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Article

Synthesis and Interfacial Properties of Bio-Based Zwitterionic Surfactants Derived from Different Fatty Acids in Non-Edible Vegetable Oils

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Abstract: Waste cooking oils and non-edible vegetable oils are abundant and renewable resources for bio-based materials which have showed great potential applications in many industries. In this study, five fatty acids commonly found in non-edible vegetable oils, including palmitic acid, stearic acid, linoleic acid, linolenic acid, ricinoleic acid, and their mixtures, were used to produce bio-based zwitterionic surfactants through a facile and high-yield chemical modification. These surfactants demonstrated excellent surface/interfacial properties with the minimum surface tensions ranging from 28.4 mN/m to 32.8 mN/m in aqueous solutions. The interfacial tensions between crude oil and surfactant solutions were remarkably reduced to lower values ranging from 0.0028 mN/m to 0.1983 mN/m without the aid of extra alkali, which particularly implied a great potential application in enhanced oil recovery. Meanwhile, these bio-based surfactants also showed good wetting properties (contact angles of ~ 51° comparing with that of double distilled water, 92.04°) and appropriate predicted biodegradability (degradation order of "weeks" for bio-based surfactants synthesized from saturated fatty acids, and "months" for those synthesized from unsaturated fatty acids). Bio-based surfactants synthesized from unsaturated fatty acids showed better interfacial properties in reducing interfacial tension between crude oil and formation water. The bio-based surfactants presented in this study are alternative substitutes for traditional petroleum-based surfactants in various surfactant application fields.

Keywords: Bio-based surfactants; zwitterionic surfactants; fatty acid; non-edible oil; interfacial properties

1 Introduction

Traditional surfactants widely used in industrial field are petroleum-based surfactants [1–5], whereas petroleum is a finite and non-renewable resource. In recent years considerable attention has been paid to the application of bio-based surfactants due to their renewable feedstock and environmental compatibility

[6–11]. The main raw materials for preparation of bio-based surfactants may include proteins [12,13], carbohydrates [14], and vegetable oils. Non-edible vegetable oils, such as castor oil, cottonseed oil, and waste cooking oil, have become platform chemicals for bio-based materials both in scientific and industrial research, owing to their universal availability, inherent biodegradability, and low cost [15,16]. Waste cooking oils were used as economical source for biodiesel [16–18] and vegetable oils were successfully converted to biopolymers [6,15,19]. Palm oil, castor oil, and other common vegetable oils in India were used for the preparation of sodium N-acyl isoleucines [13]. A novel sodium N-fatty acyl amino acid surfactant was synthesized from pupa oil, which was from waste products of the silk industry [20]. A soybean oil-based polymeric surfactant had been obtained from epoxidized soybean oil [21]. Bio-based zwitterionic surfactants synthesized from renewable raw materials had been reported to show high surface activity with low critical micelle concentration [22–24], excellent interfacial activity in reducing interfacial tension between crude oil and surfactant solution to ultra-low value [25] even in conditions of free of alkaline [23,26], thermal-stable and salt-tolerant properties [27], and well performance with polymer to be an candidate for novel surfactant-polymer binary flooding system [28,29].

There are different kinds of non-edible vegetable oils with high outputs globally. The world production of castor seed was over one million tons per year [30]. The predicted production of cottonseed oil in China in 2014 was 1.07 million tons [31]. The consumption of vegetable oils and animal fats in China in 2013 was about 30 million tons, which generated about 4.5 million tons of waste cooking oils. Different vegetable oils contain different kinds of fatty acids with varying proportions. For examples, oleic acid and linoleic acid widely exist in most vegetable oils. However, in castor oil more than 70% of fatty acids are ricinoleic acid, which is not found in other vegetable oils. In addition to unsaturated fatty acids mentioned above, saturated fatty acids such as palmitic acid and stearic acid are also found in almost all the vegetable oils. Due to the different compositions and structural diversity of non-edible vegetable oils, the knowledge about the production of bio-based zwitterionic surfactants from various fatty acids and their mixtures as starting materials is still limited. In this work, the main fatty acids commonly found in non-edible vegetable oils and waste oils, including palmitic acid, stearic acid, linoleic acid, linolenic acid, and ricinoleic acid, were used to produce bio-based zwitterionic surfactants. Moreover, the mixtures of the fatty acids with proportions mimicking those found in genetically modified soybean oil, castor oil, cottonseed oil, or rapeseed oil were also used to synthesize bio-based surfactants, which might provide the feasibility of production of bio-based zwitterionic surfactants by using directly non-edible oil as starting material. In order to explore the application potentials of these bio-based zwitterionic surfactants in daily chemicals and enhanced oil recovery, the surface tensions, interfacial tensions between crude oil and water, wetting properties, and biodegradability of these bio-based zwitterionic surfactants were evaluated in this paper.

2 Materials and Methods

2.1 Materials

Palmitic acid (AR, Shanghai Lingfeng Chemical, Shanghai, China), Stearic acid (AR, Shanghai Lingfeng Chemical, Shanghai, China), Linoleic acid (> 70%, Aladdin, Shanghai, China), Linolenic acid (> 70%, TCI, Tokyo, Japan), Ricinoleic acid (> 70%, Aladdin, Shanghai, China), $AlCl_3$ (99%, Aladdin, Shanghai, China), Benzene (AR, Shanghai Lingfeng Chemical Reagent Co., Ltd., Shanghai, China), Hydrochloric acid (AR, Shanghai Lingfeng Chemical Reagent Co., Ltd., Shanghai, China), Thionyl chloride (AR, Shanghai Lingfeng Chemical Reagent Co., Ltd., Shanghai, China), Trichloromethane (AR, Shanghai Chemical Reagent Co., Ltd., Shanghai, China), Acetone (AR, Shanghai Lingfeng Chemical Reagent Co., Ltd., Shanghai, China), *N*, *N*-dimethyl-1,3-propanediamine (99%, GC, Sigma, Shanghai, China), Methanol (AR, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), Sodium chloroacetate (99%, Aladdin, Shanghai, China), Ethanol (AR, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), Ethyl acetate (AR, Shanghai Lingfeng Chemical Reagent Co., Ltd., Shanghai, China) were used without further purification. Vegetable oils were purchased from local supermarkets.

Daqing crude oil was dehydrated and degassed. The acid value is 0.06 mg KOH/g. The density of the crude oil is 0.84 g/cm^3 and the viscosity is 19.2 mPa·s at 50°C. The main components of the crude oil are asphaltene (8.12 wt%), resins (24.12 wt%), hydrocarbons (65.88 wt%) and organic acids (0.13 wt%). Hydrocarbons were mainly alkanes with chain ranging from C13 to C31, and tricosane (C23) is the most abundant component.

2.2 Characterization

GC-MS spectra were recorded on Agilent 6890 N Network GC system and 5975 inert Mass Selective Detector. ESI HRMS spectra were recorded on the Waters LCT Premier XE Mass Spectrometers. ^{1}H NMR spectra of all the intermediates and final surfactants were recorded on a Bruker Avance 400 spectrometer (400 MHz) in $CDCl_3$ at room temperature. Tetramethylsilane (TMS) was used as reference.

2.3 Synthesis

Synthesis of *N*- palmiticamidopropyl-*N*, *N*-dimethylcarboxylbetaine (PDB) from palmitic acid was summarized as followed. A solution of palmitic acid (2.56 g, 10 mmol) in trichloromethane (10 mL) was added dropwise to a dried flask containing 0.8 mL $SOCl_2$ (11 mmol), and the mixture was stirred at 40°C for 2 h. The mixture was then distilled to remove the solvent and residue $SOCl_2$. The product was dissolved in 10 mL acetone, and 1.4 mL *N*, *N*-dimethyl-1, 3-propanediamine (11 mmol) was slowly added to the acetone solution at 0°C. The reaction mixture was then heated to 40°C and stirred for 2 h. The excess diamine and solvent were removed on a rotary evaporator giving *N*- palmiticamidopropyl-*N*, *N*-dimethyl amine (PDA), yield 96.2%. PDA were quaternized using sodium chloroacetate with a molar ratio of 1:1.25 in a solvent mixture of methanol and water ($v_{methanol}/v_{water}$ = 1:4). The mixture was refluxed at 75°C for 12 h; the mixture was vaporized off under reduced pressure, then mixed with ethanol and filtered. The filtrate was distilled to remove ethanol and purified by recrystallization in ethyl acetate. PDB was obtained with a yield of 88.3% using gravimetric method. ESI HRMS: *m/z* $[M+Na]^+$ calculated for 421.3406; found: 421.3411. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.873 (t, J = 3.40 Hz, 3H), 1.221-1.274 (m, 24H), 1.569-1.580 (m, 2H), 1.934-1.960 (m, 2H), 2.170-2.195 (m, 2H), 3.207 (m, 6H), 3.267-3.277 (m, 2H), 3.690-3.743 (m, 2H), 3.851-3.882 (m, 2H), 6.998 (br, 1H).

Stearic acid derived surfactant, *viz*. *N*-stearicamidopropyl-*N*, *N*-dimethylcarboxylbetaine (SDB), was synthesized following the method described above for PDB. The synthesis of bio-based surfactants derived from unsaturated fatty acids (linoleic acid, linolenic acid, ricinoleic acid), *N*-phenyllinoleicamidopropyl-*N*, *N*-dimethylcarboxyl betaine (PLDB), *N*-phenyllinolenicamidopropyl-*N*, *N*-dimethylcarboxyl betaine (PLDB'), and *N*-phenylricinoleicamidopropyl-*N*, *N*-dimethylcarboxyl betaine (PRDB), was carried out as the synthesis of *N*-phenyloctadecanoicamidopropyl-*N*, *N*-dimethylcarboxyl betaine (PODB) described by Zhang et al. [24] and given in Supporting Information.

The fatty acids mentioned above were further used as mixtures to mimic different vegetable oils (genetically modified soybean oil, castor oil, cottonseed oil or rapeseed oil) according to the compositions which was analyzed by GC-MS chromatography after methyl trans-esterification. Surfactants derived from the mixtures of fatty acids were obtained according to the protocol described previously for unsaturated fatty acids [24].

2.4 Surface Tension Measurement

Surface tension (SFT) measurement of different surfactant concentrations solutions was carried out by using a DCAT 21 tensiometer (Dataphysics, Germany) with the plate method [32]. Every measurement was repeated for three times. The temperature was controlled at 25.0 ± 0.1°C. The SFT between air and double distilled water was 71.8 mN/m at 25°C.

Since the critical micelle concentration values of bio-based zwitterionic surfactants are low enough therefore the activity coefficients can be approximated to 1. The concentration of surfactant can be used to replace the activity of surfactant in the normal form of Gibbs equation. Maximum surface excess concentration (Γ_{max}) was calculated by the following Gibbs Eq. (1).

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

where C is the concentration of surfactant aqueous solution in g L^{-1}, R = 8.314 J/mol/K, T = 298.15 K, SFT is expressed in mN/m, η is a constant that depends on the number of species constituting the surfactant adsorbed at the interface. For zwitterionic surfactants, it is generally assumed that the value of η should be set to 1, because no counterion adsorption is expected if the cationic and anionic portions of the molecule are genuinely internally associated [33–35]. The minimum area occupied per surfactant molecule (A_{min}) at air/water interface is related to the surface excess Γ_{max} as follows:

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

where N_A is the Avogadro constant.

2.5 Interfacial Tension Measurement

Interfacial tension (IFT) measurements between Daqing crude oil and formation water were carried out using a SVT 20 tensiometer (Dataphysics, Germany) by the spinning-drop method. The equilibrium IFT was obtained when successive values in 10 min intervals agreed to within 0.001 mN/m. Surfactant solutions were prepared with simulated formation water of Daqing oil field and the concentration of bio-based surfactant was 0.500 g/L. The IFT between Daqing crude oil and simulated formation water was 9.700 mN/m at 50°C. The measurement temperature was controlled at 50 ± 0.1°C (the average temperature of the stratum in Daqing oil field, China). The total dissolved substance of formation water is 5327.2 mg/L, including 112.7 mg/L $CaCl_2$, 42.8 mg/L $MgCl_2$, 1597.1 mg/L NaCl, 17.0 mg/L Na_2SO_4, 381.6 mg/L Na_2CO_3 and 3176.0 mg/L $NaHCO_3$. The measurements were carried out twice for every sample.

2.6 Contact Angle Measurement

Contact angles were measured by using the sessile drop technique [36]. The measurements were repeated for 5 times for every sample. The temperatures of the samples were controlled at 25 ± 1°C. Double distilled water showed an average contact angle of 92.04° on the solid substrate at 25°C.

2.7 Biodegradation Estimation

Ultimate biodegradation of the bio-based zwitterionic surfactants was calculated by EPI Suite v 4.11, BIOWIN3 biodegradation model [37], which is frequently used to estimate the degradation of organic chemicals. Ultimate biodegradation was calculated by inputting the exact molecular structure.

3 Results and Discussion

3.1 The Yield and Structural Characterization

The yields and structures of bio-based zwitterionic surfactants derived from single fatty acid are shown in Fig. 1. The yields of bio-based zwitterionic surfactants from fatty acids mixtures (mimicking fatty acids mixtures in genetically modified soybean oil, castor oil, cottonseed oil, or rapeseed oil) were 81.2% for genetically modified soybean oil-based *N*-phenylfattyamidopropyl-*N*, *N*-dimethylcarboxyl betaine (GPDB), 81.4% for cottonseed oil-based *N*-phenylfattyamidopropyl-*N*, *N*-dimethylcarboxyl betaine

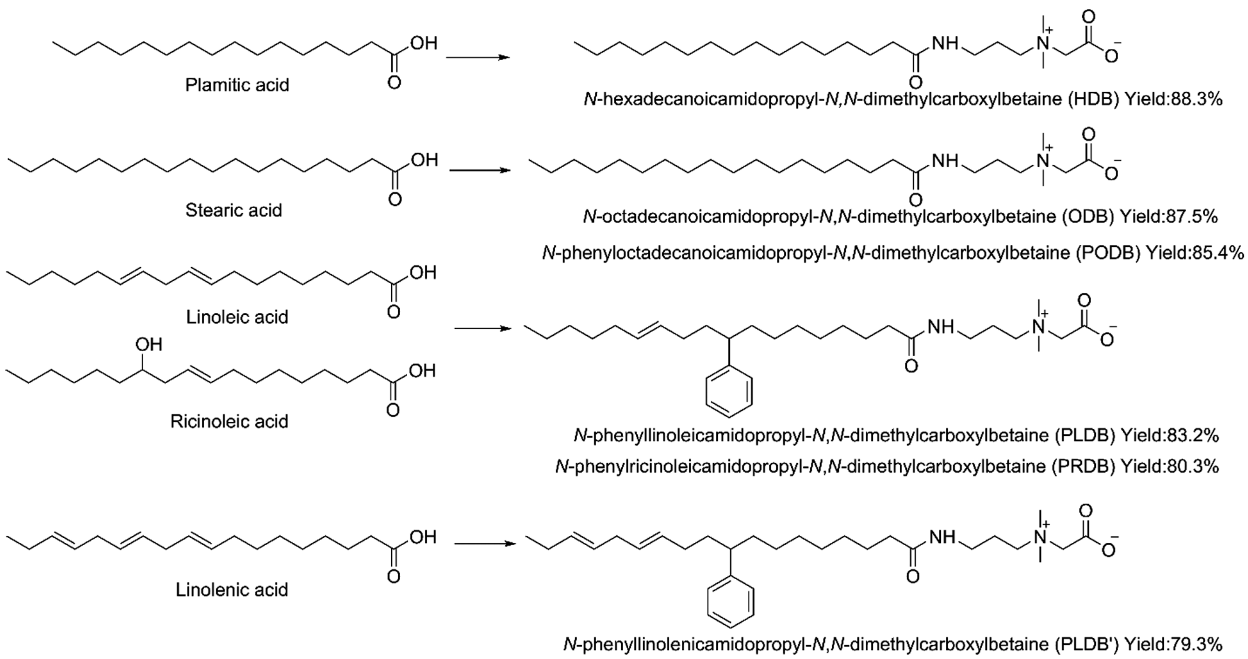

Figure 1: The yield and molecular structures of bio-based zwitterionic surfactants from different fatty acids

(CPDB), 83.3% for rapeseed oil-based *N*-phenylfattyamidopropyl-*N*, *N*-dimethylcarboxyl betaine (RPDB), 79.8% for castor oil-based *N*-phenylfattyamidopropyl-*N*, *N*-dimethylcarboxyl betaine (CPDB'), respectively.

The unsaturated fatty acids were first modified on the double bonds. Friedel-Crafts alkylation was adopted using $AlCl_3$ as catalyst to modify unsaturated acids into phenyl fatty acids. Under this reaction condition, the hydroxyl group in ricinoleic acid ((9Z, 12R)-12-hydroxy-9-octadecenoic acid) could be eliminated with the neighboring hydrogen and generate a new double bond. According to several repeated experimental data, a carbon chain structure with a double bond and a phenyl was obtained from ricinoleic acid. It seems that the yield of bio-based zwitterionic surfactants derived from saturated fatty acids is higher than those from unsaturated fatty acid mainly due to the default of Friedel-Crafts alkylation reaction. More double bonds in the raw fatty acids resulted in lower yield of bio-based surfactants. ESI-HRMS spectra and ^{1}H NMR spectra of bio-based surfactants were presented in Supporting Information.

3.2 Composition of Vegetable Oils

The composition and relative proportion of fatty acids in genetically modified soybean oil, cottonseed oil, rapeseed oil, and castor oil were shown in Tab. 1. Six main fatty acids, including saturated and unsaturated fatty acids, were identified. It can be concluded that the main components of four vegetable oils were unsaturated fatty acids and different from each other. The top three components of genetically modified soybean oil are linoleic acid, oleic acid, and palmitic acid. The top two components of cottonseed oil are linoleic acid and palmitic acid. The top two components of rapeseed oil are oleic acid and linoleic acid. The top two components of castor oil are ricinoleic acid and linoleic acid. The ratios of different fatty acids in the four mixtures were the same as those shown in Tab. 1 to mimic four vegetable oils.

3.3 Surface Properties

The SFTs of bio-based zwitterionic surfactants derived from single fatty acids were shown in Fig. 2a. SFTs dramatically reduced with the increases of bio-based surfactants concentrations (~0.01 g/L)

Table 1: The main fatty acid compositions of four vegetable oils

	Fatty Acid (wt%)					
Vegetable Oil	Palmitic Acid C16:0	Stearic Acid C18:0	Oleic Acid C18:1	Linoleic Acid C18:2	Linolenic Acid C18:3	Ricinoleic Acid C18:1(-OH)
Genetically modified Soybean Oil	11.20 ± 0.26	5.07 ± 0.31	31.67 ± 0.73	42.22 ± 2.81	9.85 ± 0.34	[a]ND
Cottonseed Oil	24.59 ± 0.53	3.29 ± 0.21	6.81 ± 0.30	65.32 ± 3.42	ND	ND
Rapeseed Oil	3.92 ± 0.18	2.86 ± 0.13	77.06 ± 3.57	17.06 ± 2.12	ND	ND
Castor Oil	1.50 ± 0.02	1.71 ± 0.03	4.81 ± 0.03	5.81 ± 0.03	ND	86.08 ± 3.65

[a]ND: not detected. Values are means with error representing standard deviation (n = 3)

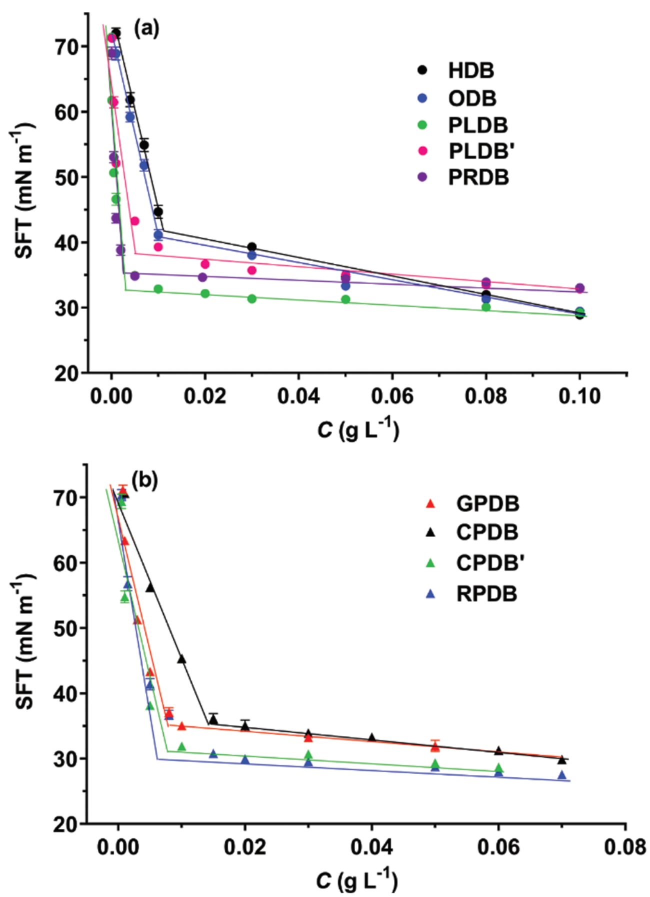

Figure 2: (a) The surface tension *vs.* concentration of bio-based zwitterionic surfactants derived from single fatty acids; (b) The surface tension *vs.* concentration of bio-based zwitterionic surfactants derived from fatty acids mixtures mimicking different vegetable oils. The error bars represent standard deviations of the mean for triplicate measurements

especially for those derived from unsaturated fatty acids. Comparing with bio-based surfactants with phenyl groups, bio-based surfactants synthesized from saturated fatty acids resulted in further reduction in SFTs at higher concentrations, which indicating the reorganization of adsorbed surfactant at surface. Surface property parameters of these bio-based zwitterionic surfactants were calculated from the plots and listed in Tab. 2. The CMCs of bio-based zwitterionic surfactants were all extremely low, ranging from 0.0027 g/L to 0.0111 g/L. The minimum of SFTs were from 28.4 mN/m to 32.8 mN/m. As for the SFT at CMC, PLDB exhibited the best surface property with the lowest value of SFT as 32.7 mN/m. Comparing HDB with ODB, the CMC values would be reduced one order of magnitude by introducing two methylenes into hydrophobic chain. The bio-based surfactants derived from oleic acid [24], linoleic acid, and ricinoleic acid showed CMC values one order of magnitude lower than that of SDB. It means that the bio-based surfactants with phenyl group (PLDB, PLDB', PRDB) exhibited better surface properties than that of SDB with the same length of hydrocarbon chain. It has been reported that a phenyl group equals to 3.5 methylenes [38,39], and the branched hydrophobic alkyl chain has a significant effect on the improvement of surface properties [1]. On the other hand, surfactants with a phenyl group in hydrophobic chains arranged compactly at surface due to the π-π stacking interaction between phenyl groups [40,41]. The surface properties of surfactant derived from oleic acid [24] were also superior to that of the surfactant with same hydrophilic group but without the modification of the double bond in oleic acid [42]. The hydrophobic chains in surfactants derived from unsaturated fatty acid are mostly *cis*-formed [12], and their molecular arrangement is incompact, resulting in higher values of SFTs. After addition of a phenyl to the double bonds, the generated single bond can rotate freely, leading to compact molecular arrangements and lower values of SFTs.

Table 2: Surface and interfacial properties of the bio-based zwitterionic surfactants

Starting material		Surfactant	CMC (g L^{-1})	SFT_{CMC} (mN m^{-1})	SFT_{min} (mN m^{-1})	Γ_{max} (μmol/m^2)	A_{min} (nm^2/ molecule)	Contact angle θ	$DIFT_{min}$ (mN m^{-1})	$DIFT_{equ}$ (mN m^{-1})
Single Fatty Acid	Palmitic Acid	HDB	0.0111	41.7	28.4 ± 0.3	3.81	0.43	50.34 ± 0.21	0.1983 ± 0.003	0.1983 ± 0.003
	Stearic Acid	ODB	0.0101	41.1	29.1 ± 0.3	3.51	0.47	49.65 ± 0.37	0.0039 ± 0.0004	0.1017 ± 0.002
	Linoleic Acid	PLDB	0.0030	32.7	28.9 ± 0.3	4.85	0.34	48.67 ± 0.029	0.0028 ± 0.0003	0.0045 ± 0.0003
	Linolenic Acid	PLDB'	0.0051	38.3	32.7 ± 0.4	4.66	0.35	50.68 ± 0.026	0.0045 ± 0.0004	0.0051 ± 0.0003
	Ricinoleic Acid	PRDB	0.0027	35.4	32.8 ± 0.2	4.76	0.35	49.21 ± 0.031	0.0068 ± 0.0004	0.0091 ± 0.0004
The Fatty Acid Mixture of Simulating Vegetable Oils	Mixture 1	GPDB	0.0079	34.9	31.1 ± 0.1	5.35	0.31	40.47 ± 0.029	0.0015 ± 0.0001	0.0015 ± 0.0001
	Mixture 2	CPDB	0.0142	35.3	29.5 ± 0.1	4.00	0.42	43.67 ± 0.028	0.0023 ± 0.0002	0.0032 ± 0.0002
	Mixture 3	RPDB	0.0063	29.8	27.1 ± 0.1	4.77	0.35	41.62 ± 0.030	0.0028 ± 0.0002	0.0053 ± 0.0003
	Mixture 4	CPDB'	0.0078	31.0	28.5 ± 0.1	4.85	0.34	47.50 ± 0.035	0.0066 ± 0.0003	0.0066 ± 0.0003

Mixture 1 mimicking the fatty acids compositions found in genetically modified soybean oil, Mixture 2 mimicking the fatty acids compositions found in cottonseed oil, Mixture 3 mimicking the fatty acids compositions found in rapeseed oil, Mixture 4 mimicking the fatty acids compositions found in castor oil. Measurement values are means with error representing standard deviation (n = 3)

In addition to zwitterionic surfactants derived from single fatty acid, the SFT curves of bio-based zwitterionic surfactants from fatty acid mixtures mimicking the compositions found in genetically modified soybean oil, cottonseed oil, castor oil, or rapeseed oil were showed in Fig. 2b. These four kinds of surfactants also showed excellent surface properties with the SFT_{min} below 31.1 mN m^{-1}. Maximum surface excess concentrations (Γ_{max}) of these surfactants were mainly bigger than that of single fatty derived ones. This could be elucidated by the synergetic effect in adsorption at surface among different structural surfactants [43,44]. RPDB (derived from mimic rapeseed oil) exhibited the best surface properties, which can be attributed to its main components, PODB and PLDB. Bio-based surfactants derived from fatty acid mixture, CPDB', exhibited nearly the same interfacial properties compared with surfactants directly produced from castor oil [23].

3.4 Interfacial Properties

The IFTs between Daqing crude oil and simulated formation water were illustrated in Fig. 3a, in which the concentration of bio-based zwitterionic surfactant derived from single fatty acid was 0.500 g/L. The minimum of dynamic interfacial tension ($DIFT_{min}$) and the equilibrium values of dynamic interfacial tension ($DIFT_{equ}$) of five bio-based zwitterionic surfactants were listed in Tab. 2. As Fig. 3a showed, dynamic interfacial tension (DIFT) gradually decreases over time first, and it then increases to a final equilibrium. Values of $DIFT_{min}$ of five bio-based zwitterionic surfactants were steadily kept at or below 10^{-3} mN/m order of magnitude for crude oil-water interfaces, except that of HDB, and the values of

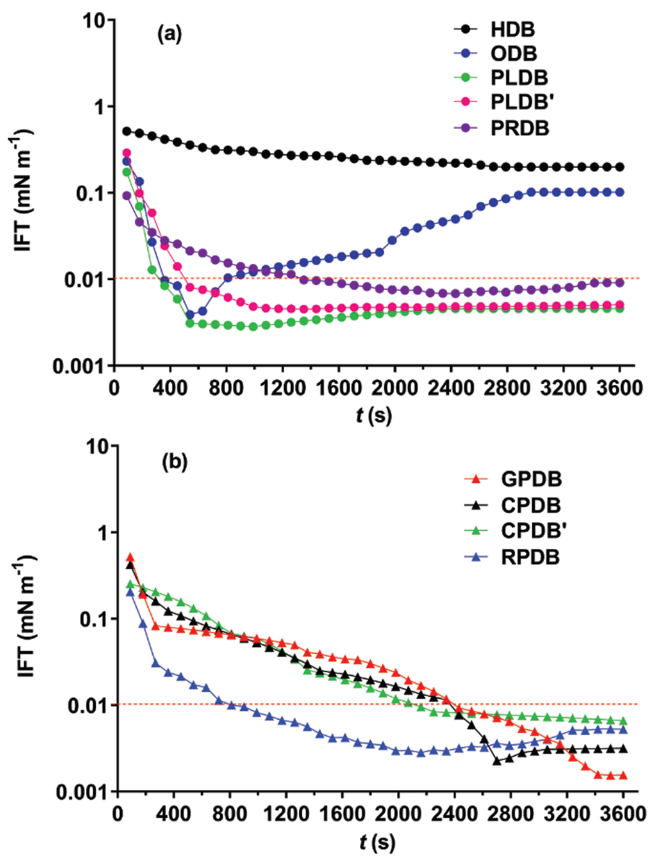

Figure 3: (a) Dynamic interfacial tensions between Daqing crude oil and bio-based surfactant solutions derived from single fatty acid at 50°C; (b) Dynamic interfacial tensions between Daqing crude oil and bio-based surfactant solutions derived from fatty acid mixtures at 50°C

$DIFT_{equ}$ were also maintained at ultra-low (< 0.01 mN/m) values, except that of HDB and ODB. When the IFT between crude oil and water arrives to ultra-low level, the efficiency of oil recovery would be remarkably improved [45,46]. The results also indicated that the surfactant molecules with a phenyl group having more excellent performance, especially in the reduction of oil-water IFT. Previous data of surface activities also showed that surfactant molecules with a phenyl could constitute a compact structure at the interface. In addition, a benzene ring substituent could increase the solubility of surfactants in oil phase and enhance the interaction between crude oil and surfactants. Surfactants with a benzene ring in molecules are widely applied in enhanced oil recovery [4,5].

The DIFT of bio-based zwitterionic surfactants derived from fatty acid mixtures mimicking different vegetable oils were listed in Fig. 3b, and the concentration of surfactants was also 0.500 g/L. Comparing with the DIFT of bio-based zwitterionic surfactants derived from independent fatty acid, the four bio-based zwitterionic surfactants from fatty acid mixtures reduced IFT much slowly, but showed more outstanding interfacial properties. The values of $DIFT_{equ}$ suggested that bio-based surfactants showed synergetic effect in reducing IFT by comparing the values of $DIFT_{equ}$ in Fig. 3b with those values of $DIFT_{equ}$ in Fig. 3a.

Surfactants used in oil recovery are mainly petroleum sulfonates [1–3], and alkyl benzene sulfonates [4,5], which are entirely derived from petroleum. Accompanying with surfactants, strong alkali (NaOH or Na_2CO_3) is added essentially to reduce oil-water IFT to ultra-low values and enhance oil recovery [47,48], which has been proved to result in well bore scaling, stratum damage, and permeability declination [49,50]. Interfacial tension between heavy oil and alkyl polyglycosides surfactant solution was reduced from ~0.12 mN/m to ~0.0013 mN/m with addition of 0.5% Na_2CO_3 [51]. Ultra-low interfacial tension (1×10^{-3} mN/m) of heavy oil/alkyl ether sulfates brine was obtained with 0.15% Na_2CO_3 while the interfacial tension was 0.027 mN/m free of Na_2CO_3 [52]. Bio-based zwitterionic surfactants synthesized from fatty acids can reduce oil-water IFT to ultra-low values without presence of extra alkali, which indicates their important applications in enhanced oil recovery.

3.5 Wetting Properties

The contact angles (θ) of bio-based zwitterionic surfactants derived from single fatty acid and fatty acids mixtures were listed in Tab. 2. Among surfactants derived from single fatty acids, PLDB exhibited the smallest contact angle, 48.67°. The lower values of SFT_{CMC}, the lower values of contact angles. Furthermore, surfactants derived from fatty acid mixtures showed more excellent wetting properties than ones from single fatty acid. The hydrophobic interface of the solid substrate (average contact angle of double distilled water, 92.04°) was converted into hydrophilic (average contact angle of formation solutions, < 51°), which play crucial role in detaching the oil films from reservoir rocks and thus lead to the increase of oil recovery.

3.6 Biodegradation Estimation

Ultimate biodegradation score for bio-based zwitterionic surfactants derived from single fatty acid was 2.92 (PDB), 2.86 (SDB), 2.65 (PLDB, PRDB), 2.65 (PLDB'), respectively. The bigger score indicates a faster speed of the expected total degradation. Scores above 2.8 were in the degradation order of "weeks", and scores between 2.0 to 2.8 were in the order of "months". These results demonstrated that bio-based zwitterionic surfactants are biodegradable. It seems that bio-based zwitterionic surfactants could be biodegraded within weeks with a C16 hydrophobic chain, and be biodegraded within months with a longer C18 hydrophobic chain and a phenyl group. Alkyl benzene sulphonates and petroleum sulphonates widely used in tertiary oil recovery, take octadecyl benzene sulphonates and octadecyl naphthalate sulphonates that with C18 hydrophobic chains for instance, show ultimate biodegradation scores of 2.66

and 2.55 respectively. Therefore, the bio-based zwitterionic surfactants synthesized in the present work exhibit comparable or even better in biodegradability with the commercial surfactants for oil recovery.

4 Conclusions

The previous method for synthesis of bio-based zwitterionic surfactants using oleic acids have been successfully extended to that using various fatty acids and their mixtures as starting materials. The bio-based zwitterionic surfactants exhibited excellent surface/interfacial properties. The surface/interfacial properties of surfactants with substituent groups, which are derived from unsaturated fatty acids, are superior to the linear ones from saturated fatty acids. The surface/interfacial properties as well as the wetting properties of surfactants derived from fatty acid mixtures are remarkably increased compared to that of single ones, due to the synergetic effect among different surfactant components. The study of fatty acids mixtures mimicking those found in vegetable oils could provide a basis for future application of bio-based surfactants derived from non-edible vegetable oil and waste oil directly. More importantly, the bio-based zwitterionic surfactant should be an alternative to petroleum-based surfactants in the fields of ecological remediation, oil spill processing, and other disposing oil contamination fields, and more specifically in enhanced oil recovery.

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Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

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