Accepted Manuscript

Investigation on interfacial/surface properties of bio-based surfactant Naliphatic amide-N,N-diethoxypropylsulfonate sodium as an oil displacement agent regenerated from waste cooking oil

Yan Zhang, Qing You, Yang Fu, Mingwei Zhao, Hongfu Fan, Yifei Liu, Caili Dai

PII:	S0167-7322(16)31738-X
DOI:	doi: 10.1016/j.molliq.2016.08.026
Reference:	MOLLIQ 6186
To appear in:	Journal of Molecular Liquids
Received date:	29 June 2016
Accepted date:	7 August 2016



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.



Investigation on Interfacial/Surface Properties of Bio-based Surfactant N-Aliphatic Amide-N,N-Diethoxypropylsulfonate Sodium as An Oil Displacement Agent Regenerated from Waste Cooking Oil

Yan Zhang^{1,2}, Qing You^{1*}, Yang Fu², Mingwei Zhao², Hongfu Fan¹, Yifei Liu², Caili

Dai^{2*}

1. School of Energy Resources, China University of Geosciences (Beijing)

2. School of Petroleum Engineering, China University of Petroleum (East China)

*Corresponding authors:

Qing You, Tel 86-10-82322754, Email <u>youqing@cugb.edu.cn</u> Caili Dai, Tel 86-532-86981183, Email <u>daicl@upc.edu.cn</u>

ABSTRACT: To regenerate the non-edible waste cooking oil and significantly reduce the negative effect on human being and the environment, a bio-based nonionic-anionic amphoteric sulfonate type surfactant with excellent interfacial and surface properties was synthesized. The interfacial tensions between crude oil and water can reach up to an ultralow value as 0.0040 mN/m without additives. With dynamic light scattering and surface tension, micelles formed by *N*-aliphatic amide-*N*, *N*-diethoxypropylsulfonate bio-based surfactant were studied. This work also systematically investigated the surface activity, adsorption behavior, and thermodynamic parameters (ΔG_m^0 , ΔG_{ads}^0 , ΔH_m^0 , ΔS_m^0 , ΔH_m^A , $\Delta C_{p,m}^0$) of micellization. According to the experimental results, it can be seen that the bio-based surfactant has an excellent surface activity, besides, the micelle formation is entropy and enthalpy co-driven at 25-45°C. Dynamic light scattering also illustrated the micelle formation. Through this research work, we expect to gain some insights into the phase behaviors of this bio-based surfactant and broaden its great potential oilfield application in enhanced oil recovery.

Keywords: bio-based surfactant, ultralow interfacial tension, surface activity, micelle formation, thermodynamic parameters

1. Introduction

Crude oil as industrial blood is the most important natural resource of the world. However, approximately two-thirds of the oil remains in an average oil reservoir after primary and secondary (water flooding) oil recovery. The residual oil is trapped in the reservoir pore structures due to capillary forces, which could be displaced by increasing microscopic displacement oil efficiency. Reducing the oil-water interfacial tension (IFT) is one of the most effective ways to remarkably increase the efficiency of oil recovery when the IFT value between the displacing fluid and crude oil reaches up to an ultralow level ($<10^{-2} \text{ mN} \cdot \text{m}^{-1}$) ^[1]. Many researches have been done to investigate the mechanism of surfactant flooding ^[2,3]. The reduction of oil-water interfacial tension is a principal mechanism for surfactant system to enhance oil recovery. Anionic surfactant (such as petroleum sulfonate with extensive source and lower cost advantage), nonionic surfactant (such as containing ethylene oxide group with high stability according to the different needs), and zwitterionic surfactant (such as betaine with good temperature resistance, salt tolerance and biodegradation) have been widely used in enhanced oil recovery ^[4, 5].

The surfactants mentioned above are mainly petroleum-based surfactants, which have the problems of the easy hydrolysis and bio-refractory for the environment. In addition, the huge consumption of the surfactant has reached about 10×10^6 tons, but mostly from petroleum-based surfactant, for an example, the proportion of the total amount of the surfactant in China is up to 85%. Due to the shortage of nonrenewable petroleum resources, both scientific and industries fields have noticed the bio-surfactant with renewable supplies and environmentally friend application. Especially in recent years, some of the bio-based surfactants derived from waste cooking oils have been reported and becomes a major focus for researchers ^[6-10].

As a sort of inedible oil, waste cooking oil has huge quantities, according to the statistics, around 4×10^{6} - 6×10^{6} tons of waste cooking oils was generated from urban food waste in China per year. Unreasonable dispose of waste cooking oil harms the environment and human beings. For an example, if disposed into the rivers, it not only results in waste, but also pollutes the water resources. In addition, some of them went back to the dining table by refining, which caused a serious threat to food security. As an inedible animal and vegetable oil, waste cooking oil contains abundant organic matter, so it is an important substitute resource for petroleum ^[11].

At present, the reutilization of the waste cooking oil mainly involves the

preparation of biological demulsifier, washing raw materials, fatty acid methyl esters (biodiesel), textile additives, etc ^[12-18]. As the most mature research area among them, the biodiesel preparation can not only be used as a new, clean and renewable bio-based energy resource, but can also act as a research basis of the non-toxic, harmless, degradable bio-based surfactants in some industrial fields, especially, in enhanced oil recovery area, the application can substitute for petroleum-based surfactants. In this case, in surfactant production, the proportion of all petroleum-based surfactants is gradually dropping off. The synthesis as well as interfacial activities of bio-based zwitterionic surfactant which is applied in enhanced oil recovery field have been studied ^[19]. However, to our best knowledge, the research about bio-based nonionic-anionic amphoteric sulfonate type surfactants derived from waste cooking oil and their utilization in enhanced oil recovery field is a virgin land to be exploited.

In this work, a bio-based nonionic-anionic amphoteric sulfonate type surfactant is synthesized. The surface/interfacial activity, adsorption property, and thermodynamic parameters of micellization of the bio-based surfactant are systematically investigated. Through this research work, we expect to gain some insight into the phase behaviors of this bio-based surfactant and broaden its great potential application area in enhanced oil recovery. Furthermore, this work also provides an important strategic significance for national energy security.

2. Experimental Section

2.1 Chemicals

Waste cooking oil was collected from canteens and restaurants. Filtration and centrifugation was performed and it acidified and filtered the upper oil phase. Besides, the upper oil phase was also, dehydrated and washed by water. The raw material was got and was used to prepare fatty acid methyl ester^[20-22]. The average carbon chain length of fatty acid methyl ester is 12 by 1H NMR method, the average formula is $C_{11}H_{23}COOCH_3$. The bio-based *N*-aliphatic amide-*N*, *N*-diethoxypropylsulfonate sodium (NDPSS) was synthesized through two-step reactions below ^[23]:

(1) Synthesis of fatty acid alkanolamide

The raw materials fatty acid methyl ester and diethanolamine (mole ratio: 1:1.1) were mixed and reacted at 100 °C for 5 h. NaOH was used as a catalyst with mass concentration of 0.5 wt %.

$$C_{11}H_{23} \xrightarrow{O}_{\mathbb{Z}} -OCH_3 + NH \xrightarrow{CH_2CH_2OH}_{CH_2CH_2OH} \xrightarrow{O}_{\mathbb{Z}} C_{11}H_{23} \xrightarrow{O}_{\mathbb{Z}} -N \xrightarrow{CH_2CH_2OH}_{CH_2CH_2OH} + CH_3OH$$

After the reaction, the solution was concentrated in rotary evaporator. After drying, the fatty acid alkanolamide is obtained. The yield is 85%.

(2) Sulfopropyl reaction

The reaction materials fatty acid alkanolamide and 1,3-propanesultone (molar ratio: 0.52:1) reacted at 80 $^{\circ}$ C for 24 h. NaOH was used as a catalyst with mass concentration of 0.8 wt %.

$$R \xrightarrow{O} CH_{2}CH_{2}OH + 2 \xrightarrow{O} S \xrightarrow{O} + 2NaOH \rightarrow R \xrightarrow{O} CH_{2}CH_{2}OCH_{2}CH_{2}CH_{2}SO_{3}Na + 2H_{2}OCH_{2}CH_{2}CH_{2}OH + 2H_{2}OH + 2H_$$

After the reaction, the solution was cooled and dried in rotary evaporator. Finally, the pale yellow solid powders was obtained and its yield is 88%. Then, the NDPSS was characterized with 1H NMR shown in support information. ¹H NMR (400 MHz, D₂O, 298 K) d: 3.89 (m, 4H), 3.44–3.35 (m, 8H), 2.96 (t, 4H, CH₂-SO₃⁻), 2.15 (t, 2H), 1.82 (m, 2H), 1.39 (m, 2H), 1.18–1.10 (m, 16H, alkyl chain), 0.81 (t, 3H, -CH₃); IR: 2924.94 cm⁻¹(-CH₃), 2853.89 cm⁻¹ (-CH₂), 1620.61 cm⁻¹ (-CO), 1347.15 cm⁻¹ (-CON), 1167.72 cm⁻¹ (C–O–C), 1192.61 cm⁻¹ $\stackrel{1}{\sim}$ 1041.09 cm⁻¹(–SO₃). 2.2 *Methods*

(1) Interfacial tension measurements

The oil/water interfacial tension (IFT) was measured by using a Texas-500C spinning drop tensionmeter in accordance with the following equation. The volumetric ratio of water to oil is about 200 in the spinning drop tensiometer. When measured values of IFT remained unchanged for half an hour, samples were assumed to be equilibrated. The measurement of the interfacial tension was performed at $50.0^{\circ}C \pm 0.5^{\circ}C$, and all of the measurements were performed for no less than twice.

$$\gamma = 3.42694 \times 10^{-7} (\rho_w - \rho_o) \omega^2 D^3 \quad L / D \ge 4$$

Where γ is the oil/water interfacial tension (mN/m); ρ_w and ρ_o are the densities of the water and oil phases (g/cm³), respectively; *w* is the rotational speed (rpm); *D* and

L are the width and length of the oil droplet (mm), respectively.

(2) Surface tension measurements

A surface tensiometer whose model is JYW-200B (Chengde Dahua Instrument Co. Ltd., accuracy ± 0.01 mN/m) was used to measure surface tension measurement with the ring method. A thermostat cell holder controlled the temperature. The surface tension was gained with a single-measurement method, and all of the measurements were performed for no less than three times.

(3) Electrical conductivity measurements

The electrical conductivities of the solutions were carried out on a low-frequency conductivity analyzer (model DDS-307, Shanghai Precision & Scientific Instrument Co., Ltd., accuracy of $\pm 1\%$). CMC of ionic micelle aggregates would be obtained by measuring the electrical conductivity. The turning point in the chart of specific conductivity versus concentration indicates the CMC.

(4) Dynamic light scattering (DLS)

A Zetasizer Nano ZS (Malvern) was used to perform the DLS measurement, and the hydrodynamic radius of micelles which formed in aqueous solution depend on the measurement. The DLS measurement was conducted at 25.0 ± 0.1 °C. A solid-state He–Ne laser (22 mW) was used to obtain the incident beam, and the scattering angle and the light wavelength are 90° and 632.8 nm, respectively. 1.5 mL of the sample solution was dropped to a small square container, and DLS data were collected from the mean values of the three measurements.

3. Results and Discussion

3.1 Interfacial Tension

Interfacial tension is an important parameter of surfactant for enhanced oil recovery. Lower interfacial tension value means better performance of the surfactant in enhanced oil recovery. The effect of enhanced oil recovery would be considerable once the interfacial tension of biomass surfactant solution and crude oil declines to an ultra-low level ($<10^{-2}$ mN·m⁻¹). The interfacial tensions of Luliang crude oil (the density is 0.860 g/cm³, the viscosity is 9.2 mPa·s at 50°C) and bine water (the salinity is 10019.34 mg/l, the density is 1.013 g/cm³; the composition: Ca²⁺ 218.36 mg/l, Mg²⁺9.74 mg/L, Na⁺+K⁺ 3623.75 mg/l, HCO₃⁻ 395.98 mg/l, CO₃²⁻ 44.1 mg/l, SO₄²⁻ 5.99 mg/l, Cl⁻ 5765.52 mg/l) with different concentrations of biomass surfactant at 50°C were shown in Figure 1. With the increase of concentrations, the minimum

value of interfacial tension between oil and solutions of biomass surfactant with different concentrations declined gradually (Figure 1). When the concentration of DNPSS surfactant is 0.4% (wt), the minimum value of (IFT_{min}) could be 0.0040 mN·m⁻¹. In oilfield applications, it is beneficial to make a lower usage of surfactants, and having ultra-low interfacial tension is one of the paramount aims. At the concentration of 0.3% (wt) NDPSS surfactant, the IFT was 0.0062 mN·m⁻¹, which also reaches up to an ultra-low level. It is common in petroleum exploitation to inject water into reservoirs to displace oil as well as to maintain the reservoir pressure as the natural pressure of the reservoir declines over the course of production. Typically, about 65% of the hydrocarbons remain unproduced after natural drive and water flooding ^[24]. The key reason of low oil rate of hydrocarbon is high interfacial tension between oil and water, which leads to big flow resistance in porous media of reservoir formation. According to the Laplace formula, the flow resistance was remarkably reduced by lowing IFT between oil and water, therefore, the purpose of enhanced oil recovery can be realized.²²



Figure 1 The IFTs between Luliang crude oil and different concentration NDPSS solutions at $50\,^\circ\!\mathrm{C}$

What is interesting is that once the concentration value of the biomass surfactant fell far below that of the single surfactant in the work before, it would be better to obtain the reduction of IFT. It is because of the synergism between the surfactant analogues. Comparing to single-chain counterparts, mixture-chain surfactants have excellent interfacial/surface performance due to the strengthened ability of molecular self-assembly. Based on the theory of surface chemistry, several surfactants were mixed frequently, aiming at reducing the dosage of surfactants as well as obtain lower

surface/ interfacial tensions. Under such a condition, the final product NDPSS surfactant was also a mixture derived from waste cooking oil exhibiting great synergism as a naturally surfactant compound system ^[25-27].

3.2 Surface Properties and Micellization

Surface tension measurement was conducted to study the surface properties of NDPSS surfactant in aqueous solution. The surface tensions of solutions *and* concentrations at 25 $^{\circ}$ C are illustrated in Figure 2. Comparing dilute NDPSS surfactant solution and pure water(72mN·m⁻¹), the surface tension value decreases sharply in dilute NDPSS surfactant solution , which indicates that NDPSS surfactant molecules are adsorbed at air-water interface. Surface tension would decline gradually while NDPSS surfactant concentration increases. Surface tension would stop decreasing and keep a constant value when the concentration of NDPSS surfactant reaches a critical value. It indicates that the air-water interface has been saturated with NDPSS surfactant molecules.

As seen in Figure 2, the arrow shows an inflection point on the plot of NDPSS surfactant concentration versus surface tension. It is critical micelle concentration (CMC) as traditionally termed. The NDPSS surfactant molecules would form micelles in aqueous solution while NDPSS surfactant concentration keeps rising. Under 25° C, the CMC value of NDPSS surfactant in aqueous solution dropped to 0.0019 mol·L⁻¹, and the surface tension at CMC was 28.0 mN·m⁻¹. The lower CMC value is, the better surface activity is. Comparing with the CMC values of other surfactants, the CMC values of NDPSS surfactant were three orders of magnitude below that of other bio-based surfactants, and the max of surface excess concentration was up to nearly two times of others' ^[28], which also means NDPSS surfactant has better surface activity.



Figure 2. Surface tension versus concentration of NDPSS solution at 25°C

From Figure 2, surface tension can decline to 27.8 mN/m because NDPSS surfactant could be adsorbed at the air-water interface. To demonstrate the surface activity, the following equation proposed the effect of surface tension reduction (Π_{cmc}):

$$\Pi_{\rm cmc} = \gamma_0 - \gamma_{\rm cmc} \qquad (2)$$

Wherein, γ_0 is the surface tension of water; γ_{cmc} is the surface tension of biomass surfactant solutions when the concentration is higher than CMC.

For the NDPSS surfactant molecules, the value of $\Pi_{\rm cmc}$ can be calculated as 44.0 mN/m according to the equation (2), and it demonstrates the good ability of decreasing surface tension of NDPSS surfactant. For other types of bio-based surfactants, such as N-phenyl fatty amidopropyl-N, zwitterionic surfactants, N-dimethylcarboxylbetaine (PFAPMB), and N-fatty acyl amino acid surfactant (SFAAA), their $\gamma_{\rm cmc}$ of surfactant aqueous solutions are 28.4, and 28.0 mN/m, respectively ^[29, 30]. Comparing with the ability to decrease surface tension of bio-based surfactants, their surface activities are similar.

As mentioned above, in Figure 2, the decrease of surface tension is because NDPSS surfactant is adsorbed at air-water interface. Thus the adsorption behavior is studied. Two parameters, the maximum surface excess concentration Γ_{max} and the minimum area A_{min} are introduced to demonstrate the adsorption phenomenon of NDPSS surfactant, they occupied each surfactant molecule in the air-water interface, and the two parameters can be calculated as follows ^[31]:

$$\Gamma_{\max} = -\frac{1}{nRT} \left(\frac{d\gamma}{d \ln c} \right)_T \quad (3)$$

Wherein, *n* indicates the amount of solute species; the concentration of solute species at the interface changes with surfactant concentration *c*; *R* indicates gas constant; *T* represents absolute temperature; γ represents surface tension; and $d\gamma/d(\ln c)$ indicates slope of surface tension γ versus ln*c* dependence when the concentration approximates CMC.

For NDPSS surfactant of aqueous solution, when *n* is taken as 2, A_{\min} can be calculated according to the following equation (4):

$$A_{\min} = \frac{1}{N_A \Gamma_{\max}} (\times 10^{23})$$
 (4)

Wherein, N_A represents Avogadro number.

As seen in Table1, the value of Γ_{max} is 3.38 µmol/m² and A_{min} is 49.1 Å² for the adsorption phenomenon of bio-based surfactant NDPSS occurs on the air-water interface at 25°C. Table 1 also clearly presents the comparison among the relevant adsorption parameters.

surfactant	cmc	$\gamma_{\rm cmc}({\rm mN/m})$	$\Pi_{\rm cmc}({\rm mN/m})$	$\Gamma_{\rm max}(\mu {\rm mol/m}^2)$	$A_{\min}(\text{\AA}^2)$
NDPSS	1.9 mmol/L	28.0	44.0	3.38	49.1
PFAPMB	0.734 mg/L	28.4	43.6	2.66	62.0
SDS	8.2 mmol/L	32.5	39.5	3.16	53.0

Table 1. Surface Properties of NDPSS and other surfactant in Aqueous Solution(25 °C)

PFAPMB, the other bio-based surfactant, its A_{\min} value is 62.0 Å² ^[30]. By comparison, in NDPSS molecules, the value of A_{\min} is lower, and the lower A_{\min} makes Γ_{\max} value a little higher, which implies NDPSS molecules pack more tightly at air-water interface. This higher packing density may be on account of the structure of NDPSS as well as the characteristics of molecular. Comparing with conventional sodium dodecyl sulfate (SDS) surfactant, NDPSS molecules also have a smaller A_{\min} and a little larger Γ_{\max} , which introduces in a better surface activity compared with SDS.

In order to further investigate the micelles which are formed of bio-based surfactant NDPSS, DLS measurement was performed, and the hydrodynamic radius of the

micelles formed in aqueous solution would depend on the result of the DLS measurement. Figure 3 shows the result of DLS measurement when NDPSS surfactant concentration is around 2 mM (slightly larger than its CMC). As seen in Figure 3, the scattering peak is quite sharp; it demonstrates the micelles formation as well as the uniform micelles' radius. The average value of hydrodynamic radius is around 9 nm.



Figure 3. Size distribution of NDPSS micelles in aqueous solution (2mmol, 25°C) 3.3 Thermodynamic Parameters of Micelle Formation

In general, temperature plays an important role in the self-assembly phenomenon of surfactant in aqueous solution. We also employed electrical conductivity measurements to study the micellar aggregation behavior of NDPSS in aqueous solution. Figure 4a presents the curve of surface tensions *vs* NDPSS concentrations under different temperatures. Table 2 shows the CMC values under the temperature of 25-45°C, which can be obtained quite easily.



Figure 4a. The conductivity versus NDPSS concentration. Figure 4b. The cmc values of NDPSS

micelles at different temperature

t/°C	25	30	35	40	45
$\frac{\text{CMC}}{(\text{mmol} \cdot \text{L}^{-1})}$	1.80	1.87	2.00	2.15	2.38
α	0.675	0.679	0.682	0.686	0.690

Table 2 CMC and Degrees of counterion dissociation at different temperature

Figure 4a shows the variations of specific electrical conductance which is a function of NDPSS concentration under different temperatures. It can be surveyed that the curves fit into two straight lines with different slopes for each temperature. The break in conductivity versus concentration plot roots in the micellizaiton of amphiphilic compounds ^[32]; in the break point, the concentration is equivalent to the CMC. At 25 °C, the CMC value is 0.0018 mol/L, which is estimated with the electrical conductivity plot illustrated in Figure 4a, and this value is close to the CMC values obtained from surface tension measurements (0.0019 mol/L at 25 °C). The minor discrepancy is mainly attributed to the fact that the CMC usually rest in the determination method.

As seen in Figure 4a, the slopes of linear region below CMC are larger than that above CMC. This is due to the counterion bound in the surface of micellar aggregates. Viewed from another perspective, the loss of ionic charges is effective since a set number of counterions are circumscribed to the micellar surface. The degree of counterion dissociation α approximates the mean value of counterions/surfactant ion which dissociates from the micelle, and the parameter can be calculated according to the ratio which is between the slopes of curves below and above the CMC. The values of α calculated for this bio-based surfactant NDPSS micelles at different temperature are shown in Table 2. The value of α increases with the increase of the temperature, probably caused by strong Brownian motion with fast ions movement. Figure 4b presents the relationship of temperature and the CMC values. It can be seen that the values of CMC increase as temperature increases due to weak hydrophobic interaction of alkane chains ^[33], and this plot conforms to a second-order polynomial; it can accord well with other surfactants in aqueous solution.

In terms of the thermodynamic parameters of the micelles generated by NDPSS in aqueous solution, according to micellization's pseudophase model, the value of ΔG_m^0 ,

standard Gibbs free energy in micelle formation can be obtained using the equation below ^[34]:

$$\Delta G_{\rm m}^{0} = (2 - \alpha) RT \ln X_{\rm cmc}$$
 (5)

Here, *R* represents gas constant; *T* represents absolute temperature; X_{cmc} represents CMC in molar fraction, and it can be transmuted from CMC. The values of ΔG_m^{0} in different temperatures can be calculated according to equation (5), which is shown in Table 3. It can be seen that the values of ΔG_m^{0} nearly keep stable as temperature increases, which implies that the formation process of micelles are spontaneous. Besides, based on ΔG_m^{0} , standard Gibbs free energy of adsorption (ΔG_{ads}^{0}) could also be obtained according to equation (6) ^[35]. In NDPSS molecules, ΔG_{ads}^{0} value at 25 °C approximates -46.95 kJ/mol.

$$\Delta G_{\rm ads}^{0} = \Delta G_{\rm m}^{0} - \Pi_{\rm cmc} / \Gamma_{\rm max} \quad (6)$$

The standard enthalpy of micellar formation ΔH_m^{0} , another thermodynamic parameter, can also depend on the Gibbs-Helmholtz equation below:

$$\Delta H_m^0 = \left[\frac{\partial (\Delta G_m^0 / T)}{\partial (1/T)}\right] \quad (7)$$

According to equation (7), function 1/T plots the values of $(\Delta G_m^{0}/T)$, and Figure 5a presents the curve. The curve in Figure 5a conforms to a second-order polynomial. ΔH_m^{0} values at different temperatures depend on the slope of tangential lines, which are shown in Table 3. According to the values of ΔG_m^{0} and ΔH_m^{0} , ΔS_m^{0} , micelle formation's standard entropy, can be calculated using equation (8); the results are listed in Table 3.

$$\Delta S_{\rm m}^{0} = (\Delta H_{\rm m}^{0} - \Delta G_{\rm m}^{0})/T \quad (8)$$

Figure 5b presents the relationship between temperatures (*T*) and thermodynamic parameters (ΔG_m^{0} , ΔH_m^{0} , and $-T\Delta S_m^{0}$). ΔH_m^{0} indicates the contributions of enthalpy change and $-T\Delta S_m^{0}$ represents the enthalpy change to standard Gibbs free energy of micelle formation. As seen in the plots, the Gibbs free energy hardly changes as temperature increases, whereas the decline of the enthalpy variation and the increase of the entropy variation are obvious. Comparing their effectiveness to ΔG_m^{0} , the two curves interests when the temperature is around 303K, which demonstrates entropy

variation has a significant effect on determining ΔG_m^0 below the temperature of 303K, and the micelle formation of NDPSS in aqueous solution is mainly entropy-driven. However, the transform of enthalpy plays a significant role int determining ΔG_m^0 over the temperature of 303K, and the micelle formation of NDPSS in aqueous solution is mainly enthalpy-driven ^[36-38]. Therefore, the micelle formation is entropy and enthalpy co-driven at 25-45°C. In that case, the arrangement of surfactant molecule on the interface was more compact. Therefore, the surface tension of the solution was lower. It is preferred to form micelles and the micelles would be much more stable. The solubilization for oil is enhanced, thus this is helpful to increase the sweep efficiency of the remaining oil from reservoir.

<i>T</i> (K)	CMC(mMol/L)	$\Delta G_{\rm m}^{0}({\rm kJ}{\cdot}{\rm mol}^{-1})$	$\Delta H_{\rm m}^{0} ({\rm kJ} \cdot {\rm mol}^{-1})$	$-T\Delta S_{\rm m}^{0}({\rm kJ}\cdot{\rm mol}^{-1})$	$\Delta S_{\rm m}^{0}(\mathbf{J}\cdot\mathbf{mol}^{-1}\cdot\mathbf{K}^{-1})$
298	1.80	-33.93	-10.97	-22.97	77.06
303	1.87	-34.27	-15.92	-18.35	60.57
308	2.00	-34.53	-20.71	-13.82	44.88
313	2.15	-34.74	-25.35	-9.39	30.01
318	2.38	-34.84	-29.84	-5.00	15.72

Table 3 Thermodynamic parameters of NDPSS micelles formed in aqueous solution



Figure 5a. The plot of $\Delta G_m^{0/T}$ and *T*. Figure 5b. The plots of thermodynamic parameters (ΔG_m^{0} , ΔH_m^{0} , and ΔS_m^{0}) and *T*

In terms of the change of entropy and enthalpy in aqueous solution, some linear relationships exist and they are usually named as entropy-enthalpy compensation ^[39-41]. It is valuable to study the relationship of enthalpy and entropy transformation

for micelle formation of NDPSS in aqueous solution. Entropy-enthalpy compensation is usually consisted of two parts: the desolvation part because of the dehydration of hydrophobic chain and the chemical part because of the aggregation of surfactant tails to generate micelles. Enthalpy change (ΔH_m^{0}) 's dependence to entropy (ΔS_m^{0}) is presented in Figure 6a. This figure illustrates that the plot of ΔH_m^{0} versus ΔS_m^{0} has a good linear relationship. The compensation of entropy andenthalpy can be described with the form below:

$$\Delta H_{\rm m}^{0} = (\Delta H_{\rm m}^{A} + T_{\rm c} \Delta S_{\rm m}^{0}) \qquad (9)$$

Wherein, T_c represents the compensation temperature as well as a measure of desolvation part; ΔH_m^A is the enthalpy which belongs to chemical part.

According to the fitting of straight line, in NDPSS micelles formation, ΔH_m^A value is -34.61 kJ/mol, T_c value is 307.7 K, and ΔS_m^A value is 112.5 J·mol⁻¹·K⁻¹(ΔH_m^0 =0). This compensation temperature resembles the surfactant reported with the same structures ^[42]. The parameters of ΔH_m^A and ΔS_m^A represent the stability of micelles. The lower the value of ΔH_m^A is , the higher the value of ΔS_m^A is, and the more stable the micelles are. Therefore, the NDPSS micelles are relatively stable.

As another thermodynamic parameter, as well as the heat capacity of micellization, $\Delta C_{p,m}^{0}$ could be obtained using the following equation (10)^[43]:

$$\Delta C_{\rm p,m}^{0} = T(\partial \Delta S_{\rm m}^{0} / \partial T) \quad (10)$$

Figure 6b presents the curve of micellization entropy which as a function of temperature, and it can be seen that the plot accords with a good linear relationship. The value of ΔC_{pm}^{0} approximates -3.06 kJ·mol⁻¹·K⁻¹, which is to the same as the slope of fitting line. The negative value of ΔC_{pm}^{0} suggests that the hydration shell is missing in the process of micellization because of the organized water molecules at the surroundings of the hydrophobic chain of surfactant.



Figure 6a. The relationship of enthalpy-entropy compensation. Figure 6b. ΔS_m^{0} versus temperature for NDPSS in aqueous solution

4. Conclusions

In conclusion, we studied the surface/interfacial properties of the bio-based surfactant NDPSS. NDPSS exhibits excellent interfacial active, and the IFTs between Luliang crude oil and NDPSS water solutions could reach up to an ultralow level, which shows great potential application as an oil displacement agent in enhanced oil recovery. NDPSS also has a quite low CMC value, which indicates an excellent surface activity. The micelle formation is spontaneous, thermodynamically stable, and is entropy and enthalpy co-driven at 25 to 45°C. Through this research work, we expect to broaden its great potential application area in enhanced oil recovery as a substitute of petroleum-based surfactants.

Acknowledgements

This work was supported by Beijing Natural Science Foundation (3154040), Fundamental Research Funds for the Central Universities (2-9-2014-007), the National Science Fund for Distinguished Young Scholars (51425406), and the Chang Jiang Scholars Program (T2014152). The authors thank Dr. Yongpeng Sun and Yining Wu editing of the English and his valuable suggestion on preparing this paper. The authors also express their appreciation to technical reviewers for their constructive comments.

Conflict of interest

The authors declare that they have no conflict of interest

Reference

[1] Wilson, L. A.. Physico-chemical environment of petroleum reservoirs in relation to oil recovery systems. Improved oil recovery by surfactant and polymer flooding, Academic Press, 1997: 1-26.

[2] Zhao, F. L.. Oilfield Chemistry. China University of Petroleum Press, 2000: 104-109.

[3] Ye, Z. B.. Principles of enhanced oil recovery. Petroleum Industry Press, 2000: 103-110.

[4] Zhou, C. H., Zhang, Q., Liu, Y., et al. Effect of Fatty Acids on Interfacial Tensions of Novel Sulfobetaines Solutions. Energy & Fuel, 2014, 28(2): 1020-1027.

[5] Qiao, W. H., Li, J., Zhu Y. Y., et al. Interfacial tension behavior of double long-chain 1,3,5-triazine surfactants for enhanced oil recovery. Fuel, 2012, 96(1): 220-225.

[6] Zhang, Q. Q., Cai, B. X., Xu, W. J.. Novel zwitterionic surfactant derived from castor oil and its performance evaluation for oil recovery. Colloids & Surfaces A, 2015, 483: 87-95.

[7] Banat, I. M.. Biosurfactants production and possible uses in microbial enhanced oil recovery and oil pollution remediation: a review. Bioresource Technology, 1995, 51(1): 1-12.

[8] Xie, W. L.. Chemistry and technology of oils chemical products, Science Press, 1998: 60-78.

[9] Zhang, Y., Dube, M. A., McLean, D., Kates, M., 2003. Biodiesel production from waste cooking oil: 1. Process design and technological assessment. Bioresource Technology, 2003, 89(1): 1-16.

[10] Wang, L. T., Dong, X. Q., Jiang, H. X., et al. Preparation of a novel carbon-based solid acid from cassava stillage residue and its use for the esterification of free fatty acids in waste cooking oil. Bioresource Technology, 2014, 158(4): 392-395.

[11] Yao, Z. L., Min, E. Z., 2010. The hazard and utilization of waste edible oils. Gas Industry, 2010, 5: 123-128.

[12] Liu, H. J., Ma, C. G. Miao, H. Q., et al. Research progress on sulfonated fatty acid methyl ester. China Oils & Fats, 2011, 36(7): 54-57.

[13] Wang, L. T., Dong, X. Q., Jiang, H. X., et al. Preparation of a novel carbon-based solid acid from cassava stillage residue and its use for the esterification of free fatty acids in waste cooking oil. Bioresource Technology, 2014, 158(4): 392-395.

[14] Du, Z. P., Wang, W. X., Tai, X. M.. Synthesis, property and application progress of fatty acid methyl ester sulfonate. China Surfactant Detergent & Cosmetics, 2012, 4: 1-6.

[15] Li, L., Zhu, Y. C.. Research and application progress of fatty acid methyl ester sulfonates. China Surfactant Detergent & Cosmetics, 2012, 4: 7-13.

[16] Zhang, L., Lan, H. B., Yun, Z. Review on preparation and analytical methods of fatty acid methyl ester sulfonate. China Surfactant Detergent & Cosmetics, 2010, 3: 210-213.

[17] Fan, W. L., Zhang, B., He, P., 2008. Study on the performance of fatty acid methyl ester sulfonate in detergent. Applied Chemical Industry, 2008, 7: 830-833.

[18] Xu, M. X.. Production and application of fatty methyl ester's derivatives, Chemical Industry, 2012, 7: 30-32.

[19] Qiao, W. H., Cui, Y. C., Zhu Y. Y., et al., 2012. Dynamic interfacial tension behaviors between Guerbet betaine surfactants solution and Daqing crude oil. Fuel, 2012, 102: 746-750.

[20] Okitsu, K., Sadanaga, Y., Takenaka, N., Maeda, Y., Bandow, H.. A two-step continuous ultrasound assisted production of biodiesel fuel from waste cooking oils: a practical and economical approach to produce high quality biodiesel fuel. Bioresource Technology, 2010, 101(14): 5394-5401.

[21] Srilatha, K., Devi, B. P., Lingaiah, N., et al. Biodiesel production from used cooking oil by two-step heterogeneous catalyzed process. Bioresource Technology, 2012, 119(7): 306-311.

[22] Zhao, G. X.; Zhu, B. X, 2003. Principles of surfactant action. China Light Industry Press: Beijing, 2003: 274.

[23] Dai, C. L., Fu, Y., You, Q., et al. Bio-based sulfonate surfactant and its synthetic method. CN103805155A, 2014.

[24] Green, D., Whillhite, G. Enhanced Oil Recovery SPE Textbook Series. Richardson, TX, 1998.

[25] Sreenu, M., Rao, B. V., Prasad, R. B. N., et al. Synthesis, surface and biological properties of sodium N-acyl isoleucines. European Journal of Lipid Science &

Technology, 2014, 116(2): 193-206.

[26] Rosen, M. J., Wang, H., Shen, P., Zhu, Y.. Ultralow interfacial tension for enhanced oil recovery at very low surfactant concentrations. Langmuir, 2005, 21(9): 3749-3756.

[27] Biswal, N. R., Paria, S.. Interfacial and wetting behavior of natural-synthetic mixed surfactant systems. RSC Advances. 2014, 4(18): 9182-9188.

[28] Blesic, M., Lopes, A., Melo, E., et al. On the self-aggregation and fluorescence quenching aptitude of surfactant ionic liquids. Journal of Physical Chemistry B, 2008, 112(29): 8645-8650.

[29] Wu, M. H., Wan, L. Z., Zhang Y. Q. A novel sodium N-fatty acyl amino acid surfactant using silkworm pupae as stock material. Scientific Reports, 2014, 4(4): 4428.

[30] Zhang, Q. Q., Cai, B. X., Xu, W. J., et al. The rebirth of waste cooking oil to novel bio-based surfactants. Scientific Reports, 2015, 5: 09971.

[31] Shanks, P. C., Franses, E. I. Estimation of micellization parameters of aqueous sodium dodecyl sulfate from conductivity data. Journal of Physical Chemistry, 1992, 96(4): 1794-1805.

[32] Wang, J. J., Wang, H. Y., Zhang, S. L.. Conductivities, volumes, fluorescence, and aggregation behavior of ionic liquids $[C_4mim][BF_4]$ and $[C_nmim]$ Br (n=4, 6, 8, 10, 12) in aqueous solutions. Journal of Physical Chemistry B, 2007, 111(22): 6181-6188.

[33] Zhao, G. X. Physical chemistry of surfactants. Peking University Press, 1984:36-60.

[34] Wadekar, M. N., Boekhoven, J., Jager, W. F., et al. Micellization behavior of aromatic moiety bearing hybrid fluorocarbon sulfonate surfactants. Langmuir, 2012, 28(7): 3397-3402.

[35] Chen, L. J., Lin, S. Y., Huang, C. C., et al., 1998. Temperature dependence of critical micelle concentration of polyoxyethylenated non-ionic surfactants. Colloids. & Surfaces A, 198, 135(1-3): 175-181.

[36] Wu, J., Li, N., Zheng, L., et al. Aggregation behavior of polyoxyethylene (20) sorbitan monolaurate (Tween 20) in imidazolium based ionic liquids. Langmuir 2008, 24(17): 9314-9322.

[37] Dong, B., Gao, Y. A., Su, Y., et al. Self-aggregation behavior of fluorescent carbazole-tailed imidazolium ionic liquids in aqueous solutions. Journal of Physical

Chemistry B, 2009, 114(114): 340-348.

[38] Singh, H. N., Saleem, S. M., Singh, R. P., Birdi, K. S.. Micelle formation of ionic surfactants in polar nonaqueous solvents. Journal of Physical Chemistry, 1980, 84(17): 2191-2194.

[39] Bedö, Z., Berecz, E., Lakatos, I.. Enthalpy-entropy compensation of micellization of ethoxylated nonyl-phenols. Colloid Polymer Science, 1992, 270(8): 799-805.

[40] Chen, L. J., Lin, S. Y., Huang, C. C.. Effect of hydrophobic chain length of surfactants on enthalpy-entropy compensation of micellization. Journal Physical Chemistry B, 1998, 102(22): 4350-4356.

[41] Wu, W. X., Lian, H. X., Ding, W., et al. Thermodynamics for micellization of anionic-nonionic gemini surfactants. Petrochemical Technology, 2013, 42(1): 39-46.

[42] González-Pérez, A., Ruso, J. M., Romero, M. J., et al. Application of thermodynamic models to study micellar properties of sodium perfluoroalkyl carboxylates in aqueous solutions. Chemical Physics, 2005, 313(1-3): 245-259.

[43] Li, N., Zhang, S., Zheng, L., Wu, J., Li, X., Yu, L., 2008. Aggregation behavior of a fluorinated surfactant in 1-butyl-3-methylimidazolium ionic liquids. Journal Physical Chemistry B, 2008, 112(112): 12453-12460.

Graphical Abstract

Investigation on Interfacial/Surface Properties of Bio-based Surfactant N-Aliphatic Amide-N,N-Diethoxypropylsulfonate Sodium as An Oil Displacement Agent Regenerated from Waste Cooking Oil

Yan Zhang^{1,2}, Qing You^{1*}, Yang Fu², Mingwei Zhao², Hongfu Fan¹, Yifei Liu², Caili



Interfacial/Surface Properties of NDPSS

Graphical abstract

Highlights

- A bio-based surfactant regenerated from waste cooking oil was synthesized \triangleright
- The interfacial tensions can reach up to an ultralow level ($<10^{-2} \text{ mN} \cdot \text{m}^{-1}$) \triangleright
- The thermodynamic parameters of micellization were systematically investigated \triangleright
- This bio-based surfactant exhibits great potential oilfield application in EOR ۶

<text>