ORIGINAL ARTICLE



# Synthesis and Surface-Active Properties of a Homologous Series of Star-Like Triple-Chain Anionic Surfactants Derived from 1,1,1-Tris(hydroxymethyl)ethane

Xu Li^1 \cdot Fenglan Xing^1 \cdot Qun Xu^1 \cdot Xiaolong Sun^1 \cdot Yuping Wang^1 \cdot Liyan Wang^1 \cdot Pinglang Wang^1

Received: 21 January 2015/Accepted: 5 October 2015/Published online: 29 October 2015 © AOCS 2015

**Abstract** A novel homologous series of trimeric anionic surfactants,  $3C_nTE3CNa$  (where *n* is a fatty acid chain length of 7, 10, or 12), with three hydrocarbon chains and three carboxylate heads connected via tri-etheric bonds were synthesized from long-chain  $\alpha$ -bromo fatty acids and a triol, 1,1,1-tris(hydroxymethyl)ethane. The obtained trimeric carboxylic acids were esterified and purified by silica gel column chromatography, then hydrolyzed with dilute sodium hydroxide solution to form a series of trimeric carboxylate surfactant products. All prepared compounds were analyzed by IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectroscopy to confirm their chemical structures. Their surface-active properties were investigated. The critical micelle concentrations (cmc) of 3C<sub>n</sub>TE3CNa were in the range of 0.12-0.71 mmol/L, and the surface tensions at the cmc  $(\gamma_{\rm cmc})$  were 29.3–34.8 mN/m.

**Keywords** Trimeric surfactants · Oligomeric surfactants · Carboxylate surfactants · Anionic surfactants · Critical micelle concentration

# Introduction

After the discovery of dimeric (gemini) surfactants and their interesting and unexpected properties [1-10], trimeric surfactants have appeared as a new class of surfactants in the scientific literature in recent years [2, 11-21]. These surfactants comprise three amphiphilic moieties connected

Pinglang Wang pinglangw@gmail.com by linker groups at the level of the head groups or very close to the head groups of each monosurfactant. The reported trimeric surfactants exhibit excellent physicochemical properties, such as low critical micelle concentration (cmc), high efficiency in reducing the surface tension of water, and good water solubility, superior to those of the corresponding monomeric and dimeric (gemini) surfactants.

By far the most investigated trimeric surfactants are trisquaternary ammonium salts, i.e., three quaternary ammonium species linked at the level of the head groups by hydrocarbon spacer(s) [16, 17, 22–24]. For example, Zana et al. [24] did the pioneering work and a synthesized trimeric surfactant of methyldodecylbis[3-(dimethyldodecylammonio)propane]ammonium tribromide, 12-3-12-3-12, which consists of three quaternary ammonium head groups and three dodecyl chains connected by two propylene spacer chains. Ikeda et al. prepared a series of quaternary ammonium salts having a methyl- or a dodecylimino group or a dimethyl- or a dodecylmethylimmonio group (trisquaternary ammonium salt) between two dodecyldimethylammonio groups from dodecylamine and epichlorohydrin [16]. Yoshimura et al. [18] synthesized methylalkylbis[3-(dimethylammonio)ethyl]ammonium tribromide. Gao et al. synthesized trimeric cationic surfactants with ester groups in spacers [19].

The reason most trimeric surfactants reported in the literature are cationic is that amines are very strong nucleophiles (even tertiary amines), making their synthesis easier, and the quaternary salts are relatively easy to purify by crystallization. On the other hand, without those advantages, anionic trimeric surfactants are relatively difficult to synthesize and purify. That is why there are few reports on the synthesis of trimeric anionic surfactants in the literature. Also, although some star-like oligomeric

<sup>&</sup>lt;sup>1</sup> College of Chemistry and Chemical Engineering, Qiqihar University, Qiqihar 161006, China

surfactants have been reported in the literature [19, 25–28], no anionic trimeric star-like surfactants were found. In this study we report the synthesis of star-like trimeric anionic surfactants using a relatively easy procedure and their surface activities.

# **Experimental Procedures**

# Materials

The following chemicals were purchased from Aladdin Industrial Corporation (Shanghai, China): thionyl chloride (99.5 %), bromine (99.99 %), sodium hydride (60 % dispersion in mineral oil), and 1,1,1-tris(hydroxymethyl)ethane (97 %). Heptanoic acid, decanoic acid, dodecanoic acid, methanol, ethyl acetate, and dichloromethane were all of analytical grade. All chemicals were used directly without further purification. Tetrahydrofuran (THF) was dried by distillation over sodium benzophenone ketyl radical. Doubly distilled water was used in all experiments.

# Characterization

The synthesized surfactant molecules were characterized by <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy using a Bruker Ascend 600 MHz spectrometer, with chemical shifts recorded as ppm in CDCl<sub>3</sub>; TMS was used as an internal standard. Fourier transform infrared (FTIR) spectra were recorded on a Thermo Nicolet Avatar 370 (USA). Surface tension was measured at 25 °C using an Auto Surface Tensionmeter JK99C (Zongchen Digital Technical Equipment Co. Ltd, Shanghai, China).

## **Evaluation of Surface Activity**

Aqueous surfactant solutions were freshly prepared with different concentrations for the measurements. The aqueous solutions were placed in small crystallizing dishes and allowed to equilibrate for at least 30 min at 25 °C in the tensionmeter before the first measurement. The surface tension was obtained by pulling the platinum ring from the solution until the meniscus broke [29]. The platinum ring was washed with ethanol, rinsed with distilled water, and heated with a flame until red hot before each test. All measurements were repeated at least three times until good reproducibility was achieved. The cmc values were taken at the intersection of the linear portions of the plots of the surface tension against the logarithm of the surfactant molar concentration.

#### Foaming Ability and Stability

The foaming ability and stability were measured according to the foam rising volume method. Thus, 20.0 mL of the test trimeric anionic surfactant solution (0.1, 0.5, 1.0, 1.5 wt%) was placed in a 50-mL graduated cylinder. The cylinder was plugged and continuously oscillated 25 times. The foam volume (milliliters) above the solution level was read and recorded as  $V_0$  immediately after shaking. Each sample was allowed to stand undisturbed for 5 min and the new foam volume above the solution level was recorded as  $V_5$ . The foaming ability was evaluated from the  $V_0/20$  ratio, i.e., the foam volume generated from each milliliter of surfactant aqueous solution. The foam stability was reflected by the ratio of  $V_5/V_0$ , meaning the percentage of the remaining foam volume over the original foam volume after 5 min.

# Synthesis of Novel Trimeric Carboxylate Surfactants

#### Synthesis of $\alpha$ -Brominated Fatty Acids (**I-a-c**)

Fatty acid (100 mmol) and thionyl chloride (9.3 mL, 130 mmol) were placed in a dry, 100-mL, three-necked, round-bottom flask, equipped with a condenser (the top of the condenser was connected to a drying tube and two empty filter flasks in series with Tygon tubing to avoid the risk of moisture suck-back into the reaction; the open end of the tubing was inserted into a base solution, NaOH, 30%, to absorb acid gas generated from the reaction), under a nitrogen atmosphere and heated at 80 °C until no HCl gas evolution (bubbling through the NaOH solution) was observed (took ca. 1.5 h). Bromine (24.0 g, 150 mmol) was slowly added over 4 h, then held at 65 °C overnight (16 h). The reaction mixture was slowly poured into ice and mixed with ethyl acetate (35 mL). The layers were separated and the organic phase was washed with water (30 mL  $\times$  3), dried over MgSO<sub>4</sub>, and filtered. The filtrate was evaporated to obtain the crude product which was distilled using an oil pump (sand bath temperature 160 °C). The resulting product was a pale orange liquid (the yield of I-a = 91 %, I-b = 86.1 %, I-c = 95 %) (Scheme 1). The structures were confirmed by <sup>1</sup>H NMR. **I-a**  $\delta$ : 0.90 (t, J = 7.0, 3 H), 1.35–1.51 (m, 6 H), 1.99–2.10 (m, 2 H), 4.25 (q, J = 6.6, 1 H); **I-b**: 0.86 (t, J = 7.0, 3H), 1.43-1.531 (m, 12 H), 1.97-2.13 (m, 2 H), 4.25 (t, J = 7.4, 1H); **I-c**: 0.89 (t, J = 7.0, 3 H), 1.47–1.96 (m, 16 H), 1.97-2.12 (m, 2 H), 4.24 (q, J = 7.2, 1 H).

Scheme 1 Syntheses of the trimeric carboxylate surfactant molecules



#### Preparation of Intermediates (II-a-c)

Sodium hydride (0.528 g, 13.2 mmol) and 5 mL of dry tetrahydrofuran were added to a flame-dried, 100-mL, round-bottom flask. The mixture was stirred at room temperature for 10 min. A solution of 1,1,1-tris(hydroxymethyl)ethane (0.240 g, 2.0 mmol in 5 mL of THF) was added dropwise, stirred at room temperature for 1 h, and then placed in an ice bath. A solution of intermediate I (6.6 mmol in 5 mL of dry THF) was added dropwise into the reaction. The mixture was stirred in the ice bath for 30 min, heated to 65 °C, and stirred for 24 h at that temperature. The reaction mixtures turned into milky solutions which were cooled to room temperature. A small amount of water was added and the THF was removed by evaporation under reduced pressure. After cooling to room temperature, the reaction mixture was acidified to pH 1 (pH paper) with 5 % hydrochloric acid and extracted with ethyl acetate (15 mL  $\times$  3). The combined organic phases were dried over MgSO<sub>4</sub> and filtered. The filtrates were evaporation under reduced pressure. The pale yellow liquid was esterified in 15 mL of methanol using three drops of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). The mixture was heated to reflux for 15 h, and then the round-bottom flask was placed in an ice bath and a small amount of NaHCO3 was added to neutralize the acid catalyst. The excess methanol and other

volatiles were evaporated under reduced pressure. The residue was dissolved in 30 mL of ethyl acetate, washed with water (15 mL  $\times$  3), and then dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The filtrate was evaporated under reduced pressure. The products **II-a-c** were pale yellow viscous oils, which were purified by silica gel column chromatography using a mixed solvent of 5 % of ethyl acetate in hexane as an eluent. The obtained product was a colorless oil. The yields of II-a, II-b, and II-c were 63.4 %, 55.1 %, and 49.7 %, respectively. The structures of the compounds IIa-c were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and IR spectra. II-a <sup>1</sup>H NMR,  $\delta$ : 0.88 (t, J = 7.0, 3 H, CH<sub>3</sub>), 1.04 (s, 9 H), 1.28-1.54 (m, 18 H), 1.69 (q, J = 7.5, 6 H), 3.34(d, 1 H), 3.42 (d, 1 H), 3.73 (s, 9 H), 3.79 (t, J = 6.3, 3 H); <sup>13</sup>C NMR: 173.6, 79.7, 73.3, 51.6, 41.3, 33.0, 31.5, 25.1, 22.5, 17.0, 14.0; IR (film, cm<sup>-1</sup>): 2955.5 and 2862.1 (CH<sub>2</sub>, CH<sub>3</sub>), 1751.6 (C=O), 1460.7 and 729.6 (CH<sub>2</sub>), 1346.8 (CH), 1196.8–1300.2 (C–O–C). **II-b** <sup>1</sup>H NMR,  $\delta$ : 0.89 (t, J = 6.9, 3 H), 1.02 (s, 9 H), 1.22–1.41 (m, 36 H), 1.68 (q, J = 7.2), 3.32 (d, 1 H), 3.72 (d, 1 H), 3.72 (s, 9 H), 3.78 (t, J = 6.6, 3 H); <sup>13</sup>C NMR: 173.6, 79.6, 73.3, 51.6, 41.2, 33.0, 31.8, 29.4, 29.3, 29.2, 25.4, 22.6, 17.0, 14.1; IR (film, cm<sup>-1</sup>): 2953.0, 2925.8, 2856.4 (CH<sub>3</sub>, CH<sub>2</sub>), 1755.1 (C=O), 1465.1 and 722.5 (CH<sub>2</sub>), 1348.8 (CH), 1198.1-1131.8 (C-O–C). II-c <sup>1</sup>H NMR,  $\delta$ : 0.88 (t, J = 6.9, 3 H), 1.02 (s, 9 H), 1.26-1.43 (m, 48 H), 1.68 (q, J = 6.9, 6 H), 3.32 (d, 1 H),

3.40 (d, 1 H), 3.72 (s, 9 H), 3.78 (t, J = 6.3, 3 H); <sup>13</sup>C NMR: 173.6, 79.7, 73.3, 51.6, 41.2, 33.0, 31.9, 29.6, 29.5, 29.4, 29.4, 25.5, 22.7, 17.1, 14.1; IR (film, cm<sup>-1</sup>): 2959.0, 2924.8, 2854.9 (CH<sub>3</sub>, CH<sub>2</sub>), 1755.5 (C=O), 1466.0 and 723.5 (CH<sub>2</sub>), 1345.6 (CH), 1197.9–1115.0 (C–O–C).

## Preparation of Final Products (III-a-c)

The intermediate II (1.0 mmol) and THF (10 mL) were added to a three-necked, 50-mL round-bottom flask equipped with a condenser. Sodium hydroxide aqueous solution (5 %, 10 mL) was introduced and the mixture heated to reflux for 6 h. The reaction mixture was cooled and evaporated under reduced pressure to remove most of the THF. Water was added and the mixture was washed with dichloromethane (10 mL  $\times$  3). The aqueous phase was concentrated under reduced pressure, crystallized in a refrigerator, and centrifuged. The resulting solid was dried in a vacuum oven at 60 °C for 5 h to obtain a white solid. The yields of III-a (3C<sub>7</sub>TE3CNa), III-b (3C<sub>10</sub>TE3CNa), and III-c (3C<sub>12</sub>TE3CNa) were 83.1 %, 81.3 %, and 79.5 %, respectively. **III-a** <sup>1</sup>H NMR,  $\delta$ : 0.87 (t, J = 7.0, 3H), 1.04 (s, 9 H), 1.31–1.46 (m, 18 H), 1.71–1,78 (m, 6 H), 3.25 (d, 1 H), 3.66 (d, 1 H), 3.82 (q, J = 4.8, 3 H); IR (film, J)cm<sup>-1</sup>): 3426.6 (H<sub>2</sub>O), 2955.7, 2931.0 and 2858.4 (CH<sub>3</sub>, CH<sub>2</sub>), 1577.6 and 1426.4 (COO<sup>-</sup>), 1324.9 (CH), 1096.3 (C–O–C), 731.8 cm<sup>-1</sup> (CH<sub>2</sub>); **III-b** <sup>1</sup>H NMR,  $\delta$ : 0.88 (t, J = 6.9, 3H, 1.02 (s, 9 H), 1.26–1.31 (m, 36 H), 1.37–1.45 (m, 6 H), 3.26 (d, 1 H), 3.65 (d, 1 H), 3.82 (q, J = 4.8, 3H); IR (film, cm<sup>-1</sup>): 3440.1 (H<sub>2</sub>O), 2956.7, 2923.8 and 2854.5 (CH<sub>3</sub>, CH<sub>2</sub>), 1581.4 and 1424.8 (COO<sup>-</sup>), 1324.9 (CH), 1109.2 (C–O–C), 731.8 (CH<sub>2</sub>); **III-c** <sup>1</sup>H NMR,  $\delta$ : 0.89 (t, J = 6.9, 3 H), 1.02 (s, 9 H), 1.26–1.44 (m, 48 H), 1.73-1.78 (m, 6 H), 2.17 (d, 1 H), 3.65 (d, 1 H), 3.82 (q, J = 4.8, 3 H); IR (film, cm<sup>-1</sup>): 3432.5 (H<sub>2</sub>O), 2923.8, 2853.8 (CH<sub>3</sub>, CH<sub>2</sub>), 1593.7 and 1417.7 (COO<sup>-</sup>), 1467.7 (CH<sub>2</sub>), 1322.8 (CH), 1102.9 (C–O–C), 717.6 (CH<sub>2</sub>).

# **Results and Discussion**

## Synthesis and Purification

The first step in preparing the trimeric anionic surfactants is to convert the long-chain fatty acids to  $\alpha$ -bromo fatty acids. Instead of the Hell–Volhard–Zelinsky reaction [30–32] using phosphorus or phosphorus tribromide (PBr<sub>3</sub>), we used thionyl chloride which is a more convenient and easier to handle reagent. The reaction generates the acyl chloride from carboxylic acids which react with bromine to produce  $\alpha$ -bromo fatty acids. However, we found that the acids were not easy purified by either crystallization (too many impurities co-exist) or silica gel column chromatography (the bands on the column tailed too long and overlapped together). So they were esterified with methanol using a catalytic amount of sulfuric acid. The methyl esters were easily purified by silica gel chromatography with no tail phenomena on the column observed. The pure ester was then easily hydrolyzed and purified by crystallization. Overall, syntheses of the trimeric anionic surfactants, step by step, were smooth and successful with high quality products and good yields.

#### **Equilibrium Surface Tensions**

All three trimeric anionic surfactants,  $3C_7TE3CNa$ ,  $3C_{10}$ -TE3CNa, and  $3C_{12}TE3CNa$ , showed good water solubility at room temperature. The surface tension isotherms as a function of the logarithm of the concentration are shown in Fig. 1. The surface tension decreased gradually with increasing surfactant concentration and reached a clear break point, which was taken as the cmc.

Of the three trimeric anionic surfactants,  $3C_{10}TE3CNa$  was the most efficient at lowering the surface tension of aqueous solutions. Its surface tension at the cmc ( $\gamma_{cmc}$ ) was 29.3 mN/m, lower than those of the  $3C_7TECNa$  and  $3C_{12}TE3CNa$ , 34.7 and 31.5 mN/m, respectively. Also, the cmc of  $3C_{10}TE3CNa$ , 0.12 mmol/L, was the lowest of the three surfactants. The cmc of  $3C_7TECNa$  and  $3C_{12}TE3CNa$  were 0.71 and 0.21 mmol/L, respectively.

The results show that increasing the hydrocarbon chain length from hexyl to nonyl caused a lowering of the cmc and  $\gamma_{cmc}$ , whereas an increase from nonyl to undecyl resulted in a little less surface activity. A possible reason



**Fig. 1** Correlation of the surface tension and the logarithm of concentration for aqueous solutions of the surfactants  $3C_n$ TE3CNa (*black square n* = 7; *black triangle n* = 12; *black circle n* = 10) at 25 °C

why  $3C_{10}$ TE3CNa shows the greatest surface activity is that  $3C_7$ TE3CNa seems to show weak hydrophobicity for intermolecular attraction owing to its short hydrocarbon chain length, resulting in higher surface tension and cmc values. On the other hand,  $3C_{12}$ TE3CNa seems to have higher surface tension than that of  $3C_{10}$ TE3CNa owing to strong intramolecular attraction between the three hydrocarbon chains. In the case of  $3C_{10}$ TE3CNa, the intra- and intermolecular interactions balance favorably and compact micelles can form owing to strong hydrophobic interactions.

Interestingly,  $\gamma_{\rm cmc}$  values of trimeric surfactants with C<sub>8</sub>, C<sub>10</sub>, and C<sub>12</sub> hydrocarbon chains reported in the literature had a similar trend, i.e., C<sub>10</sub> < C<sub>12</sub> < C<sub>8</sub> [15, 18]. In one report, the trimeric surfactants were made using a triamine linker reacted twice to generate surfactant molecules with a hydrocarbon chain length of 8, 10, or 12; their  $\gamma_{\rm cmc}$  values were 39.9, 33.3, and C<sub>12</sub> = 36.9 mN/m, respectively [14]. Another example was trimeric surfactants of quaternary ammonium bromide with hydrocarbon chain lengths of 8, 10, or 12; their  $\gamma_{\rm cmc}$  values were 35.1, 25.8, and 36.4 mN/m, respectively, although the  $\gamma_{\rm cmc}$  values of C<sub>8</sub> and C<sub>12</sub> were similar [17].

Comparing with the cmc values of the monomeric anionic surfactant sodium dodecanoate, 5.51-6.22 g/L $(2.5 \times 10^{-2}-2.8 \times 10^{-2} \text{ mol/L})$ , in water at 25 °C [33– 35], the cmc value of the corresponding trimeric surfactant  $3C_{12}$ TE3CNa is only 0.163 g/L ( $2.1 \times 10^{-4} \text{ mol/L}$ ), about two orders of magnitude lower than that of sodium dodecanoate on a molar basis. Similarly, the cmc value of  $3C_{10}$ TE3CNa is only 0.087 g/L ( $1.3 \times 10^{-5} \text{ mol/L}$ ), much less than that of sodium decanoate, 5.548 g/L( $2.9 \times 10^{-2} \text{ mol/L}$ ) [36]. The cmc values for the corresponding dimeric anionic surfactants were not found in the literature. The big differences in the cmc values between the monomeric and the corresponding trimeric anionic surfactants indicate that the trimeric anionic surfactants are much more effective in adsorbing at the air-water interface. Removing the hydrophobic parts of the surfactant molecules from contact with water quickly lowers the free energy of the interface (surface tension) as the concentration of the surfactants increases, and the surfactants start aggregating into micelles when the surface becomes saturated.

# Foaming Ability and Stability of Trimeric Anionic Surfactants

Foaming ability and foam stability for the three trimeric anionic surfactants were studied as a function of concentration in distilled water at room temperature. The ratios of the initial foam volumes  $V_0$  (at time 0 min after oscillation) and the surfactant solution volume (20 mL) are an indicator of the surfactant foaming ability, and the ratio of foam volume after standing for 5 min ( $V_5$ ) and the initial foam volume ( $V_0$ ) reflect foam stability. The results of foaming ability and foam stability of the three trimeric surfactants are listed in Table 1.

As shown in Table 1, the foaming ability ( $V_0/20$ ) of  $3C_7TE3CNa$  increased from 54 to 74 % as its concentration increased from 0.1 to 0.5 wt%, and as the concentration continued increased to 1.0 and 1.5 wt%, it slightly decreased to 61, and 57 %. For  $3C_{10}TE3CNa$  and  $3C_{12}$ -TE3CNa as their concentration increased from 0.1 to 1.5 wt%, their foaming abilities increased from 58 to 108 % and 74 to 122 %, respectively. It is a common feature for the three surfactants that the effect of concentration on foaming ability is most notable when their concentration increased from 0.1 to 0.5 wt%. The increases of foaming ability were 37, 55, and 43 % for  $3C_7TE3CNa$ 

Surfactants	Concentration (wt%)	Foam volume (mL)		$V_0/20~(\%)$	$V_5/V_0~(\%)$
		V <sub>0</sub> (0 min)	V <sub>5</sub> (5 min)		
3C <sub>7</sub> TE3CNa	0.1	10.8	10.5	54	97.2
	0.5	14.7	14.0	74	95.2
	1.0	12.1	11.8	61	97.5
	1.5	11.3	11.0	57	97.3
3C <sub>10</sub> TE3CNa	0.1	11.6	10.7	58	92.2
	0.5	18.0	18.0	90	100.0
	1.0	19.0	17.3	95	91.1
	1.5	21.5	19.7	108	91.6
3C <sub>12</sub> TE3CNa	0.1	14.8	14.5	74	98.0
	0.5	21.2	19.4	106	91.5
	1.0	25.8	24.8	129	91.6
	1.5	24.3	23.0	122	94.7

**Table 1** Foam properties of the trimeric anionic surfactants

 $3C_{10}TE3CNa$ , and  $3C_{12}TE3CNa$ , respectively, then slowly increased as the concentration further increased to 1.0 and 1.5 wt% except for  $3C_7TE3CNa$ , which decreased slightly. The foaming ability increases with increasing hydrocarbon chain length at the same concentration levels. The data in Table 1 shows that all three surfactants had high foam stability ( $V_5/V_0$ ), ranging from 92 to 100 %.

# Conclusions

Trimeric anionic surfactants were successfully synthesized by reacting  $\alpha$ -bromo fatty acids ( $\alpha$ -bromoheptanoic acid,  $\alpha$ bromodecanoic acid, and  $\alpha$ -bromododecanoic acid) with 1,1,1-tris(hydroxymethyl)ethane in the presence of sodium hydride, followed by esterification with methanol, silica gel column purification, and hydrolyzation in dilute base solution to form the desired products .The syntheses, step by step, were smooth with high quality products and good yields.

The cmc values of the trimeric anionic surfactants  $3C_nTE3CNa$  (n = 7, 10, 12) are much lower than those of the corresposting monomeric anionic surfactants, sodium dodecanoate and sodium decanoate. Their cmc values are only 1.5-3.0 wt% of those of the latter's, or about two orders of magnitude lower than those of the corresponding monomeric surfactants on a molar basis, indicating that the prepared trimeric anionic surfactants are much more effective in lowering the free energy of the air–water interface than the corresponding monomeric surfactants. All three trimeric anionic surfactants showed high foaming ability, which increases with increasing hydrocarbon chain length at the same concentration level.

**Acknowledgments** The authors gratefully acknowledge the financial support from the fund for supporting the Specially Appointed Professor from the Qiqihar University.

# References

- Menger FM, Littau CA (1991) Gemini surfactants: synthesis and properties. J Am Chem Soc 113(4):1451–1452
- Zana R (2002) Dimeric and oligomeric surfactants. Behavior at interfaces and in aqueous solution: a review. Adv Colloid Interface Sci 97:205–253
- Su S, Lin H, Lai Y (2012) Surface activity and cleavability of gemini surfactants featuring hydrophilic spacer groups. J Surfactants Deterg 15(6):745–750
- Rosen MJ, Tracy DJ (1998) Gemini surfactants. J Surfactants Deterg 1(4):547–554
- Rosen MJ (1993) Geminis: a new generation of surfactants. ChemTech 23(3):30–33
- Zana R, Benrraou M, Rueff R (1991) Alkanediyl-α,ωbis(dimethylalkylammonium bromide) surfactants. 1. Effect of the spacer chain length on the critical micelle concentration and micelle ionization degree. Langmuir 7(6):1072–1075

- Aiad I, Emam D, El-Deeb A, Abd-Alrahman E (2013) Novel imidazolium-based gemini surfactants: synthesis, surface properties, corrosion inhibition and biocidal activity against sulfatereducing bacteria. J Surfactants Deterg 16(6):927–935
- Grotha C, Nydéna M, Holmberga K, Kanickyb JR, Shahc DO (2004) Kinetics of the self-assembly of gemini surfactants. J Surfactants Deterg 7(3):247–255
- Kuliszewska E, Brecker L (2014) Gemini surfactants foam formation ability and foam stability depends on spacer length. J Surfactants Deterg 17(5):951–957
- Xu Q, Wang L, Xing F (2011) Synthesis and properties of dissymmetric gemini surfactants. J Surfactants Deterg 14(1):85–90
- Menger FM, Angel de Greiff AJ, Jaeger DA (1984) Synthesis and properties of three triple-armed amphiphiles. J Chem Soc 8:543–544
- Danino D, Talmon Y, Levy H, Beinert G, Zana R (1995) Branched threadlike micelles in an aqueous solution of a trimeric surfactant. Science 269:1420–1421
- Esumi K, Goino M, Koide Y (1996) Adsorption and adsolubilization by monomeric, dimeric or trimeric quaternary ammonium surfactant at silica/water interface. Part 1: adsorption phenomenon. J Colloid Interface Sci 183:539–545
- Abdul-Raouf MES (2011) Synthesis, surface-active properties, and emulsification efficiency of trimeric-type nonionic surfactants derived from tris(2-aminoethyl)amine. J Surfactants Deterg 14(2):185–193
- Yoshimuraa T, Kimurab N, Onitsukab E, Shosenjib H, Esumia K (2004) Synthesis and surface-active properties of trimeric-type anionic surfactants derived from tris(2-aminoethyl)amine. J Surfactants Deterg 7(1):67–74
- Kim T, Kida T, Nakatsuji Y, Ikeda I (1996) Preparation and properties of multiple ammonium salts quaternized by epichlorohydrin. Langmuir 12(26):6304–6308
- Esumi K, Taguma K, Koide Y (1996) Aqueous properties of multichain quaternary cationic surfactants. Langmuir 12(16): 4039–4041
- Yoshimura T, Yoshida H, Ohno A, Esumi K (2003) Physicochemical properties of quaternary ammonium bromide-type trimeric surfactants. J Colloid Interface Sci 267(1):167–172
- Liu XG, Xing X, Gao Z (2014) Synthesis and physicochemical properties of star-like cationic trimeric surfactants. Colloids Surf A Physicochem Eng Asp 457:374–381
- Yang F et al (2010) Synthesis and surface activity properties of alkylphenol polyoxyethylene nonionic trimeric surfactants. Appl Surf Sci 257:312–318
- Yoshimura T, Esumi K (2003) Physicochemical properties of ring-type trimeric surfactants from cyanuric chloride. Langmuir 19(8):3535–3538
- Alami E, Levy H, Zana R (1993) Alkanediyl-α,ω-bis(dimethylalkylammonium bromide) surfactants. 2. Structure of the lyotropic mesophases in the presence of water. Langmuir 9(4):940–944
- Alami E, Beinert G, Marie P, Zana R (1993) Alkanediyl-α,ωbis(dimethylalkylammonium bromide) surfactants. 3. Behavior at the air–water interface. Langmuir 9(6):1465–1467
- Zana R, Levy H, Papoutsi D, Beinert G (1995) Micellization of two triquaternary ammonium surfactants in aqueous solution. Langmuir 11(10):3694
- Neto V, Granet R, Mackenzie G, Krausz P (2008) Efficient synthesis of "star-like" surfactants via "click chemistry" [3+2] copper (I)-catalyzed cycloaddition. J Carbohydr Chem 27(4):231–237
- Stébé M, Istratov V, Langenfeld A, Vasnev VA, Babak VG (2003) Syntheses and properties of novel non-ionic fluorinated multichains "star-like" surfactants. J Fluor Chem 119(2): 191–205

- Yoshimura T, Kusano T, Iwase H, Shibayama M, Ogawa T, Kurata H (2012) Star-shaped trimeric quaternary ammonium bromide surfactants: adsorption and aggregation properties. Langmuir 28(25):9322–9331
- Wu C, Hou Y, Deng M, Huang X, Yu D, Xiang J, Liu Y, Li Z, Wang Y (2010) Molecular conformation-controlled vesicle/micelle transition of cationic trimeric surfactants in aqueous solution. Langmuir 26(11):7922–7927
- Harkins WD, Jordan HF (1930) A method for the determination of surface and interfacial tension from the maximum pull on a ring. J Am Chem Soc 52:1751–1772
- Hell C (1881) A new method for the bromination of organic acids. Ber Dtsch Chem Ges 14:891–893
- 31. Volhard JJ (1887) Preparation of  $\alpha$ -brominated acids. Justus Liebigs Ann Chem 242:141–163
- Zelinsky N (1887) A convenient preparation of α-bromopropionic acid ester. Ber Dtsch Chem Ges 20:2026
- 33. Amato ME, Caponetti E, Chillura Martino D, Pedone L (2003) <sup>1</sup>H and <sup>19</sup>F NMR investigation on mixed hydrocarbon–fluorocarbon micelle. J Phys Chem B 107(37):10048–10056
- Morigaki K, Dallavalle S, Walde P, Colonna S, Luisi PL (1997) Autopoietic self-reproduction of chiral fatty acid vesicles. J Am Chem Soc 119(2):292–301
- Malliaris A, Paleos CM, Dais P (1987) Effect of functionalization on aggregational and organizational characteristics of the sodium salts of *N*-dodecylsuccinamic and *N*-dodecylmaleamic acids. J Phys Chem 91:1149–1152
- 36. Shima M, Yohdoh K, Yamaguchi M, Kimura Y, Adachi S, Matsuno R (1997) Effects of medium-chain fatty acids and their acylglycerols on the transport of penicillin V across Caco-2 bioscience cell monolayers. Biotechnol Biochem 61(7):1150–1155

**Fenglan Xing** is currently a professor at Qiqihar University, Qiqihar, China. Her research interest is synthesis of surfactants and investigation of their physicochemical properties.

**Qun Xu** is a researcher at Qiqihar University, China. His research interest is synthesis of surfactants and fine chemicals.

**Xiaolong Sun** is a graduate student pursuing a master's degree at Qiqihar University, Qiqihar, China. His main research interests are synthesis and characterization of gemini surfactant molecules.

**Yuping Wang** is a graduate student pursuing a master's degree at the Qiqihar University, China. Her main research interests are synthesis and evaluation of gemini surfactants.

Liyan Wang received her Ph.D. in 2008 at Niigata University in Japan. She has worked at the Key Laboratory of Fine Chemicals of the Qiqihar University, China. She has been involved in surfactant applications and synthesis.

**Pinglang Wang** earned his Ph.D. in 1987 and is a specially appointed professor at the Qiqihar University, China. His research interest is in synthetic organic chemistry.