ORIGINAL ARTICLE



A Novel Alkyl Sulphobetaine Gemini Surfactant Based on Striazine: Synthesis and Properties

Ruixia Niu¹ · Chao Wang¹ · Zhigang Sun² · Biao Long¹ · Hua Song¹ · Weidong Ren¹ · Daqiang Wang¹ · Junyao He¹

Received: 4 August 2016/Accepted: 12 June 2017/Published online: 3 August 2017 © AOCS 2017

Abstract A series of alkyl sulphobetaine Gemini surfactants C_n -GSBS (n = 8, 10, 12, 14, 16) was synthesized, using aliphatic amine, cyanuric chloride, ethylenediamine, N.N'-dimethyl-1,3-propyldiamine and sodium 2-chloroethane sulfonate as main raw materials. The chemical structures were confirmed by FT-IR, ¹H NMR and elemental analysis. The Krafft points differ markedly with different carbon chain length, for C8-GSBS, C10-GSBS and C₁₂-GSBS are considered to be below 0 °C and C₁₄-GSBS, C16-GSBS are higher than 0 °C but lower than room temperature. Surface-active properties were studied by surface tension and electrical conductivity. Critical micelle concentrations were much lower than dodecyl sulphobetaine (BS-12) and decreased with increasing length of the carbon chain from 8 to 16, and can reach a minimum as low as 5 \times 10⁻⁵ mol L⁻¹ for C₁₆-GSBS. Effects of carbon chain length and concentration of Cn-GSBS on crude oil emulsion stability were also investigated and discussed.

Keywords Gemini surfactants · Synthesis · S-triazine · Surface activity · Emulsification

Ruixia Niu niuruixia999@sina.com

Introduction

Gemini surfactants represent a class of amphiphilic compounds consisting of two hydrophilic and two hydrophobic groups linked by a spacer [1, 2]. They have attracted considerable attention from industrial and academic research groups [3, 4], because of their unique physiochemical properties, such as 1–2 orders of magnitude lower critical micelle concentration (cmc), higher surface activity, better wetting and foaming properties, as compared with corresponding conventional monomeric surfactants [5–7].

There are also many studies focusing on the synthesis and surface properties of Gemini surfactants [8-11]. Among them, Gemini surfactants based on s-triazines are environmentally friendly, as the triazine ring is easily biodegradable. For the s-triazine derived Gemini surfactants, triazine works as a linkage of the hydrophilic, hydrophobic and spacer groups. Recently, research shows that there are remarkable differences in surface activity for different substitution patterns of the triazine nucleus [12]. However, most studies on s-triazine-derived Gemini surfactants focus on quaternary ammonium Gemini surfactants, only a few investigations concern betaine Gemini surfactants, especially sulphobetaine Gemini surfactants [13-15]. There is not enough data to establish the relationship between the structure of s-triazinederived sulphobetaine Gemini surfactants and their properties. Thus, it is very important to synthesize novel sulphobetaine Gemini surfactants with different structures and study their properties.

Here, we synthesized a novel alkyl sulphobetaine Gemini surfactants C_n -GSBS from cyanuric chloride, for whose three chlorines can react with $-NH_2$ step by step at high yield [16, 17]. The Krafft temperatures (T_k) and cmc values of C_n -GSBS were investigated. In addition, the effects of the concentration and carbon chain length of C_n -

¹ College of Chemistry and Chemical Engineering, Northeast Petroleum University, Daqing 163318, Heilongjiang, China

² Department of Applied Chemistry, College of Science, Northeast Agricultural University, No. 59 Timber Street, Harbin, China



GSBS on emulsion stability were investigated in detail. The Gemini surfactants possess a novel structure, as shown in Scheme 1.

Herein, the series of alkyl-monosubstituted trizines is defined as C_n -GSBS-I (n = 8, 10, 12, 14 or 16), where n represents the hydrocarbon chain lengths. The series of intermediates, which are obtained by substitution of ethylenediamine with two equivalent of C_n -GSBS-I, are defined as C_n -GSBS-II. The series of intermediates, which are obtained by substitution of N,N-dimethylpropane-1,3diamine from C_n -GSBS-II, are defined as C_n -GSBS-III. Correspondingly, the target surfactants obtained by quaternisation of C_n -GSBS-III using sodium 2-chloroethanesulfonate are defined as C_n -GSBS.

Experimental

Materials and Equipment

Ethylenediamine, aliphatic amine and sodium 2-chloroethanesulfonate were all purchased from TianJin DaMao Chemical Co., Ltd. and all were of analytical grade. Cyanuric chloride and N,N'-dimethyl-1,3-propyl-diamine were obtained from Aladdin and had purities of 99.0 and 99.5%, respectively. Deionized water was used in all measurements. Crude oil for emulsion studies was obtained from the Daqing Oil Field of China.

A Bruker Advance II 400 MHz NMR spectrometer (Bruker, France), a Bruker-Tensor 27 spectrometer, a Vario

EL Spectrometer (Elementer, Germany) and a Bruker Apex IV FTMS (Bruker, Switzerland) were used to identify the structures of the products. A model YYS-150 inverted biological microscope was used to measure the emulsion particle size distribution (Yiyuan Optical instrument Co., LTD, Shanghai).

Synthesis

The series of surfactants were synthesized in four steps, as shown in Scheme 1.

Synthesis of 2-Aliphaticamino-4, 6-Dichloro-1,3,5-Triazine (C_n-GSBS-I)

First, 0.1 mol of cyanuric chloride and 50 mL of acetone were added into a 250 mL three-necked, round-bottom flask equipped with a thermometer and magnetic stirrer, then 0.11 mol of aliphatic amine dissolved in acetone was added into the flask dropwise, using an ice bath and maintaining pH 7–9 by adding 10% Na₂CO₃. The process was monitored by thin layer chromatography (TLC) on silica gel plates using an eluent system ethyl acetate/petroleum ether = 1:10 (by volume). After the reaction finished, the organic phase was separated, washed by 0.5 mol/ L of HCl and deionized water, then filtered and dried. The dried filter cake was recrystallized twice from heptane to get 2-aliphaticamino-4,6-dichloro-1,3, 5-triazine $(C_n -$ GSBS-I).

Compounds	¹ H NMR (400 MHz, DMSO, δ in ppm)	$FT-IR (cm^{-1}, KBr)$	Elementary analysis (found/calculated)/%		
			С	Н	Ν
C ₁₂ -GSBS	 3.950 [NHCH₂CH₂] 1.270 [CH₃(CH₂)₉CH₂] 3.420 [NHCH₂CH₂(CH₂)₉] 3.664 [NHCH₂CH₂(CH₂)₉] 0.891 [CH₃CH₂] 	3290, 2960, 2860, 1579, 1460, 1380, 1170, 1060, 759, 719	51.13/51.22	0.08/0.08	0.19/0.20
	3.950 [NH (CH ₂) ₃ N(CH ₃) ₂] 1.270 [NH CH₂CH₂NH] 3.950 [NH (CH ₂) ₃ N(CH ₃) ₂] 1.590 [NH(CH ₂) ₃ N(CH ₃) ₂] 2.228 [NH(CH ₂) ₃ N(CH ₃) ₂]				

Table 1 The assignment of ¹H-NMR, IR spectra and EA results of C₁₂-GSBS

Synthesis of 1, 2-*N*,*N*-(2-Aliphaticamino-4-Dichloro-1,3,5-Triazine) Ethylenediamine (C_n-GSBS-II)

 C_n -GSBS-II was synthesized by mixing a solution of 0.12 mol of ethylenediamine and 50 mL of acetone solution and 0.1 mol of C_n -GSBS-I. The temperature was maintained at 45 °C and pH 8, by adding 10 wt% Na₂CO₃ aqueous solution. The process was monitored by TLC on silica gel plates and eluent system ethanol/ethyl acetate = 1:5 (by volume). When the reaction was completed, the mixture was concentrated *in vacuo*, refrigerated, precipitated and filtered. The filter cake was quick rinsed 3–4 times with acetone and water, respectively, (to remove the ethylenediamine and C_n -GSBS-I residue on the white solid). The white solid was then dried in a vacuum oven at 80 °C.

Synthesis of 1, 2-*N*,*N*-(2-Aliphaticamino-4-(*N*,*N*-Dimethyl-1,3-Propane Diamine)-1,3,5-Triazine) Ethylenediamine (C_n-GSBS-III)

C_n-GSBS-III was synthesized by mixing a solution of excess N,N-dimethyl-1,3-propylene amide (as reactant, solvent and acid-binding agent) and 0.05 mol of C_n-GSBS-II. The mixture was maintained at 105 °C for 7 h, then was cooled to room temperature. Deionized water was added until a white solid precipitated, then it was filtered. The white solid, C_n-GSBS-III, was recrystallized three times from an acetone–acetonitrile mixture ($V_{acetone}/V_{acetonitrile} = 1:6$). The purified C_n-GSBS-III was dried in a vacuum oven at 80 °C.

Synthesis of 1, 2-*N*,*N*-(2-Aliphaticamino-4-(4-Sulfoethyl-*N*,*N*-Dimethyl-1,3-Propane Diamine)-1,3,5-Triazine) Ethylenediamine (C_n-GSBS)

 C_n -GSBS was synthesized by mixing a solution of 1 mol of sodium 2-chloroethanesulfonate and 50 mL of dimethyl

sulfoxide solution with 0.05 mol of C_n -GSBS-III. The temperature was maintained at 75 °C for 5 h. When the reaction was completed, dimethyl sulfoxide was removed by reduced pressure distillation, and the residue was dissolved in ethanol to collect the final product (C_n -GSBS). Ethanol was then removed by vacuum distillation, and C_n -GSBS was recrystallized three times from an acetone–ethanol mixture ($V_{acetone}/V_{ethanol} = 6:1$). The purified C_n -GSBS was dried in a vacuum oven at 80 °C. The purity of the product was determined by two-phase titration methods; the purities of C_n -GSBS (n = 8, 10, 12, 14, 16) were 94, 98, 97, 93 and 96%, respectively.

The chemical structures and purities of C_n -GSBS were confirmed by ¹H NMR, FT-IR and EA. The series of surfactants have similar chemical structures; representative, detailed spectral data of C_{12} -GSBS are listed in Table 1.

Measurements

Determination of Krafft Temperature (T_k) , Critical Micelle Concentration (cmc), Surface Tension at the cmc (γ_{cmc}) and A_{min}

Electrical conductivity was used to determine the values of T_k and cmc of C_n -GSBS. A DDS-307 low-frequency conductivity analyzer (Shanghai Precision & Scientific Instrument Corporation) was used to measure the conductivity of the surfactant solutions, which had a constant concentration of 0.1 wt%. The value of T_k was determined from the abrupt increase in the electrical conductivity as a function of temperature [18]. The value of cmc was measured by the electrical conductivity-concentration curve at constant temperature.

The T_k measurements were performed at different temperatures, and the conductivity, K values, were measured about 10 min after the predicted temperature was reached. The T_k point corresponds to the complete clarification of the surfactant suspension and to the upper break in the conductivity plots [18]. At the T_k point, the suspension of solid C_n -GSBS clarifies and the conductivity plot of K versus the C_n -GSBS concentration C shows a break. The value of cmc can be determined from the break [19, 20]. Using a microliter syringe, a certain amount of concentrated stock surfactant aqueous solution (about ten times cmc) was added progressively to water. Then the solution was thoroughly stirred and the value of K was measured at 25 ± 0.05 °C [21].

The surface tension method was used to determine the value of cmc of C_n -GSBS. Aqueous solutions of C_n -GSBS surfactants were prepared at different concentrations from 0.000001 to 0.1 mol L⁻¹ using distilled water. The surface tensions (γ) of these solutions were measured at 25 ± 0.1 °C by a QBZY-1 automatic surface tensionmeter (Shanghai Fangrui instrument Co., Ltd., China) using the Wilhelmy plate method, according to the procedure described by Wang [22]. The accuracy of the measurements was within ±0.1 mN/m. The temperature was controlled by a thermostat waterbath. The platinum plate was always cleaned and heated to a red/orange color with a Bunsen burner before use. All the measurements were repeated three times and averaged.

The change of surface tensions along with the log of surfactant concentrations (γ -lg*C*) was plotted, and the value of cmc was determined from the break point [23].

The maximum surface excess, Γ_{max} , at the air-water interface was calculated by the Gibbs adsorption isotherm equation [1, 24]:

$$\Gamma_{\max} = \frac{-1}{2.303 n R T} \left(\frac{\mathrm{d}\gamma}{\mathrm{d} \, \mathrm{lg} \, c} \right)_T,\tag{1}$$

where the value of *n* (a constant determined by the number of species constituting the surfactant and adsorbed at the interface) is taken as 2, *R* is the gas constant (8.314 J mol⁻¹ K⁻¹), *T* is the absolute temperature (K), and $d\gamma/dlgC$ is the slope below the cmc in the surface tension plots [25].

The minimum average area occupied per surfactant molecule A_{\min} (nm²) at the air/water interface at saturated adsorption was calculated using Eq. (2), where N_A is Avogadro's number [13].

$$A_{\min} = (N_{\rm A} \Gamma_{\max})^{-1} \times 10^{14}.$$
 (2)

Emulsion Stability

Emulsion stability was investigated by mixing surfactant solution and crude oil in a graduated cylinder with a

stopper at 45 °C. Then 10 mL of surfactant aqueous solution containing 0.001 wt% of C_n -GSBS, and 2.5 wt% Na₂CO₃ and 10 mL of crude oil was poured into a 50 mL cylinder. The cylinder was inverted up and down twenty-five times successively, then rested at 45 °C. Emulsion stability was evaluated by the time required of 2.5 mL water separation from the emulsion. The experiment was repeated three times [26].

Foaming Properties Measurements

Foaming properties were determined by the Ross-Miles method at 30 °C, the foaming ability and foam stability was estimated by measuring the initial foam height H_0 and the half-life $t_{1/2}$ (the time it takes half of the initial foam to disintegrate). The inside wall of the foaming column was rinsed with water and then with sample solution, and then 50 mL sample solution was run down the inside wall of the foaming column. The removable pipet was filled with 200 mL of sample solution (1.5 g L^{-1}) and placed on a rubber stopper at the head of the foaming column. The solution was then allowed to fall from a specified distance (90 cm) into the foaming column. The foam height H_0 was measured immediately after the pipet was emptied, and the half-life was recorded. The volume of foam produced was taken as the foaming ability of the surfactant. Each experiment was repeated three times at a given surfactant solution.

Results and Discussion

Krafft Temperature (T_k)

The values of T_k of C_n -GSBS are listed in Table 2. The T_k values of C_8 -GSBS, C_{10} -GSBS and C_{12} -GSBS are considered to be below 0 °C, and the values of T_k of C_{14} -GSBS and C_{16} -GSBS are higher than 0 °C but lower than room temperature, which means C_n -GSBS has good water solubility throughout the series.

Critical Micelle Concentration (cmc)

Here, two methods were used to measure the cmc value of C_n -GSBS, the electrical conductivity and the surface tension measurements.

Figure 1 shows the variation of the electrical conductivity *K* with the C_n-GSBS (n = 8, 12, 16) concentration at 25 °C. From Fig. 1, we can see the distinguishable linear dependencies variation along with the increase of C_n-GSBS concentration, cmc values can be taken as the break points in the plots and are collected in Table 2.

Table 2 Krafft temperature and surface properties of C_n-GSBS

Surfactants	$T_{\rm k}$ (°C)	cmc ^a (mM)	cmc ^b (mM)	$\gamma_{\rm cmc}~({\rm mN/m})$	$10^{10}\Gamma_{\rm max} \ ({\rm mol/cm}^2)$	$A_{\min} (\mathrm{nm}^2)$	pC ₂₀
C ₈ -GSBS	Below 0	0.201	0.33	32.26	1.06	1.56	3.70
C ₁₀ -GSBS	Below 0	0.143	0.28	33.18	0.89	1.87	3.84
C ₁₂ -GSBS	Below 0	0.112	0.24	34.13	0.74	2.25	3.95
C14-GSBS	<3	0.097	0.18	35.67	0.44	3.79	4.01
C ₁₆ -GSBS	<15	0.051	0.12	37.55	0.65	2.54	4.29
BS-12 [8, 15]	5.5	1.800	_	36.52	_	_	_
SDS [1]	-	8.2	-	39.20	3.16	0.53	3.05

cmc^a, by surface tension method

cmc^b, by electrical conductivity method



Fig. 1 Change of specific conductivity *K* with molality of C_n -GSBS at 25 °C (the plot of C_{12} -GSBS and C_{16} -GSBS have been shifted upward by 30 and 100 for the sake of clarity)

From Fig. 1, we can see at low concentration range below cmc, the rate of change K is higher with increasing concentration, but above the cmc, the rate of change of K with increasing concentration became smaller, which is consistent with the prior study done by V. Chauhan [27]. According to Li, there may be two reasons for the slope decline of the curve: (1) the confinement of a fraction of the counterions on the micelle surface results in an effective loss of free anions or (2) the micelles can also contribute to charge transport to a lesser extent than the free ions owing to their lower mobility [28].

The variation of surface tension (γ) versus logarithm of surfactant concentration (lg*C*) is plotted in Fig. 2, the values of cmc are taken as the break points of the γ -lg*C* curves.

All obtained T_k , cmc, γ_{cmc} and minimum surface area (A_{min}) of C_n -GSBS are described in Table 2, sodium dodecyl sulfate (SDS) [1].

These results indicate that the values of cmc of Gemini surfactants C_8 -GSBS to C_{16} -GSBS are about one or two orders of magnitude lower than single stranded



Fig. 2 Change of surface tension with the logarithm of C_n -GSBS concentration for at 298 K

sulphobetaine (BS-12). The values of cmc measured by electrical conductivity measurements are all bigger than those obtained by surface tension method; similar results have been observed in the literature on Gemini surfactants [21]. The value of cmc of a conventional ionic surfactant is known to decrease with increasing number of carbon atoms in the hydrophobic groups up to about a hexadecyl group [10, 29]. In this work, the value of cmc of C_n -GSBS decreases from 2.01×10^{-4} to 5.1×10^{-5} mol L⁻¹ with increasing the hydrocarbon chain from 8 to 16, which is in agreement with this tendency. The critical surface tensions $(\gamma_{\rm cmc})$ of C_n-GSBS are lower than that of the monomeric surfactant BS-12. This shows that the Gemini surfactant adsorbs strongly at the air-water interface, and orients itself so as to cause effective surface activity. The increase in the hydrophobic chain length renders the Gemini surfactant slightly less surface active, probably due to a strong cohesion by the two long hydrocarbon chains.

The value of A_{\min} can explain how the surfactant molecules exist on the air-water interface, and can show their orientation and packing state. Both Γ_{\max} and A_{\min} values are listed in Table 2. When the length of the

Table 3 Emulsion stability of synthesized Gemini surfactants C_n -GSBS and BS-12

Surfactants	Emulsion stability (s)
C ₈ -GSBS	602
C ₁₀ -GSBS	615
C ₁₂ -GSBS	631
C ₁₄ -GSBS	642
C ₁₆ -GSBS	650
BS-12	480

hydrophobic chain increased from C_8 to C_{14} , the A_{min} values increased from 1.56 to 3.79 nm², and for C_{16} -GSBS the A_{min} decreased slightly. The results suggest that the alkyl sulphobetaine Gemini surfactant C_n -GSBS packs loosely at the air–water interface.

Generally, pC_{20} is used to measure the efficiency of adsorption of surfactants at the air-water interface; the larger the value of pC_{20} , the greater the tendency to adsorb at the air-water interface, relative to its tendency to form micelles, and the higher efficiency to reduce the surface tension [1, 30]. From Table 2, it is evident that the values of pC_{20} of C_n -GSBS increase when increasing the hydrocarbon chain length from 8 to 16, which is in line with expectation [31, 32]. This result suggests that the longer the hydrocarbon chains of the C_n -GSBS, the stronger the adsorption at the air-water interface.

Emulsion Stability

The measured results for crude oil emulsion stability are listed in Table 3. It was found that the emulsion stability of C_n -GSBS is better than that of BS-12, and the emulsion stability increases monotonously with the increase of hydrophobic carbon length from 8 to 16 [33, 34]. This indicates that C_n -GSBS has the ability to emulsify the remaining oil in a formulation and can be used as an oil displacement agent.

Foam Properties

The foam ability and foam stability of different surfactants (C_n -GSBS, AOS) are shown in Fig. 3.

It can be seen from Fig. 3 that the foam abilities of C_n -GSBS are lower than AOS, but the foam stabilities are much better that that of AOS. Moreover, the foam abilities of C_n -GSBS have no obvious change along with the change of the hydrophobic carbon length, but their foam stabilities increase with increasing the hydrophobic carbon length. The excellent foam stabilities of C_n -GSBS may be caused



Fig. 3 Foam ability and foam stability of C_n -GSBS surfactants compared with AOS

by the specific molecular structure. As a kind of Gemini surfactant, the GSBS series has a larger molecular crosssection, longer hydrophobic chains and a strong polar anionic sulfonic group, which will contribute to binding the water in the foam liquid membrane effectively, and thus preventing the liquid unloading of the foam liquid film.

Conclusion

A series of novel alkyl sulphobetaine Gemini surfactants derived from *s*-triazine (C_n -GSBS, n = 8, 10, 12, 14, 16) have been synthesized, and their structures were confirmed by FT-IR, ¹H NMR and elemental analysis. Compared with conventional alkylbetaine surfactant, this kind of surfactant exhibits lower T_k , lower cmc, γ_{cmc} , greater efficiency in reducing surface tension, and good crude oil emulsification ability. Foam stability in the series is strong compared to an alpha olefin sulfonate reference. The results obtained from this work would also serve as a foundation for potential applications of these compounds in the field of crude oil recovery.

References

- 1. Rosen MJ, Kunjappu JT. Surfactants and interfacial phenomena. 4th ed. Hoboken: John; 2012.
- Xu Q, Wang L, Xing F. Synthesis and properties of dissymmetric Gemini surfactants. J Surfactants Deterg. 2011;14(1):85–90.
- Murguía MC, Cristaldi MD, Porto A, Di Conza J, Grau RJ. Synthesis, surface-active properties, and antimicrobial activities of new neutral and cationic trimeric surfactants. J Surfactants Deterg. 2008;11(1):41–8.
- Zhou M, Zhao J, Hu X. Synthesis of Bis [N, N'-(alkylamideethyl) ethyl] triethylenediamine bromide surfactants and their oilfield application investigation. J Surfactants Deterg. 2012;15(3):309–15.
- 5. Dharaiya N, Patriati A, Kuperkar K, Putra EGR, Bahadur P. Spectral and scattering microstructural investigation in cationic

gemini surfactants(12-s-12) induced by p-tolulidine. Colloids Surf A. 2012;396(7):1–7.

- 6. Zana R, Xia J. Gemini surfactants: synthesis, interfacial and solution-phase behavior, and applications. New York: Marcel Dekker; 2004.
- Hujun X, Hui G, Peng K, Dandan C. Synthesis and properties of a novel liner alkylated diphenylmethane sulfonate Gemini surfactant. J Surfactants Deterg. 2013;16:57–61.
- Chen H, Zhu B. A new anionic oxalamide lauryl succinate sodium sulfonate gemini surfactant: microwave-assisted synthesis and surface activities. J Surfactants Deterg. 2014;17:937–42.
- Zhu YP, Masuyama A, Okahara M. Preparation and surface-active properties of amphipathic compounds with two sulfate groups and two lipophilic alkyl chains. J Am Oil Chem Soc. 1990;67:459–63.
- Yoshimura T, Esumi K. Synthesis and surface properties of anionic gemini surfactants with amide groups. J Colloid Interface Sci. 2004;276:231–8.
- Du X, Lu Y, Li L, Wang J, Yang Z. Synthesis and unusual properties of novel alkylbenzene sulfonate gemini surfactants. Colloids Surf A. 2007;290:132–7.
- Li X, Hu ZY, Zhao HL, Zhao SF, Cao DL. Synthesis and properties of novel alkyl sulfonate gemini surfactants. J. Surfactants Deterg. 2010;13:353–9. doi:10.1007/s11743-010-1188-5.
- Qiao W, Peng H, Zhu Y, Cai H. Synthesis and surface activity properties of symmetric double chains alkylbetaine surfactants derived from s-triazine. Colloids Surf A. 2012;405:45–50. doi:10. 1016/j.colsurfa.2012.04.034.
- Xie KL, Sun Y, Hou AQ. Diffusion properties of reactive dyes into net modified cotton cellulose with triazine derivative. J Appl Polym Sci. 2007;103:2166–71. doi:10.1002/app.25097.
- Xue Z, Hu Z, Zhu H, Chen L. Synthesis and surface activity properties of cleavable s-triazine fatty sulfonate surfactants. China Surfactant Detergent Cosmet. 2008;3:151–5.
- Petrova-Meladinova PM, Konstantinova TN. On the synthesis of some reactive triazine azo dyes containing tetramethylpiperidine fragment. Dyes Pigm. 2005;67:63–9.
- Konstantionova TN, Petrova P. On the synthesis of some bifunctional reactive triazine dyes. Dyes Pigm. 2002;52:115–20.
- Zana R, Lévy H, Danino D, Talmon Y, Kwetkat K. Mixed micellization of cetyltrimethyl ammonium bromide and an anionic dimeric (Gemini) surfactant in aqueous solution. Langmuir. 1997;13:402–8.
- Van Biesen G, Bottaro CS. Linear solvation energy relationships of anionic dimeric surfactants in micellar electrokinetic chromatography I. Effect of the length of a hydrophobic spacer. J Chromatogr A. 2007;1157:437–45.
- Van Biesen G, Bottaro CS. Liner solvation energy relationships of anionic dimeric surfactants in micellar electrokinetic chromatography II. Effect of the length of a hydrophilic spacer. J Chromatogr A. 2008;1180:171–8.
- Tai S, Gao Z, Liu X, Zhang Q. Synthesis and properties of novel alkyl sulfate Gemini surfactants. Eur J Lipid Sci Technol. 2012;114:1062–9.
- 22. Wang Q, Zhang SX, Geng B, Zhang L, Zhao J, Shi J. Synthesis and surface activities of novel monofluoroalkyl phosphate surfactants. J Surfactants Deterg. 2012;15:83–8.
- Chen L, Hu Z, Zhu H, Xue Z. Synthesis of cleavable aryl sulfonate anionic surfactants and a study of their surface activity. J Surfactants Deterg. 2008;11(2):97–102.
- Yoshimura T, Sakato A, TsuchiyaK Ohkubo T, Sakai H, Abe M, Esumi K. Adsorption and aggregation properties of amino acidbased *N*-alkyl cysteine monomeric and *N*,*N*[']-dialkyl cystine gemini surfactants. J Colloid Interface Sci. 2007;308(2):466–73.

- Chai M, Zheng Z, Bao L, Qiao W. CO₂/N₂ triggered switchable surfactants with imidazole group. J Surfactants Deterg. 2014;17(3):383–90.
- Huber K. Interactions in mixed interfaces of binary surfactant solutions. J Colloid Interface Sci. 1991;147(2):321–32.
- Chauhan V, Singh S, Bhadani A. Synthesis, characterization and surface properties of long chain β-hydroxy-γ-alkyloxy-*N*methylimidazolium surfactants. Colloids Surf A. 2012;395(395):1–9.
- Li XW, Gao YA, Liu J, et al. Aggregation behavior of a chiral long-chain ionic liquid in aqueous solution. J Colloid Interface Sci. 2010;343(1):94–101.
- MiZhou M, Zhong X, Zhao J, Wang X. Synthesis and surface active properties of 1,1,1,1-tetra-(2-oxypropyl sulfonate-3-alkylether -propoxy) neopentanes. J Surfactants Deterg. 2013;16(3):285–90.
- Li P, Chen Q, Zhao J, Wang H, Li C, Hu Z, Cao D, et al. Synthesis and properties of X-type alkyl sulfonate gemini surfactants derived from cyanuric chloride. J Surfactants Deterg. 2011;15(4):449–56.
- 31. Cui ZG. Fundamentals of surfactants, colloids, and interface chemistry. 1st ed. Beijing: Chemical Industry Press; 2013.
- 32. Rosen MJ. Surfactants and interfacial phenomena. 2nd ed. New York: Wiley; 1989.
- Fu Z, Liu M, Xu J, Wang Q, Fan Z. Stabilization of water-inoctane nano-emulsion. Part I. Stabilized by mixed surfactant systems. Fuel. 2010;89(10):2838–43.
- 34. Kang L, Xu B, Wang Y, Li Y, Shan X, An F, Liu J. Stability mechanism of W/O crude oil emulsion stabilized by polymer and surfactant. Colloids Surf A Physicochem Eng Asp. 2011;384(1–3):555–60.

Ruixia Niu received her B.Sc., M.Sc. and Ph.D. degrees from the Northeast Petroleum University in Daqing, People's Republic of China and worked at the College of Chemistry & Chemical Engineering at Northeast Petroleum University as a research chemist. She is an associate professor at the Provincial Key Laboratory, Oil & Gas Chemical Technology. She has been involved in surfactant and detergent science and technology for the past 15 years.

Chao Wang graduated from Northeast Petroleum University. He is currently involved in research on arylalkyl sulfonate surfactant applications and synthesis as a postgraduate at Northeast Petroleum University.

Zhigang Sun graduated from Northeast Petroleum University. He is currently involved in research on surfactant applications and synthesis at Department of Applied Chemistry, College of Science, Northeast Agricultural University.

Biao Long received his B.Sc. and M.Sc. degrees from Northeast Petroleum University. He is currently involved in research on surfactant applications and synthesis as a postgraduate for a doctor's degree at Northeast Petroleum University.

Hua Song received her B.Sc., M.Sc. and Ph.D. degrees from Northeast Petroleum University in Daqing, People's Republic of China and worked at the College of Chemistry & Chemical Engineering at Northeast Petroleum University as a research chemist. She is a professor at the Provincial Key Laboratory Oil & Gas Chemical Technology. Her research field is desulfurization catalyst, synthesis and applications of surfactants and polymers. **Weidong Ren** is a postgraduate from Northeast Petroleum University in China and is studying at the College of Chemistry & Chemical Engineering—his speciality is the research and application of arylalkyl sulfonate surfactant.

Daqiang Wang is a postgraduate from Northeast Petroleum University in China and is studying at the College of Chemistry & Chemical

Engineering—his speciality is the research and application of arylalkyl sulfonate surfactant.

Junyao He is a postgraduate from Northeast Petroleum University in China and is studying at the College of Chemistry & Chemical Engineering—her speciality is the research and application of arylalkyl sulfonate surfactant.