitterionic surfactant, *N,N*-dimethyl-*N*-[2-hydroxy-3-sulfo-propyl]-*N*-benzyloxyoctadecanoyl-1,3-propanediamine (SPBOPA), was successfully prepared through a simple and efficient method. Biobased zwitterionic surfactant SPBOPA exhibited good interfacial activity and could reduce the crude oil/water interfacial tensions to as low as 5.2×10^{-4} mN/m. The surfactant could also reduce the IFT to ultralow level in a wide concentration range, at high concentrations of NaCl up to 50 g/L, Ca²⁺ up to 2000 mg/L, and high temperatures up to 100 °C without extra alkali. In addition, this surfactant exhibited thermal stability, excellent antidilution, and adsorption resistance. Meanwhile, SPBOPA exhibited much lower toxicity and suitable biodegradability times. All results showed that the biobased zwitterionic surfactant SPBOPA had great application potential as a highly efficient and eco-friendly surfactant in enhanced oil recovery (EOR).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c04642>.

Additional experimental details, characterizations, and methods, including photographs of the experimental setup and results (PDF)

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Author Contributions

J.-Q.L. performed the data curation, formal analysis, and writing of the original draft. H.I.M. wrote, reviewed, and edited the manuscript. H.-z.G. and B.-Z.M. supervised the experiment. S.-Z.Y. performed the formal analysis and writing, reviewing, and editing of the manuscript and supervised the experiment. All authors have read and agreed to the submitted version of the manuscript.

Notes

The authors declare no competing financial interest.

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