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Design and Surface/Interfacial Properties of Asymmetric Triazine Carboxyl Betaine Surfactants

Lishuai Jing · Weihong Qiao · Limei Luo · Huan Peng

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Abstract The design, synthesis and interfacial behaviors of six asymmetric carboxyl betaine surfactants (BC_{m-n}, m, $n = 8$, 10, 12, or 14, $m \neq n$) derived from s-triazine, which were prepared from cyanuric chloride, aliphatic amines, *N*,*N*-dimethylpropane-1,3-diamine, followed by the reaction with sodium chloroacetate, are reported. The structures were confirmed by MS, ^{1}H NMR and FT-IR. Compared with symmetric surfactants (BC_{n-n}, $n = 8, 10, 12$, or 14) we previously synthesized, the asymmetric series show superior surface activity. The γ_{CMC} of surfactants BC_{10-8}, BC_{12-8}, BC_{14-8} and BC_{12-10} is all below 30 mN/m. The minimum alkane carbon number of these ten surfactants is determined to be between 10 and 14. The interfacial behaviors between the alkanes and the solutions of triazine carboxyl betaine surfactants show that surfactants with a total carbon number in hydrophobic chains between 16 and 22 exhibit the ability to reduce the interfacial tension to an ultra-low value (10^{-3} mN/m). The surfactants with longer hydrocarbon chains display strong affinity to the alkanes with longer chains.

Keywords Triazine · Betaine surfactant · Minimum alkane carbon number · Interfacial tension

Introduction

Carboxyl betaine is a kind of attention-grabbing surfactant. Due to the decisive advantages of carboxyl betaine surfactants over general surfactants, such as the reduction in skin and eye irritation, salt tolerance, good biodegradation, and temperature resistance, it has been applied more and more in cosmetics [1, 2], detergents [3], fiber process agents [4], etc. Carboxyl betaine has also been concerned in enhanced oil recovery (EOR) in recent years [5–7]. Sulfonate surfactants, showing excellent interfacial tension properties and relatively lower cost, were studied for many years [8–11]. However, the underground experimental studies of heavy alkyl sulfonates by Daqing Oil Field, China, have shown serious undesired effects, such as blocking of small pores in porous rocks and pipelines in injection systems, due to the formation of insoluble precipitates by the reaction of a strong alkali with ions in connate water and sandstones [12–14]. The strong demands of petroleum energy motivate people to study other kinds of lower alkali or alkali-free surfactants in addition to sulfonates.

As is well known, surface/interfacial properties are very important for surfactants. To mobilize residual oil saturation, the primary requirement is a sufficiently low interfacial tension (IFT) to give a capillary number large enough to overcome the capillary forces [15]. Accordingly generating an ultralow interfacial tension in the reservoir to eliminate capillary trapping becomes the most challenging to develop for EOR [16]. Jean-Louis Salager et al. carried out a review of almost 40 year's work since the 1970s about attaining ultralow interfacial tension and three-phase behavior with surfactant formulation for EOR [17, 18]. The minimum interfacial tension occurrence is discussed at so-called correlations for optimum formulation to be related to the interfacial curvature. Capillary number theory [19, 20] also indicates that the ultralow interfacial tension between the displacement fluid and crude oil will enhance oil recovery greatly.

Carboxyl betaine surfactants carrying s-triazine possess distinctive surface properties and interfacial activities between the water and oil phases [21–23]. Single chain and double-chain symmetric s-triazine surfactants [24–27] can

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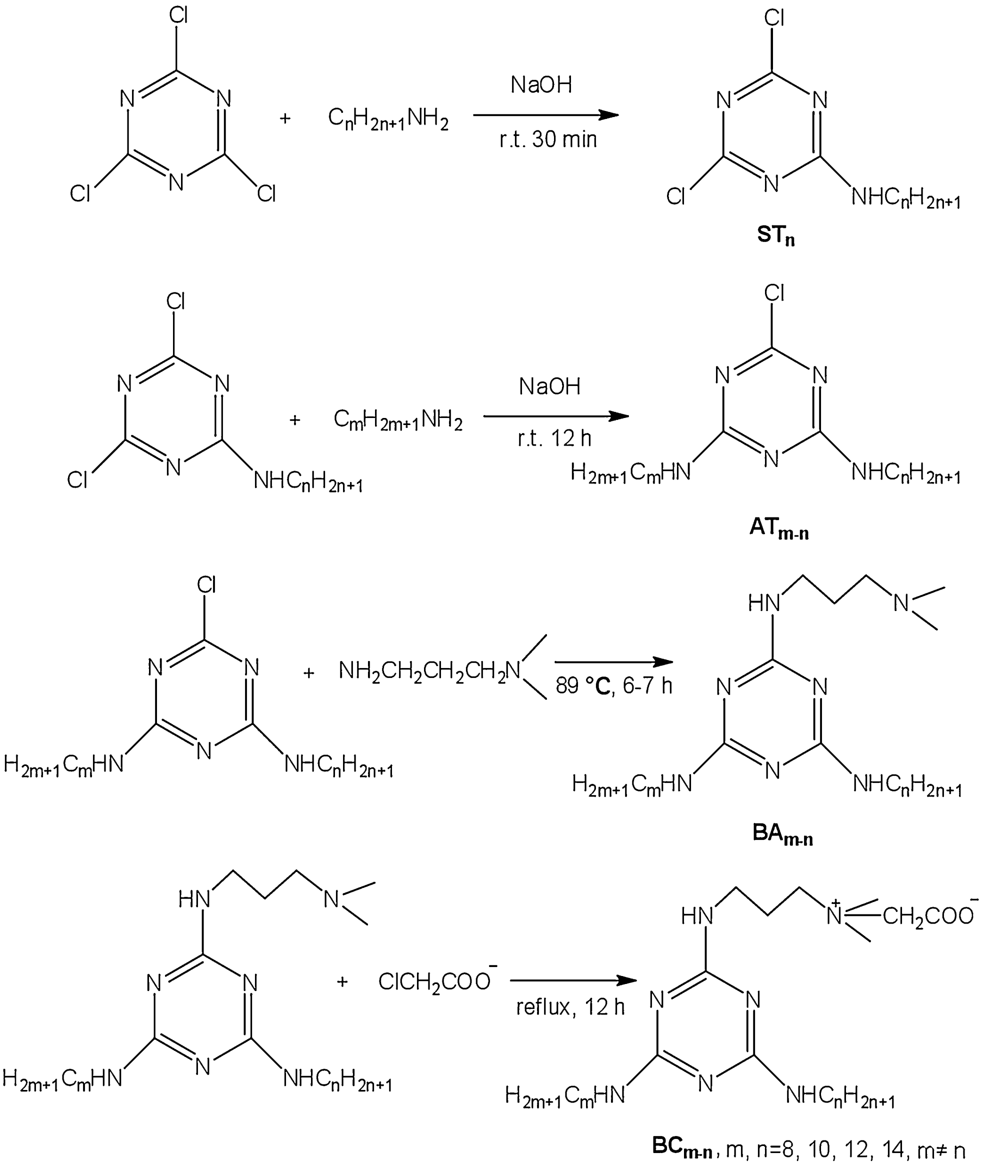
L. Jing · W. Qiao (✉) · L. Luo · H. Peng
State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China
e-mail: qiaoweihong@dlut.edu.cn



Scheme 1 Synthesis of BC_{m-n}

show a lot of outstanding properties by virtue of different hydrocarbon chains. Generally, the branched hydrocarbon chain surfactants show lower surface/interfacial tension [28], but there are few studies of asymmetric s-triazine surfactants [21, 22]. Triazine carboxyl betaine surfactants are mild and friendly to the environment, and could be used in many fields. Furthermore, triazine carboxyl betaine surfactants will overcome the occurrence of damage and erosion of equipment if used in surfactant flooding with a weak alkali or alkali-free system for EOR.

Herein, we designed and synthesized six novel carboxyl betaine surfactants derived from s-triazine and investigated their physico-chemical properties such as surface tension (γ_{CMC}), critical micelle concentration (CMC), the minimum average area per surfactant molecule (A_{min}), the alkane carbon number for the minimum interfacial tension. Scheme 1 shows the synthesis route of novel surfactants BC_{m-n}. The three chlorines of the cyanuric chloride react with $-NH_2$ step by step with a high yield, and the synthesis is simple and easily controllable. It is anticipated that these surfactants could perform better in the absence of alkali when interacting with the crude oil.

Experimental

Materials and Equipment

Octylamine, dodecylamine, tetradecylamine, and *N*,*N*-dimethylpropane-1,3-diamine were obtained from Jiangsu

Feixiang Chemical Co., Ltd., China and had a purity of 98.0 %. Decylamine (Beijing Xudong chemical plant, China) and chloroacetic acid (Tianjin Huchen chemical plant, China) were of analytical grade and had a purity of 99.0 and 99.5 %, respectively. Cyanuric chloride (Shanghai Hengdailao Trade Co., Ltd., China) has a purity of 97 %. Sodium hydroxide, chloroform, ethanol and methanol were of analytical grade. Deionized water was used in all measurements. The symmetric double chains carboxyl betaine surfactants BC_{n-n} ($n = 8$, 10, 12, 14) were prepared previously in our laboratory [23].

The mass spectrum was obtained with liquid chromatography/quadrupole time of flight tandem mass spectrometer (Micromass Britain, LC/Q-TOF–MS) and high performance liquid chromatography/mass selective detector (HP, America, HP1100LC/MSD). ^{1}H-NMR spectra were recorded on a Bruker 400 MHz instrument (Bruker, France, Model AVANCEII 400 MHz). Infrared spectroscopy was performed with a FT-IR spectrometer (Thermo 60Nicolet, America, Model NEXUS). The surface tensions were measured by tensiometer (Bowing Industry Corporation, America, Model TX-500C) by the spinning drop principle. Melting points were measured with a Micro-melting point apparatus (Ningbo Yongxin Optical Co., Ltd., China, Model X-4). The interfacial tensions (IFT) between the aqueous solutions of the surfactants and alkanes were measured with TX-500C full range tensiometer (Bowing Industry Corporation, USA).

Synthesis

The six asymmetric carboxyl betaine surfactants were synthesized in four steps, as shown in Scheme 1. Herein, the series of alkyl-monosubstituted trizine are defined as ST_n ($n = 8$, 10, 12, or 14), where n represents the hydrocarbon chain lengths. The series of alkyl-disubstituted trizine are defined as AT_{m-n} ($m, n = 8, 10, 12, \text{or } 14, m \neq n$), where m and n represent different hydrocarbon chain lengths, respectively. The series of intermediate which are obtained by substitution of *N,N*-dimethylpropane-1,3-diamine from AT_{m-n} are defined as BA_{m-n}. Correspondingly, the target surfactants obtained by quaterisation of BA_{m-n} by sodium chloroacetate are defined as BC_{m-n}.

Here we describe the synthesis process using the synthesis of *N*-(4-dodecyl amino-6-decylamino-1,3,5-triazine-2-yl)-*N*′-carboxymethyl-*N*′, *N*′-methyl propane-1,3-diamine (BC_{12-10}) as an example.

Synthesis of 2-Dodecylamino-4,6-dichloro-1,3,5-triazine (ST_{12})

Dodecylamine (0.01 mol, 1.85 g) in chloroform (20 mL) was added dropwise to a solution of cyanuric chloride (0.01 mol, 1.84 g) in chloroform (20 mL), and then 8 mL aqueous solution of 5–10 % (wt%) sodium hydroxide was added to keep the pH at 7–10. The mixture was stirred for 30–40 min at room temperature. After removal of the solvent, the resulting white crude product was recrystallized from chloroform/methanol (1:5, by vol) and purified (3.09 g, yield 92.7 %) 2-dodecylamino-4,6-dichloro-1,3,5-triazine (ST_{12}) was obtained as a white solid.

Synthesis of 2-Dodecylamino-4-decylamino-6-chloro-1,3,5-triazine (AT_{12-10})

Decylamine (1.46 g, 0.00927 mol) in chloroform (20 mL) was dropped into a 20-mL solution of ST_{12} (3.09 g) in chloroform followed by adding the aqueous solution of 5–10 % (wt%) sodium hydroxide to maintain the pH at 7–10. The reaction was continued for 12 h at room temperature. After that, the solvent was removed via rotary evaporation and the resulting white solid crude product was recrystallized from chloroform/methanol (5:1, by vol) to give 3.90 g (yield 92.6 %) 2-dodecylamino-4-decylamino-6-chloro-1,3,5-triazine.

Synthesis of *N*-(4-Dodecylamino-6-decylamino-1,3,5-triazine-2-yl)-*N*′,*N*′-dimethyl-1,3-propanediamine Triazine (BA_{12-10})

N, N-dimethyl-1,3-propanediamine (20 mL) was added to AT_{12-10} (3.90 g) under stirring and heating. AT_{12-10} was dissolved at *ca.* 60 °C and the mixture was allowed to react for 6–7 h at 89 °C. Thereafter the excess *N,N*-dimethyl-1,3-diamine was evaporated under reduced pressure. The remaining yellow product was transferred into a beaker with 50 mL deionized water, refrigerated, precipitated, and filtered. The filter cake was washed with deionized water three times until the pH of washing water was 7–8. Then the filter cake was dissolved in chloroform and dried with anhydrous Na_2SO_4 overnight. After filtration, the mixture was concentrated in vacuo to yield *N*-(4-dodecylamino-6-decylamino-1,3,5-triazine-2-yl)-*N*′,*N*′-dimethyl-1,3-propanediamine (BA_{12-10}, 3.61 g 80.9 %) as a white powder.

Synthesis of *N*-(4-Dodecylamino-6-decylamino-1,3,5-triazine-2-yl)-*N*′-carboxymethyl-*N*′,*N*′-dimethyl-1,3-propanediamine (BC_{12-10})

Sodium chloroacetate (0.97 g, 0.00834 mol) aqueous solution (15 mL) was added to the solution of BA_{12-10} (3.61 g) in 40 mL ethanol under stirring. The mixture was stirred for 12 h under reflux, then the water was removed by freeze-drying after removing the ethanol. The white residue was dissolved in 20 mL ethanol and the unreacted sodium chloroacetate was removed via centrifugation.

After removing the solvent, the collected upper ethanol solution gave a yellow residue which was purified *via* column chromatography ($CHCl_3$/MeOH (1:1, by vol)). 3.29 g *N*-(4-dodecylamino-6-decylamino-1,3,5-triazine-2-yl)-*N*′-carboxymethyl-*N*′,*N*′-dimethyl-1,3-propanediamine (BC_{12-10}) was obtained as a white power (yield 82.0 %).

BC_{12-10}: TOF–MS (positive): *m*/*z* 578.5 $[M + H]^+$, 600.5 $[M + Na]^+$. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.86$–0.89 (*t*, 6H, $2CH_3CH_2$), 1.26 [*m*, 32H, $CH_3(CH_2)_7CH_2$, $CH_3(CH_2)_9CH_2$], 1.49 (*s*, 4H, $CH_3(CH_2)_9CH_2CH_2$, $CH_3(CH_2)_7$ CH_2CH_2), 1.92 [*s*, 2H, $(CH_3)_2NCH_2CH_2CH_2NH$], 3.16–3.45 [*s*, 6H, $(CH_3)_2N(CH_2)_3NH$], 3.54–4.13 [*m*, 10H, $(CH_3)_2NCH_2(CH_2)_2NH$, $OOCCH_2(CH_3)_2NH_2$, $(CH_3)_2NCH_2CH_2CH_2NH$, $CH_3(CH_2)_8CH_2NH$, $CH_3(CH_2)_{10}CH_2NH$]. FT-IR (film): νN–H 3,296.23 cm^{-1} (s), νC–H 2,919.25 cm^{-1} (s), 2,850.46 cm^{-1} (s), νC=N 1,531.01 cm^{-1}, νC=O 1,631.78 cm^{-1} (s), δN–H 1,579.44 cm^{-1}, νC–O 1,367.97 cm^{-1}, δCH_2 ($n \geq 4$) 721.33 cm^{-1} (m).

BC_{14-8}: yield 86.6 %, m.p.137–138 °C, MS: *m*/*z* 578.7153 $[M + H]^+$, 1,156.4218 $[2M + H]^+$. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.86$–0.90 (*t*, 6H, $2CH_3CH_2$), 1.26 [*m*, 32H, $CH_3(CH_2)_5CH_2$, $CH_3(CH_2)_{11}CH_2$], 1.53 (*s*, 4H, $CH_3(CH_2)_{11}CH_2CH_2$, $CH_3(CH_2)_5CH_2CH_2$), 2.03 [*s*, 2H, $(CH_3)_2NCH_2CH_2CH_2NH$], 3.5–4.0 [*s*, 6H, $(CH_3)_2N(CH_2)_3NH$], 3.0–3.5 [*m*, 10H, $(CH_3)_2NCH_2(CH_2)_2NH$, $OOCCH_2(CH_3)_2NH_2$, $(CH_3)_2NCH_2CH_2CH_2NH$, $CH_3(CH_2)_6CH_2NH$, $CH_3(CH_2)_{12}CH_2NH$]. FT-IR (film): νN–H 3,283.63 cm^{-1} (s), νC–H 2,955.81 cm^{-1} (s), 2,852.87 cm^{-1} (s), νC=N 1,523.36 cm^{-1}, νC=O 1,631.97 cm^{-1} (s), δN–H 1,566.48 cm^{-1}, νC–O 1,364.66 cm^{-1}, δCH_2 ($n \geq 4$) 720.96 cm^{-1} (m).

BC_{14-10}: yield 84.5 %, m.p.167–168 °C, MS (positive): *m*/*z* 606.5 $[M + H]^+$, 629.5 $[M + Na]^+$, ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.86$–0.90 (*t*, 6H, $2CH_3CH_2$), 1.26 [*m*, 36H, $CH_3(CH_2)_7CH_2$, $CH_3(CH_2)_{11}CH_2$], 1.53 (*s*, 4H, $CH_3(CH_2)_{11}CH_2CH_2$, $CH_3(CH_2)_7CH_2CH_2$), 1.49 [*s*, 2H, $(CH_3)_2NCH_2CH_2CH_2NH$], 2.94, 3.5–4.0 [*s*, 6H, $(CH_3)_2N(CH_2)_3NH$], 3.19–3.27 [*m*, 10H, $(CH_3)_2NCH_2(CH_2)_2NH$, $OOCCH_2(CH_3)_2NH_2$, $(CH_3)_2NCH_2CH_2CH_2NH$, $CH_3(CH_2)_8CH_2NH$, $CH_3(CH_2)_{12}CH_2NH$], FT-IR (film): νN–H 3,300.66 cm^{-1}(s), νC–H 2,955.86 cm^{-1} (s), 2,850.37 cm^{-1} (s), νC=N 1,526.69 cm^{-1}, νC=O 1,629.46 cm^{-1} (s), δN–H 1,575.06 cm^{-1}, νC–O 1,368.39 cm^{-1}, δCH_2 ($n \geq 4$) 721.03 cm^{-1} (m).

BC_{14-12}: yield 82.1 %, m.p. 177–178 °C, TOF–MS (positive): *m*/*z* 634.8009 $[M + H]^+$, 1,268.5796 $[2M + H]^+$, ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.86$–0.89 (*t*, 6H, $2CH_3CH_2$), 1.26 [*m*, 40H, $CH_3(CH_2)_9CH_2$, $CH_3(CH_2)_{11}CH_2$], 1.48–1.92 (*s*, 4H, $CH_3(CH_2)_{11}CH_2CH_2$, $CH_3(CH_2)_9CH_2CH_2$), 3.17–3.26 [*s*, 2H, $(CH_3)_2NCH_2CH_2CH_2NH$], 3.86–4.17 [*s*, 6H, $(CH_3)_2N(CH_2)_3NH$], 3.0–3.5 [*m*, 10H, $(CH_3)_2NCH_2(CH_2)_2NH$, $OOCCH_2(CH_3)_2NH_2$, $(CH_3)_2NCH_2CH_2CH_2NH$, $CH_3(CH_2)_9CH_2NH$, $CH_3(CH_2)_{12}CH_2NH$], FT-IR (film): νN–H 3,309.10 cm^{-1} (s), νC–H 2,955.69 cm^{-1} (s), 2,849.78 cm^{-1} (s), νC=N 1,527.56 cm^{-1}, νC=O 1,629.06 cm^{-1} (s), δN–H 1,577.04 cm^{-1}, νC–O 1,368.28 cm^{-1}, δCH_2 ($n \geq 4$) 721.28 cm^{-1} (m).

BC_{12-8}: yield 83.4 %, m.p.121–123 °C, TOF–MS (positive): *m*/*z* 550.5778 $[M + H]^+$, 1,100.1472 $[2M + H]^+$. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.85$–0.89 (*t*, 6H, $2CH_3CH_2$), 1.25 [*m*, 28H, $CH_3(CH_2)_5CH_2$, $CH_3(CH_2)_9CH_2$], 1.49 (*s*, 4H, $CH_3(CH_2)_9CH_2CH_2$, $CH_3(CH_2)_5CH_2CH_2$), 1.92 [*s*, 2H, $(CH_3)_2NCH_2CH_2CH_2NH$], 3.17–3.27 [*s*, 6H, $(CH_3)_2N(CH_2)_3NH$], 3.54–4.13 [*m*, 10H, $(CH_3)_2NCH_2(CH_2)_2NH$, $OOCCH_2(CH_3)_2NH_2$, $(CH_3)_2NCH_2CH_2CH_2NH$, $CH_3(CH_2)_6CH_2NH$, $CH_3(CH_2)_{10}CH_2NH$]. FT-IR (film): νN–H 3,291.84 cm^{-1} (s), νC–H 2,955.84 cm^{-1} (s), 2,852.44 cm^{-1} (s), νC=N 1,524.94 cm^{-1}, νC=O1627.00 cm^{-1} (s), δN–H 1,565.54 cm^{-1}, νC–O 1,362.96 cm^{-1}, δCH_2 ($n \geq 4$) 721.19 cm^{-1} (m).

BC_{10-8}: yield 80.5 %, m.p. 103–104 °C, TOF–MS (positive): *m*/*z* 544.1287 $[M + Na]^+$, ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.85$–0.89 (*t*, 6H, $2CH_3CH_2$), 1.25 [*m*, 24H, $CH_3(CH_2)_5CH_2$, $CH_3(CH_2)_7CH_2$], 1.49 (*s*, 4H, $CH_3(CH_2)_7CH_2CH_2$, $CH_3(CH_2)_5CH_2CH_2$), 1.91–1.99 [*s*, 2H, $(CH_3)_2NCH_2CH_2CH_2NH$], 3.95–3.59 [*s*, 6H, $(CH_3)_2N(CH_2)_3NH$], 3.21–3.26 [*m*, 10H, $(CH_3)_2NCH_2(CH_2)_2NH$, $OOCCH_2(CH_3)_2NH_2$, $(CH_3)_2NCH_2CH_2CH_2NH$, $CH_3(CH_2)_6CH_2NH$, $CH_3(CH_2)_{10}CH_2NH$]. FT-IR (film): νN–H 3,300.70 cm^{-1} (s), νC–H 2,956.83 cm^{-1} (s), 2,853.52 cm^{-1} (s), νC=N 1,525.01 cm^{-1}, νC=O 1,628.64 cm^{-1} (s), δN–H 1,563.85 cm^{-1}, νC–O 1,356.49 cm^{-1}, δCH_2 ($n \geq 4$) 721.80 cm^{-1} (m).

Measurements

Determination of CMC, γ_{CMC} and A_{min}

The surface tensions of the aqueous solutions of the six surfactants were measured by tensiometer at 25 ± 0.1 °C until the error between two successive measurements was within 0.2 mN/m. The aqueous solutions were sonicated for 1 h for getting homogeneous and clear solutions before measurement and the pH of the solutions were at 7–8. The curves of surface tension versus logarithm of surfactant concentrations (γ-lg$C$) were plotted and the CMC values were determined from the break points. The surface tensions at CMC (γ_{CMC}) were also obtained from the curves of γ-lg$C$. The maximum surface excess, Γ_{max}, at the air–water interface was calculated by Gibbs adsorption equation [29]:

$$\Gamma_{\max} = \frac{-1}{2.303nRT}\left[\frac{d\gamma}{d\lg C}\right]_T \tag{1}$$

where the value of n (a constant determined by the number of species constituting the surfactant and adsorbed at the interface) is taken as 1, R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (K), and $d\gamma/d\lg C$ is the slope below the CMC in the surface tension plots.

The minimum average area occupied by per surfactant molecule $A_{\min}$ (nm^2) at the air/water interface at saturated adsorption was calculated using Eq. (2), where N_A is Avogadro's number.

$$A_{\min} = \frac{10^{14}}{N_A \Gamma_{\max}} \tag{2}$$

Interfacial Tension Measurement

The surfactant solution as the outer phase was injected into the centrifuge tube by syringe, and 1–2 μL alkane as the inner phase was injected into the surfactant solution. Then the centrifuge tube was put into the TX-500C full range tensiometer with a specific rotation speed (5,000 rpm) at 45 °C. The interfacial tension was obtained from Eq. (3):

$$\gamma = 3.425 \times 10^{-7} (\rho_h - \rho_d)\, \omega^2 D^3, \quad L/D \geq 4 \tag{3}$$

where γ is the oil–water interfacial tension in mN/m, ω is the angular speed in rad/s, ρ_h, ρ_d is the density of outer phase and inner phase in g/cm^3, respectively, D is the oil drop width (diameter) and L is the length of the oil drop in mm.

Results and Discussion

Equilibrium Surface Tension

The surface tensions of the aqueous solutions of the six surfactants BC_{m-n} were measured by tensionmeter at 25 ± 0.1 °C, shown in Figs. 1, 2, 3, 4. Table 1 lists the values of CMC, γ_{CMC}, and $A_{\min}$ of BC_{m-n}.

Obviously, the CMC, γ_{CMC}, and $A_{\min}$ variation of asymmetric triazine carboxyl betaine surfactants are consistent with classic interface theory. $A_{\min}$ increases as the length of hydrocarbon chains increases, which indicates BC_{m-n} packs loosely at the interface resulting from that the long hydrophobic chain is more likely to coil [30]. For surfactants BC_{m-8}, with the growth of m CMC and γ_{CMC} decrease. For surfactants BC_{m-10}, with the growth of the m, the CMC decreases, too, while γ_{CMC} increases with m increasing from 12 to 14. This can be attributed to the fact that the hydrocarbon chains of BC_{14-10} are too long, which generates the small steric hindrance between the long hydrocarbon chains of BC_{14-10}. The long hydrocarbon chains rotate freely and easily, thus possibly cover each other. Some methyl groups may cover other methyl groups, and more methylene groups expose to air. As a

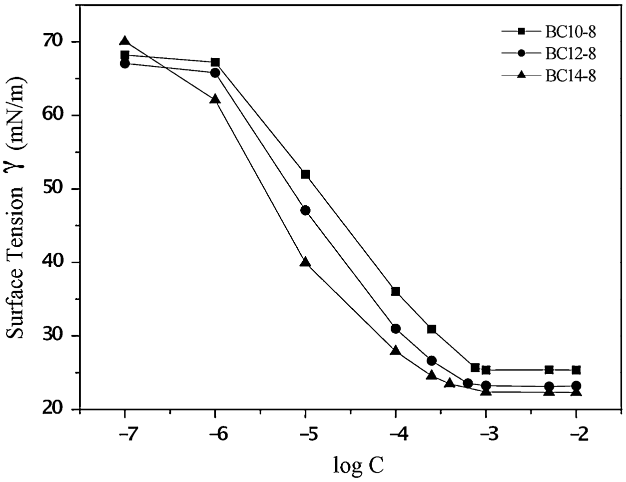


Fig. 1 Surface tension (γ) versus log$C$ of BC_{m-8} at 25 °C

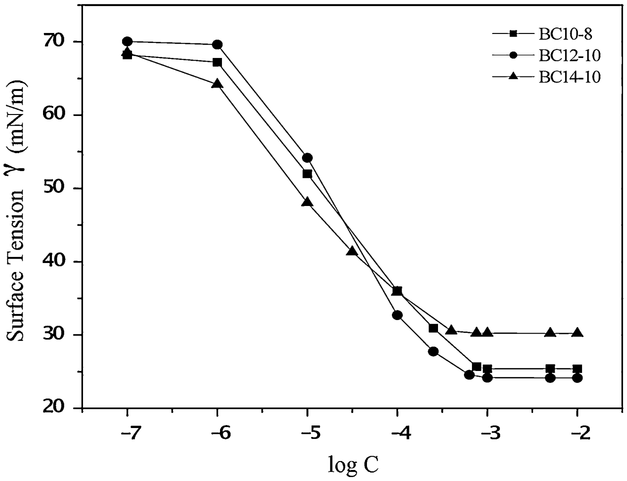


Fig. 2 Surface tension (γ) versus log$C$ of BC_{m-10} at 25 °C

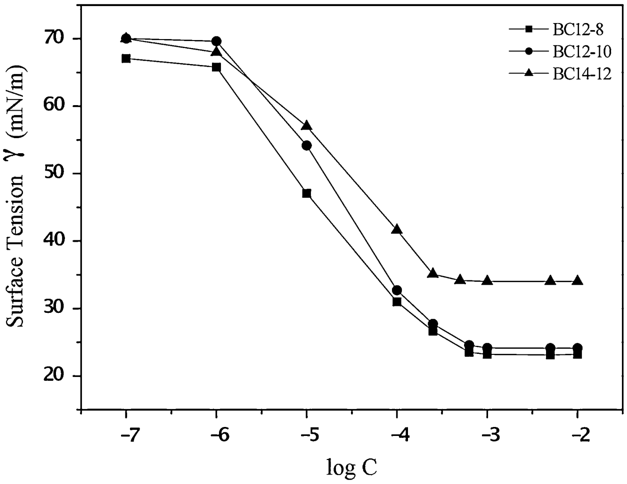


Fig. 3 Surface tension (γ) versus log$C$ of BC_{m-12} at 25 °C

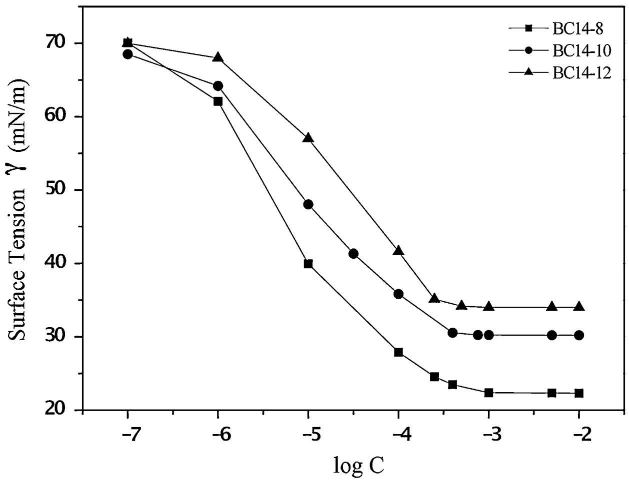


Fig. 4 Surface tension (γ) versus log$C$ of BC_{m-14} at 25 °C

Table 1 Physico-chemical properties of BC_{m-n}

Surfactants BC_{m-n}	CMC/ (molL^{-1})	γ_{CMC}/ (mN/m)	Γ_{max}/ (10^{-10}mol cm^{-2})	A_{min}/ (nm^2)
BC_{10-8}	6.31×10^{-4}	25.4	3.57	0.465
BC_{12-8}	5.01×10^{-4}	23.2	3.24	0.513
BC_{14-8}	3.16×10^{-4}	22.3	2.98	0.557
BC_{12-10}	3.98×10^{-4}	24.1	3.15	0.527
BC_{14-10}	2.82×10^{-4}	30.2	2.89	0.575
BC_{14-12}	2.51×10^{-4}	34.0	2.76	0.602

consequence, the γ_{CMC} of BC_{14-10} is larger than that of BC_{12-10} as the surface energy of methylene group is larger than that of the methyl group. For the surfactants BC_{m-12} and BC_{m-14}, with the growth of m, the CMC decreases, whereas γ_{CMC} increases. The water solubility of these two series of surfactants at 25 °C is dependent on the hydrocarbon chain length, which affects the regularity of the surface tension. With the increase of m, the water solubility of BC_{m-12} and BC_{m-14} decreases, which leads to the decrease of CMC and increase of γ_{CMC}. Compared to the symmetric surfactants, these asymmetric surfactants show better surface properties which mainly reflect in that the largest γ_{CMC} of asymmetric surfactants can reach 34 mN/m while that of symmetric surfactants can reach 43.1 mN/m [23]. Double asymmetric hydrophobic chains cross each other and arrange themselves at the air–water interface more closely. Furthermore, branched surfactants usually inhibit micellization and give low γ_{CMC}. Consequently, the surface properties of asymmetric surfactants are superior to that of the symmetric ones. The γ_{CMC} of BC_{8-8}, BC_{10-10}, BC_{10-8}, BC_{12-8}, BC_{14-8} and BC_{12-10} are all below 30 mN/m. It is surprising that these surfactants show better surface properties, although the total carbon numbers in hydrocarbon chains are as high as 16–22.

Alkane Selectivity and Minimum Alkane Carbon Number

The minimum alkane carbon number of a surfactant, as an important index of the interfacial properties, means the carbon number of an alkane which gives minimum IFT against the aqueous surfactant solution. Minimum alkane carbon number of surfactants relates to the concentration, structure of surfactant and other factors. To determine the minimum alkane number of each surfactant, the interfacial tensions between a series of alkanes and an aqueous solution of surfactant at 0.1 % by weight were measured, respectively. The interfacial properties between the alkanes and water are presented in the Figs. 5, 6, 7, 8. Table 2 summaries the minimum alkane carbon number n_{min} for the synthesized triazine carboxyl betaine surfactants.

From Figs. 5, 6, 7, and 8, the triazine carboxyl betaine surfactants BC_{m-n} can be divided into two groups. Namely, the first group of surfactants include BC_{8-8}, BC_{10-8}, BC_{12-8}, BC_{12-10}, BC_{10-10} and BC_{14-8}, with a total carbon number of hydrocarbon between 16 and 22. The interface tension versus the corresponding alkane number exhibits a minimum close to or in 10^{-3} mN/m order of magnitude at the preferred ACN; whereas the minimum interfacial tension of the second group of surfactants, BC_{12-12}, BC_{14-14}, BC_{14-12} and BC_{14-10}, all with a total carbon number of hydrocarbon more than 22, is merely close to 0.1 mN/m. The results can be used to predict the IFT behavior between the surfactants solutions and crude oils: the first group of surfactants may perform better than the second group of surfactants.

From Table 2, the n_{min} of these triazine carboxyl betaine surfactants increases from 10 to 14 as the carbon number of hydrocarbon chain increases from 8 to 14. The datum corroborates the results of correlations studies [31, 32] that the more hydrophobic surfactant prefers the alkane of

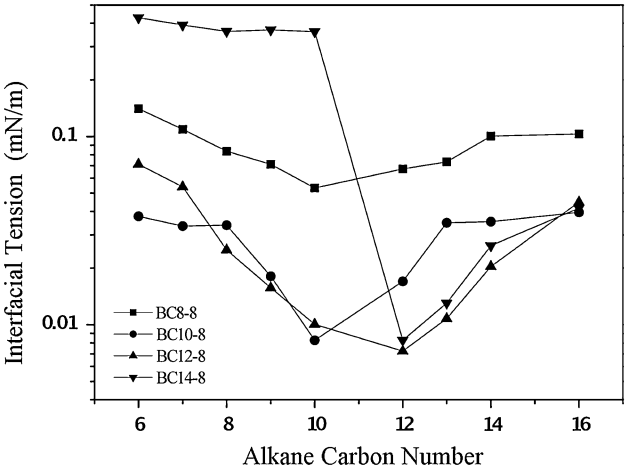


Fig. 5 Interfacial tension versus ACN curve for BC_{m-8}

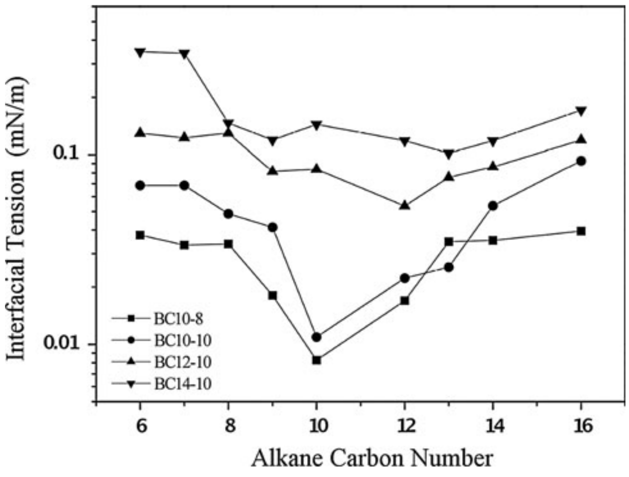


Fig. 6 Interfacial tension versus ACN curve for BC_{m-10}

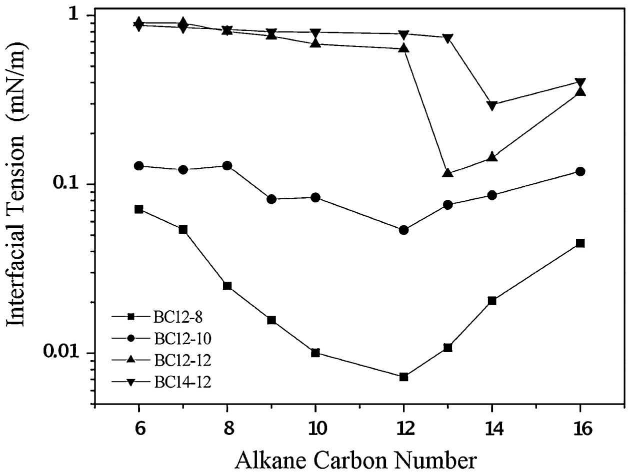


Fig. 7 Interfacial tension versus ACN curve for BC_{m-12}

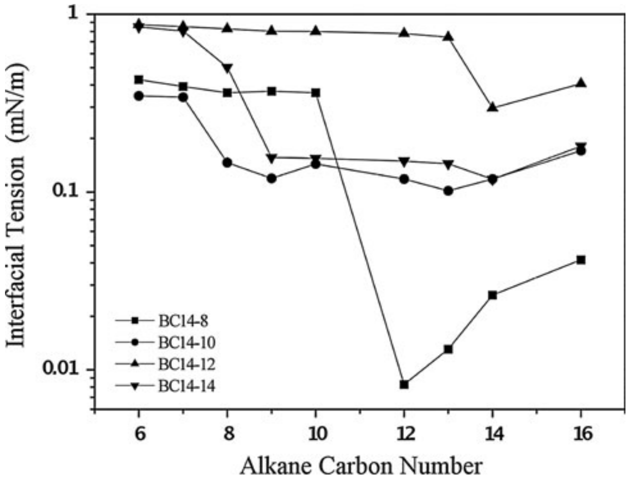


Fig. 8 Interfacial tension versus ACN curve for BC_{m-14}

Table 2 The minimum alkane carbon number ($n_{\min}$) for 1,3,5-triazine betaine surfactants

Surfactants	$n_{\min}$	Surfactants	$n_{\min}$
BC_{8-8}	10	BC_{12-10}	12
BC_{10-8}	10	BC_{14-10}	13
BC_{12-8}	12	BC_{12-12}	13
BC_{14-8}	12	BC_{14-12}	14
BC_{10-10}	10	BC_{14-14}	14

longer hydrocarbon chains, like alkyl benzene sodium sulfonates [33, 34]. In the system containing relatively pure SOW (surfactant/oil/water) components and in the absence of alcohol, the increase of correlations σ can decrease lower IFT between water and alkane for a given ACN ($\sigma = -\ln S^{*} + K\ \mathrm{ACN}$) [17].

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Author Biographies

Lishuai Jing is a Master's student at the School of Chemical Engineering, Dalian University of Technology, China. His research deals with the synthesis and the properties of surfactants.

Weihong Qiao is a professor at the School of Chemical Engineering, Dalian University of Technology, China. She received her Master's and her Ph.D. degrees in applied chemistry at Dalian University of Technology. Her research interests include the interfacial behavior of surfactants, the application mechanism of surfactants, synthesis and application of surfactants for EOR and development of functional surfactants.

Limei Luo is currently an engineer at the Chemical Analysis Testing Centre, Dalian University of Technology, China. Her research interests deal with molecular spectral analysis.

Huan Peng is a Master's student at the School of Chemical Engineering, Dalian University of Technology, China. His research deals with the synthesis and the properties of surfactants.