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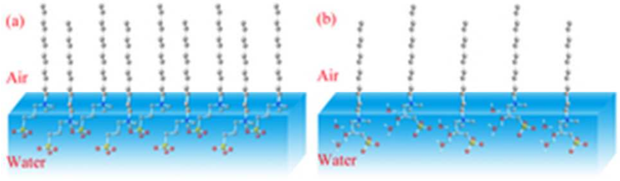

Distribution schematic of (a) propyl sulfobetaine CnSB and (b) hydroxypropyl sulfobetaine CnHSB of surfactant molecules vertically staggering at the air-water interface at concentration above CMC
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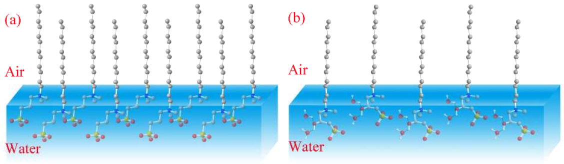
Molecular structure has important effect on surfacial and interfacial properties of sulfobetaine surfactant at air-water and crude oil-water interface



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ARTICLE

The Structure Effect on the Surfacial and Interfacial Properties of Zwitterionic Sulfobetaine Surfactants for Enhanced Oil Recovery

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Surfacial and interfacial properties of five zwitterionic surfactants, including three propyl sulfobetaines CSB (the carbon atom number of alkyl chain is 12, 14 and 16, respectively) and two hydroxypropyl sulfobetaine surfactants CHSB (the carbon atom number of alkyl chain is 12 and 14, respectively), have been studied at the air-water and oil-water interfaces. Surface activity of these surfactants at the air-water interface in aqueous solutions has been investigated by the Wilhelmy plate method at 30 ºC and ambient pressure. The values of critical micelle concentration (CMC) and surface tension at CMC (γ_{CMC}) were determined from the surface tension measurements. The obtained results indicate that the CMC and surface tension strongly depend on the surfactant molecular structure. An increase in the alkyl chain length results in the decrease of CMC and γ_{CMC} values. The presence of hydroxyl group causes the increase of CMC values and the decrease of γ_{CMC} values. The hydroxypropyl sulfobetaine surfactants have better surfacial properties. In addition, interfacial activity at the oil-water interface among the crude oil-reservoir water-surfactant systems has been investigated by spinning drop method under harsh reservoir conditions of high temperature (90 ºC) and high salinity (11.52×10^4 ppm, including 7040 ppm Ca^{2+} and 614 ppm Mg^{2+}). It's interesting that transient minimum dynamic interfacial tension (DIT_{min}) can be observed in specific concentration range. The time to reach DIT_{min} is different with surfactant molecular structure and surfactant concentration. Hydroxypropyl sulfobetaine surfactant C_{14}HSB shows excellent interfacial properties. It can reduce interfacial tension (IFT) between oil and water to ultralow level at very low concentration, and the ultralow IFT phenomenon only occurs in certain concentration range, from 0.03 to 0.10 wt%. In this work, hydroxypropyl sulfobetaine surfactants exhibit remarkable ability and are good candidates for chemical agent to enhance oil recovery of harsh reservoirs.

Introduction

Zwitterionic surfactant possesses both positive charged cationic hydrophilic group and negative charged variable anionic hydrophilic group attached to each molecule. The cationic moiety is based on primary, secondary, or tertiary amines or quaternary ammonium group. The variable anionic moiety includes carboxylic acid, sulfonic acid, sulfuric acid ester and phosphoric acid ester, which may not be adjacent to the cationic site. Zwitterionic surfactants have been widely used in the field of cosmetics, washing products and underlie virtually every aspect of our daily lives [1-4]. Their colloidal behaviors in aqueous solutions have been extensively investigated within a specific range of temperature through surface tension, conductivity and light scattering measurements [5-9]. Recently, increasing research has indicated that zwitterionic surfactant has been used in chemical enhanced oil recovery (EOR) because of their excellent water solubility, remarkable interfacial properties, high foam stabilities, insensitivity to temperature and the presence of salinity, and synergistic effect with ionic and anionic surfactants [10-13]. Especially sulfobetaine surfactant, with anionic sulfonic groups in hydrophilic headgroups, is a hot and promising research focus in EOR for harsh reservoirs with high temperature and high salinity [14-16].

To the usage of surfactants for EOR, the investigation of the interfacial properties at the oil-water and oil-water-rock interfaces are the most relevant [17]. Interfacial phenomena of surfactant solution are more complex under the reservoir conditions. The effects of properties and compositions of crude oil and reservoir rock are absolutely huge and cannot be ignored [18]. One of the most commonly and simply measured parameters of interfacial behavior is the interfacial tension (IFT) between crude oil and surfactant solution. For the displacement of crude oil in the pores and capillaries of petroleum reservoir rock, it is generally required to reduce IFT to ultralow level (less than 10^{-2} mN/m) through theoretical consideration and practical laboratory scale experiments [19]. Ultralow IFTs can be achieved with appropriate surfactants by adsorbing at the oil-water interface, which can increase capillary numbers by several orders of magnitude and effectively displace residual crude oil from the reservoir [20]. Laboratory experiments and oilfield applications confirm that sulfobetaine surfactant can reach ultralow IFTs as a single-component chemical flooding agent [21-25], avoiding chromatographic separation due to different adsorption capacity of each component of multicomponent displacing fluids. Ultralow IFTs were obtained in a wide range of sulfobetaine concentration from 0.01 to 0.3 wt% for Daqing reservoirs with temperature 98 ºC, salinity of 220,000 mg/L and divalent ions of 2,300 mg/L. But these researches only focus on selecting optimum surfactants to certain reservoir conditions and carrying out a series of performance evaluation.

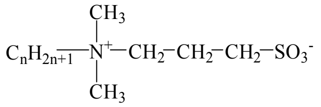
Many experimental researches have been focused on the dynamic interfacial tension (DIT) behaviors between crude oil and single-component sulfobetaine surfactant flooding systems. The studies of the DIT give information not only for the adsorption rate but also for the mechanism of adsorption of surfactant molecules, thus helping to reveal the factors governing the adsorption process. In order to better study interfacial behaviors of surfactants at the oil-water interface, it's necessary to investigate their surfacial ability. A large number of researches about sulfobetaine surfactant were concentrated on their thermodynamics of micellization [8, 26, 27]. The micelles are formed when surfactant concentration in aqueous solutions reaches the critical micelle concentration (CMC). At this point, various properties of a surfactant solution are noted, including conductivity, osmotic pressure and turbidity [28]. CMC can be affected by various factors including surfactant species (hydrophobic volume, chain length and headgroup area), temperature, pressure, ionic strength, pH, etc. These factors also have some effect on IFT behaviors. The study of CMC is helpful to gain a better insight of many physical and chemical properties of surfactants.

In our laboratory, excellent performance of sulfobetaine surfactants have been confirmed in chemical EOR process, but lacking systematic theoretic investigation on the surfacial and interfacial properties. So in this work, five sulfobetaine surfactants possibly used in EOR with excellent ability of temperature resistance and salt tolerance are chosen to investigate the influence of molecular structure on surfacial and interfacial properties. Firstly surfacial properties are studied at the air-water interface at 30 ºC in aqueous solution. Secondly interfacial properties are studied at the oil-water interface in the crude oil-reservoir water-surfactant system under harsh reservoir conditions of high temperature and high salinity. The research results will be contributed to the screening of surfactant flooding agent for harsh reservoirs.

Experimental

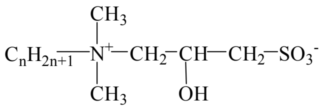
Materials

Three propyl sulfobetaine surfactants, dodecyldimethylammonio propanesulfonate ($C_{12}SB$), dimethylmyristylammonio propanesulfonate ($C_{14}SB$), dimethylpalmitylammonio propanesulfonate ($C_{16}SB$), and two hydroxypropyl sulfobetaine surfactants, dodecyldimethylammonio hydroxyl propanesulfonate ($C_{12}HSB$) and dimethylmyristylammonio hydroxyl propanesulfonate ($C_{14}HSB$), were supplied by Promise Song Industry (Shanghai, China) and used with further purification. Hydrochloric acid was dropped in the commercial product dissolved in hexane, giving hydrochloric acid salts as white solids; the solids were washed with acetone, and then recrystallized twice from methanol. Finally, white crystal powder was obtained after vacuum desiccation at 60 ºC.
Molecular structures are shown in Scheme 1.



$$C_nH_{2n+1}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}-CH_2-CH_2-CH_2-SO_3^-$$

Propyl sulfobetaine surfactants C_nSB (n=12, 14 and 16)



$$C_nH_{2n+1}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-SO_3^-$$

Hydroxypropyl sulfobetaine surfactants C_nHSB (n=12, 14)

Scheme 1. Molecular structures of sulfobetaine surfactants

Reservoir water and crude oil were supplied by the Tarim Oilfield in West China. The total dissolved solids (TDS) were 11.52 × 10^4 ppm with high concentration up to 7654 ppm of divalent metal ions, Ca^{2+} and Mg^{2+}. The composition of water is listed in Table 1. The crude oil was treated by dehydration and degassing. Its viscosity and density are 7.8 cP and 0.825 g/mL at 90 ºC.

Table 1. Quality analysis of the reservoir water of Tarim Oilfield

Ions	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
Concentration (ppm)	36660	7040	614	70560	245.3	103

Methods

SURFACE TENSIONS

The aqueous solutions of sulfobetaine surfactants were prepared at different concentrations from 0.01 mmol/L to 10 mmol/L using distilled water. The surface tensions of these solutions were measured at 30 °C by Dataphysics DCAT41 Contact Angle/Surface Tension Meter (the German Dataphysics Company, Germany) using the Wilhelmy plate method. Temperature was controlled by thermostat water bath. All measurements were repeated three times and averaged.

To further study the effect of temperature on the surface activity, the maximum surface excess concentration Γ_{max} and the minimum area A_{min} occupied per surfactant molecule at the air-water interface are proposed and determined as follows:

$$\Gamma_{\mathrm{max}} = -\frac{1}{\mathrm{nRT}}\left(\frac{\mathrm{d}\gamma}{\mathrm{d}\ln \mathrm{c}}\right)_{\mathrm{T}} \qquad (1)$$

$$A_{\mathrm{min}} = \frac{1}{\mathrm{N_A}\Gamma_{\mathrm{max}}}(\times 10^{23}) \qquad (2)$$

where n is the number of solute species, whose concentrations at the interface change with the surfactant concentration c; the value of n is taken as 1 for amphoteric surfactant in aqueous solution; R is the gas constant (8.314 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$); T is the absolute temperature; γ represents the surface tension; $\mathrm{d}\gamma/\mathrm{d}(\ln c)$ is the slope of surface tension γ *vs* ln c dependence when the concentration is near CMC; and N_A is Avogadro's constant (6.022×10^{23} $\mathrm{mol^{-1}}$).

OIL-WATER INTERFACIAL TENSIONS

Solutions of sulfobetaine surfactants were prepared at different concentration from 0.01 wt% to 0.5 wt% by reservoir water. They were sealed in tubes and observed visually clear after the age of 24 h at 90 °C. The interfacial tensions between crude oil and these solutions were measured at 90±0.1 °C by TX-500C spinning drop interface tensiometer (USA KINO Industry Co., LTD, USA). The rotational speed was at 6000 rpm and the interfacial tension was calculated from the Vonnegut approximation as reported elsewhere [29]. Samples were assumed to be equilibrated when the measured IFT values were unchanged at the period of measurement (30 min at least).

Results and discussion

Surface Tension

The surface tensions of five sulfobetaine surfactants as a function of concentration at 30 °C were determined and plotted in Figure 1. The CMC and surface tension at CMC (γ_{CMC}) values were estimated from the breakpoints of these plots and listed in Table 2. The γ_{CMC} values indicate the ability of surfactants to lower surface tensions and accordingly the CMC indicates the efficiency. The γ_{CMC} values of $C_{12}SB$, $C_{14}SB$ and $C_{16}SB$ were 38.64, 35.79 and 33.45 mN/m, respectively. The long-chain sulfobetaine surfactants provided higher ability in lowering the surface tension of water than short-chain ones.

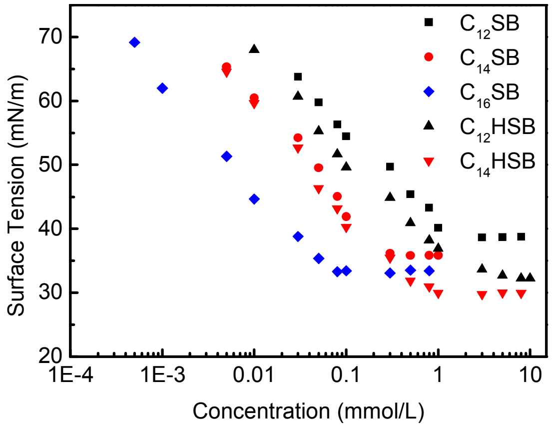


Figure 1. Variation of surface tensions as a function of concentration of sulfobetaine surfactants at 30 ºC

Table 2. Surface-active properties of sulfobetaine surfactants at 30 ºC

Surfactant	CMC (mmol/L)	γ_{CMC} (mN/m)	Γ_{max} ($\mu mol/m^2$)	A_{min} ($\AA^2$)
$C_{12}SB$	1.383	38.64	2.612	63.57
$C_{14}SB$	0.233	35.79	2.815	58.98
$C_{16}SB$	0.064	33.45	2.769	59.96
$C_{12}HSB$	3.389	32.30	2.152	77.17
$C_{14}HSB$	0.708	29.89	2.636	62.99

As far as C_nSB concerned, the relationship of surface activities and the alkyl chain length can be seen from Table 2. The CMC and γ_{CMC} values decrease gradually with the number of carbon atoms in the alkyl chain length from 12 to 16 at 30 °C. This may be due to an increase in the hydrophobic effect [30] with the increase in alkyl chain length, which promotes the micellization and the aggregation of sulfobetaine molecules. Here, the CMC values of $C_{12}SB$, $C_{14}SB$ and $C_{16}SB$ were 1.383, 0.233 and 0.0647 mmol/L, respectively. In general, the CMC value of surfactants is the sign of surface properties, which follows the principle: the smaller the CMC value, the superior the surface activity. This means that C_nSB with longer alkyl chain length has the excellent ability of micellization at low concentrations. The relationship between the CMC and the alkyl chain length of C_nSB was shown in Figure 2. It is known that the variation of the CMC with the alkyl chain length can often be described by the empirical equation as follows:

$$\text{Log}\, CMC = \text{A} - \text{B}n \tag{3}$$

where A and B are constants and *n* is the number of carbon atoms in the alkyl chain length. The Log *CMC* decreases with increasing alkyl chain length and the B value was 0.35, which was lower than those of sulfobetaine surfactants C_nSB (B=0.44 or B=0.48) [8, 31]. This indicates that the CMC of sulfobetaines in this work decreases more for each addition of two carbons in hydrocarbon chain.

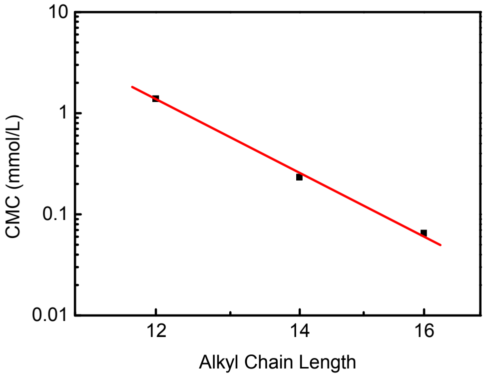


Figure 2. Relationship between CMC and alkyl chain length of C_nSB

The difference in molecular structure between C_nSB and C_nHSB is spacer groups in polar group, i.e. propyl and hydroxypropyl. From Figure 1 and Table 2, there is an increase in the CMC values and a decrease in the γ_{CMC} values as a result of the introduction of the hydroxyl group. It can be concluded that the hydroxyl group in the hydrophilic headgroup has an effect on the CMC and γ_{CMC}. Similar conclusions had been drawn that the introduction of the hydroxyl group to erucyl dimethyl amidopropyl sulfobetaine (EDAS) made an increase in CMC from 5.02 to 5.64 mmol/L and a decrease in γ_{CMC} from 35.34 to 31.41 mN/m [32]. The hydroxyl group in the spacer group enhances the solubility of hydroxypropyl sulfobetaine as the hydrophilicity increases through hydrogen bond formation between the hydroxyl group and water molecules. As the hydrophilicity increases, a higher concentration is needed to form micelles, which leads to a slightly higher CMC.

In our work, the variations of surface activities reveals that there is a stronger tendency of solubility for C_nHSB with a flexible, hydrophilic spacer group, rather than C_nSB with a rigid, hydrophobic one. Because of the stronger intramolecular electrostatic attraction between the positive and negative charge centers caused by the flexible spacer group, the electrostatic repulsion between the headgroups of the C_nHSB molecules becomes relatively weaker [33]. Accordingly, the headgroups in C_nHSB molecules can pack together more tightly than in C_nSB ones [34]. This can be confirmed from the A_{min} values in Table 2. The larger A_{min} values possessed by C_nHSB were the result of hydrogen bonds formation between hydroxyl groups and water molecules at the air-water interface combined with the flexible headgroups (see Figure 3).

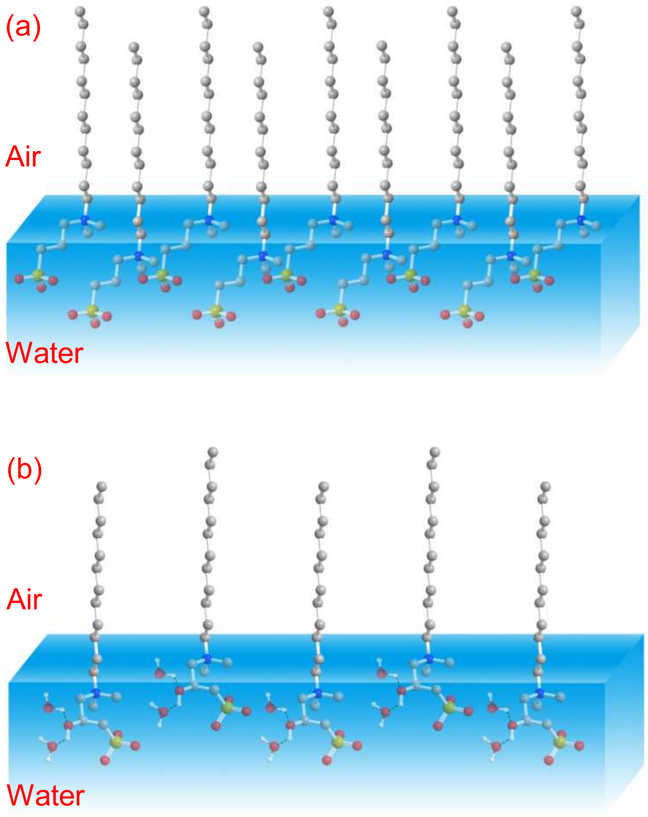


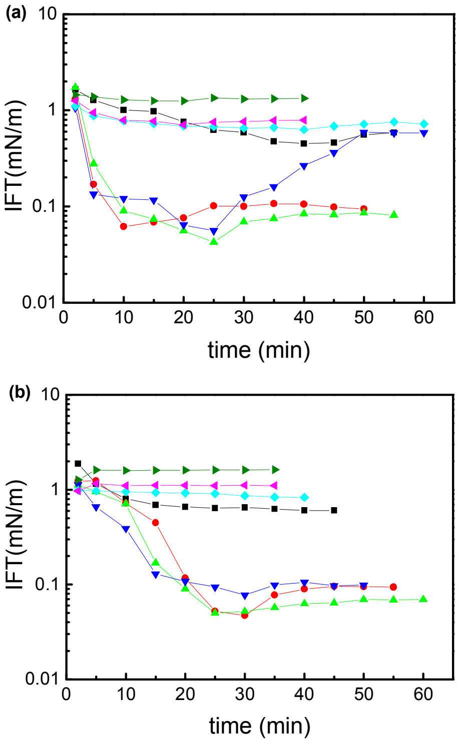
Figure 3. Distribution schematic of (a) propyl sulfobetaine C_nSB and (b) hydroxypropyl sulfobetaine C_nHSB of surfactant molecules vertically staggering at the air-water interface at concentration above CMC

In general, surfactants with same hydrophobic tail chain and similar hydrophilic headgroup in the molecular structure behave similar surface activities[19]. The nature of the headgroups has a tiny effect on surface activity. In this work, there was an obvious decrease in the γ_{CMC} values of C_nHSB, which implies that hydroxypropyl sulfobetaine has stronger surface activity than propyl sulfobetaine due to the introduction of hydroxyl group in the spacer group.

Interfacial Tension

OCCURRENCE OF MINIMUM DYNAMIC INTERFACIAL TENSION

Minimum dynamic interfacial tension (DIT_{min}) and equilibrium interfacial tension (DIT_{eq}) are major parameters for evaluating the interfacial properties of surfactants. Taylor et al.[35] proposed that oil recovered through the surfactant-enhanced alkali flooding of linear Berea sandstone cores correlates better with the DIT_{min} value than with DIT_{eq} value. During the experimental period of DIT, there do not exist salting-out effect at 90 ºC in surfactant solutions prepared by reservoir water with high salinity and high hardness (11.52×10^4 ppm, including 7040 ppm Ca^{2+} and 614 ppm Mg^{2+}). The DIT value between crude oil and reservoir water in absence of surfactant is always above 10 mN/m. The interaction energy across the interface must be large. This means that the nature of the material at both sides of the interface must be very similar [19]. Since oil and water have very different natures, the presence of surfactants will make similar natures at both sides of the interface after surfactants adsorb at the oil-water interface. Thus DIT will decrease sharply. Besides the chemical nature of surfactant, surfactant concentration has a strong effect on DIT. The effect of five sulfobetaine surfactant concentrations on DIT with time was shown in Figure 4.



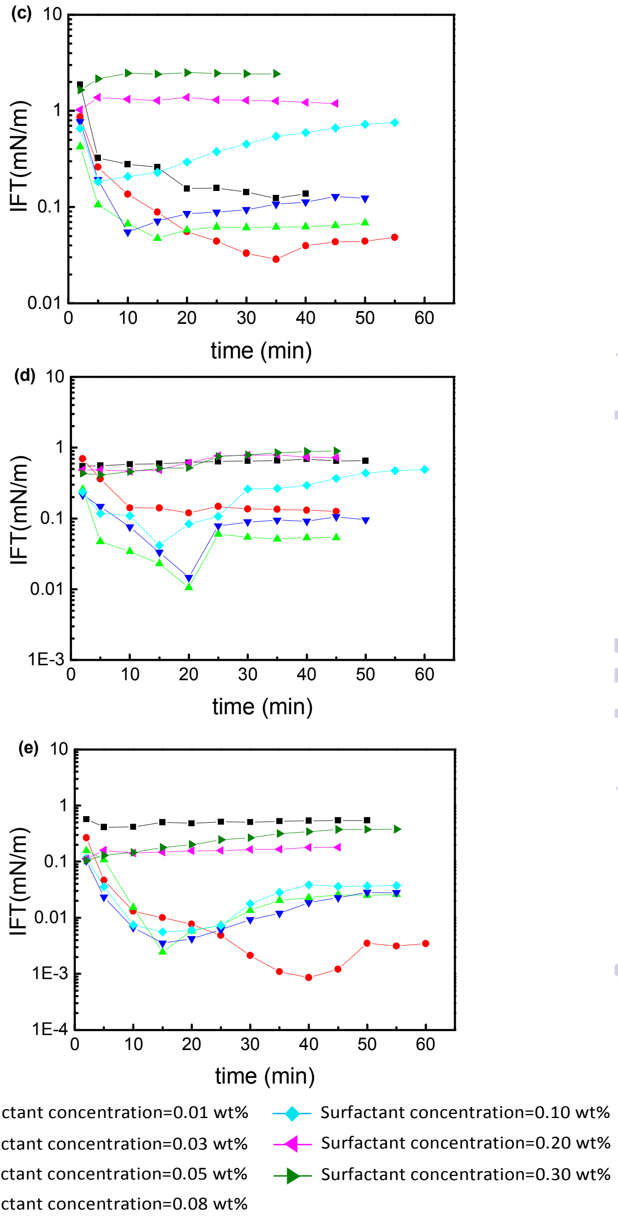
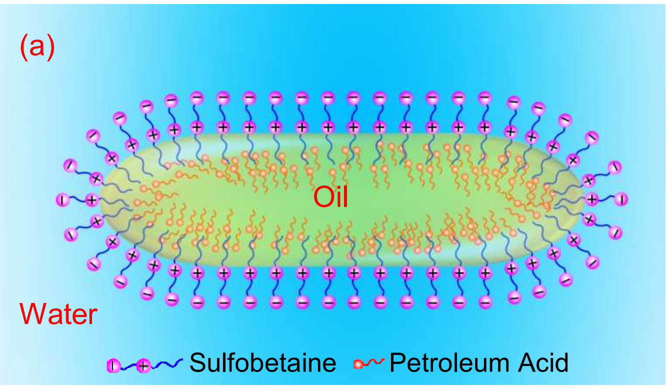


Figure 4. Variation of the DIT between crude oil and reservoir water at 90 ºC with time for sulfobetaine surfactants at different concentrations. a. $C_{12}SB$, b. $C_{14}SB$, c. $C_{16}SB$, d. $C_{12}HSB$, e. $C_{14}HSB$.

As shown in Figure 4, for a given surfactant, two interesting DIT behaviors were observed. The one is that not all surfactant systems show the occurrence of DIT_{min}. It does not occur in very low and high concentration range where DIT values always remain higher. The other is that DIT in low surfactant concentration range from 0.03 to 0.10 wt%, decreases very rapidly over time to a transient DIT_{min}, followed by a gradual increase to DIT_{eq}. The occurrence of DIT_{min} in oil-water-surfactant systems was reported in many researches [36, 37]. It may be related to the intermolecular interaction between the surface-active species present (i.e. petroleum acid) in crude oil and the added surfactants in aqueous solution. Considering surfactant diffusion-controlled adsorption, possible explanations for the occurrence of the $\mathrm{DIT_{min}}$ are that: (1) Due to adsorption velocity is larger initially than desorption velocity at the fresh oil-water interface, the rapid diffusion of added surfactant (from the aqueous phase) and surface-active species (from the oil phase) to the oil-water interface, and the interaction between each other (see Figure 5a), that results in an optimum mixed surfactant layer at the interface at an optimum concentration and ratio. This can greatly decrease IFT to $\mathrm{DIT_{min}}$. (2) Subsequent diffusion of surface-active species at the interface into the bulk phase to form mixed micelles with the added surfactant (see Figure 5b), which increases IFT from $\mathrm{DIT_{min}}$ to $\mathrm{DIT_{eq}}$ until adsorption-desorption equilibrium is reached. No evidence shows that $\mathrm{DIT_{min}}$ can be reached at lower surfactant concentrations than 0.03 wt%, due to the concentration of added surfactant not enough to form a monolayer at the oil-water interface. However, it is interesting to observe the lack of $\mathrm{DIT_{min}}$ at higher surfactant concentration. In general, the greater the amount of surfactant solubilized in the oil-water system, the more similar the natures of the two phases approach each other, the smaller the resulting IFT between the two phases [19]. Accordingly, in the crude oil-reservoir water-surfactant systems with higher surfactant concentration, DIT should be reached lower IFT. But the results here are that the values of DIT are always high during the experiment process. These phenomena are probably due to the rapid diffusion of the surface-active species at the interface into the bulk phase, where high concentration of surfactant results in the instantaneous formation of an optimum mixed surfactant layer followed by adsorption-desorption equilibrium.



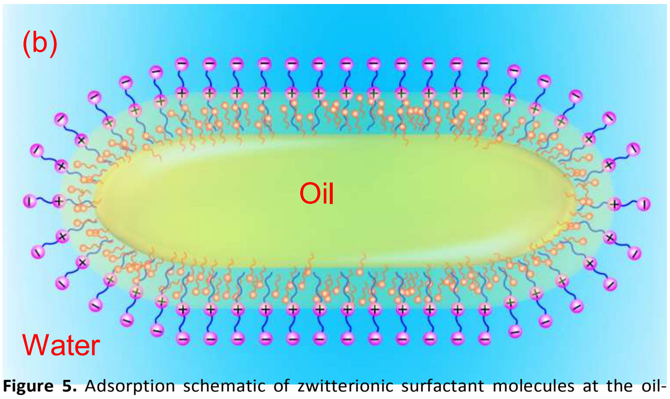


Figure 5. Adsorption schematic of zwitterionic surfactant molecules at the oil-water interface. (a) the interaction between added surfactant and petroleum acid, which decreases IFT to $\mathrm{DIT_{min}}$, (b) subsequent diffusion of the petroleum acid at the interface into the bulk phase to form mixed micelles with the added surfactant, which increases IFT from $\mathrm{DIT_{min}}$ to γ_{eq}.

TIME TO REACH $\mathrm{DIT_{min}}$

It is obviously observed from Figure 4 that the amount of time is required for each oil-water-surfactant system to reach $\mathrm{DIT_{min}}$. An increase in DIT with time is over a period generally from 10 to 30 minutes. It is also found from Figure 4 that the time to reach $\mathrm{DIT_{min}}$ varies with surfactant concentration where $\mathrm{DIT_{min}}$ exists. Many literatures indicate that the time to reach $\mathrm{DIT_{min}}$ decreased with increasing surfactant concentrations [36, 38]. Our results have similar rules by and large. The higher the surfactant concentration, the larger the concentration gradient between the bulk phase and the oil-water interface. Hence the faster the diffusion to the oil-water interface, the smaller the time in which DIT reaches the minimum values.

Göbel and Joppien [39] reported that in the longer time range the plots of the dynamic interfacial tension γ of Triton X-100 versus $1/\sqrt{t}$ show linear dependence in four cases (air, cyclohexane, n-heptane and n-hexadecane) by drop-volume method. The relationship is as follows:

$$\left(\frac{d\gamma}{d(1/\sqrt{t_{ads}})}\right)_{t\to\infty} = \frac{RT\Gamma_c^2}{c_0}\sqrt{\frac{\pi}{4D}} \qquad (3)$$

where t_{ads} is the adsorption time, c_0 is bulk phase concentration, D is the diffusion coefficient, R and T are the gas constant and the thermodynamic temperature, respectively. Concentration dependent adsorption (Γ_c) of the surfactant can be calculated from the relationship of the maximum adsorbed amount (Γ_∞) at the oil-water interface and capillarity parameter b: $\Gamma_c = \Gamma_\infty[bc_0/(1+bc_0)]$. From the three known quantities c_0, Γ_c and slope of the curve in a γ vs $1/\sqrt{t}_{ads}$ plot, it is possible to compute effective diffusion coefficients for the transport of surfactant to the interface. However, less reports have revealed molecular thermodynamic model on the basic of IFT measured by spinning drop method in the oil-water-surfactant systems. Explicit relationships have not been found between the adsorption properties described above in the measurement of surface tensions of five sulfobetaine surfactants and the comprehensive effects of testing environment (temperature, the complex composition of crude oil and reservoir water, etc) on surfactant adsorption-desorption equilibrium and on molecular interaction among oil-water-surfactant system. If mass transport is occurring at an appreciable rate compared to the time required for the oil drop to come to thermal equilibrium, the DIT calculated is path dependent. Unfortunately, because we have no method to determine the comprehensive effects of testing environment during the experiment, we cannot resolve this issue. It is difficult to calculate thermodynamic parameters of surfactants at the oil-water interface**.** The variation of DIT in crude oil-reserve water-surfactant system will be studied further from the perspective of thermodynamics.

THE EFFECT OF MOLECULAR STRUCTURE ON IFT

The values of DIT_{min} and DIT_{eq} of five sulfobetaine surfactants were extracted from Figure 4 and shown in Figure 6. Because these surfactants fail to get DIT_{min} at high concentration range, Figure 6a just shows DIT_{min} obtained at low concentration range. The values of DIT_{min} and the optimum surfactant concentration at the DIT_{min} ($C_{o\text{-}min}$), and the values of minimum DIT_{eq} ($DIT_{eq\text{-}min}$) and the optimum surfactant concentration at the minimum DIT_{eq} ($C_{o\text{-}eq}$) are listed in Table 3.

Comparing different molecular structure of sulfobetaine surfactants from the results of Figure 6 and Table 3, alkyl chain length has effect on the ability of lowering IFT values. Surfactant hydrophobicity increase with the increase in alkyl chain length. For propyl sulfobetaine surfactants, increasing alkyl chain length lead to a little better interfacial properties. IFT values reduce at the same order of magnitude. When alkyl chain length increases from 12 to 16. the values of DIT_{min} and DIT_{eq} just reduce from 0.042 to 0.028 mN/m and from 0.081 to 0.048 mN/m, respectively. However, for hydroxypropyl sulfobetaine surfactants, $C_{14}HSB$ has shown far better interfacial properties than $C_{12}HSB$ When alkyl chain length increases from 12 to 14. The values of DIT_{min} and DIT_{eq} reduce obviously by orders of magnitude from 0.010 to 0.0009 mN/m and from 0.053 to 0.003 mN/m, respectively. The increase in alkyl chain length and the addition of the hydroxyl group in the spacer group possibly make $C_{14}HSB$ moderate hydrophilic-lipophilic ability. So $C_{14}HSB$ has better solubility both in the bulk phase and the oil phase. The higher the density of the surfactant at the oil-water interface layer, the greater the intermolecular interaction between the surface-active species present and the added surfactants, the lower the IFT [40].

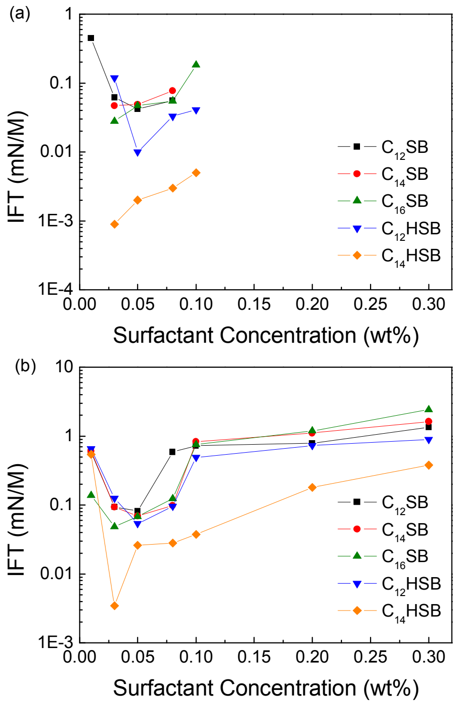


Figure 6. Variation of the DIT_{min} and DIT_{eq} between crude oil and reservoir water at 90 ºC as a function of surfactant concentrations. a. DIT_{min}, b. DIT_{eq}.

Table 3. Variation of the DIT_{min} and DIT_{eq} (in mN/m) between crude oil and reservoir water at 90 °C as a function of sulfobetaine surfactants

Surfactant	DIT_{min} (mN/m)	$C_{o\text{-}min}$ (wt%)	$DIT_{eq\text{-}min}$ (mN/m)	$C_{o\text{-}eq}$ (wt%)
$C_{12}SB$	0.042	0.05	0.081	0.05
$C_{14}SB$	0.047	0.03	0.069	0.05
$C_{16}SB$	0.028	0.03	0.048	0.03
$C_{12}HSB$	0.010	0.05	0.053	0.05
$C_{14}HSB$	0.0009	0.03	0.003	0.03

OPTIMUM CONCENTRATION TO REACH DIT_{min}

Besides the chemical nature of the surfactant, relative changes in surfactant concentrations affected the DIT of the crude oil-reservoir water-surfactant systems. Figure 6a shows that DIT_{min} increased with increasing surfactant concentration in low concentration range. Figure 6b shows that DIT_{eq} firstly decreases and then increases with increasing surfactant concentration. It is supposed that increasing surfactant concentration would result in producing the micelles in both aqueous phase and oil phase. The consequent decrease in the adsorption capacity of the surface-active species at the interface due to the solubilization of micelles, leads to the increase of DIT_{min} and DIT_{eq} with increasing surfactant concentration. From the above results, it indicates that for a given surfactant, there exists a range of optimum surfactant concentration towards certain crude oil at certain reservoir condition. Especially C_{14}HSB, exhibits excellent interfacial behavior to reduce IFTs to 0.0009 ~ 0.005 mN/m at optimum surfactant concentration from 0.03 to 0.10 wt%. The similar phenomenon was observed with many surfactants which had better interfacial properties and achieved ultralow IFT at low concentration than at high concentrations [41, 42]. Although the values of DIT_{min} and DIT_{eq} of other four sulfobetaine surfactants was relatively high and no ultralow IFT appears in the range of testing concentration, they still have optimum concentration to reach DIT_{min}.

As is well known, the reduction of effective concentration caused by surfactant adsorption on reservoir rock surface is a major problem in field application of surfactant flooding [13, 43]. The variation of surfactant concentration brings about the change of IFTs and then affects oil displacement efficiency. Accordingly, injection concentration should be higher than the experimental results through laboratory tests. It can overcome the loss of surfactant adsorption to some extent during flooding process and maintain IFT between crude oil and reservoir water in a low or ultralow region. In spite of inevitable adsorption problem, sulfobetaine surfactants are still promising chemical agents for EOR, particularly under harsh conditions with high temperature and high salinity.

Conclusions

This work show that molecular structure has great effect on surfacial and interfacial properties of surfactants. The surface tension of three propyl sulfobetaine surfactants and two hydroxypropyl sulfobetaine surfactants were analyzed at 30 ºC in comparison with the results of different molecular structures, including the alkyl chain length and hydroxyl group. The CMC values decreased with increase in alkyl chain length and increased by the addition of hydroxyl group. The γ_{CMC} values decreased with increase in alkyl chain length and the addition of hydroxyl group. Interface activity of these surfactants at the oil-water interface was also investigated under harsh reservoir conditions of high temperature (90 ºC) and high salinity (11.52×10^4ppm, including 7040 ppm Ca^{2+} and 614 ppm Mg^{2+}). DIT_{min} occurs in specific concentration range and the time to reach DIT_{min} varies with surfactant concentration. The magnitude of DIT values varied with surfactant molecule structure and surfactant concentration. C_{14}HSB not only shows the property of lower surface tension, but also has stronger ability to reduce IFT between crude oil and reservoir water. It can reduce DIT to ultralow level over an optimum range of low concentration from 0.03 to 0.10 wt% under harsh conditions. In evaluating displacement agent composition used in chemical flooding, the ability of lowering IFT plays an important role. So hydroxypropyl sulfobetaine surfactants have potential wide applications in EOR.

Acknowledgements

The work was supported by National Science Fund for Distinguished Young Scholars (51425406), National Natural Science Foundation of China (51174221, 21303268), Doctoral Fund from National Ministry of Education (No. 20120133110010), China Postdoctoral Science Foundation funded project (2013T60689) and the Graduate Innovation Fund from China university of petroleum (YCX2014015).

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