ORIGINAL ARTICLE

# Synthesis and Properties of a Novel Linear Alkylated Diphenylmethane Sulfonate Gemini Surfactant

Xu Hujun · Geng Hui · Kang Peng · Chen Dandan

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**Abstract** The linear alkylated diphenylmethane sulfonate (C<sub>12</sub>-DSDM) was synthesized by a four-step reaction with lauric acid, diphenylmethane and chlorosulfonic acid as raw materials. The structure of the final product was characterized by MS. The air–liquid surface tensions at various temperatures and salt solutions (NaCl) were measured by using the drop-volume technique and the thermodynamic parameters of the micellization were calculated. The results show that the critical micelle concentration (CMC) and  $\gamma_{CMC}$  of the surfactant are 1.452 mmol L<sup>-1</sup> and 38.49 mN m<sup>-1</sup> at 298 K. With an increase in temperature, the CMC gradually increases, the  $\gamma_{CMC}$  and the maximum surface adsorption capacity  $\Gamma_{max}$  decrease. The free energy of micelle formation is negative (-51.2 to -60.5 kJ mol<sup>-1</sup>).

**Keywords** Linear alkylated diphenylmethane sulfonate · Surface activity properties · Thermodynamic properties

# Introduction

Gemini surfactants have two hydrophobic groups and two hydrophilic groups in one molecule, and display a high surface activity. In the past decade, there have been many reports about cationic gemini surfactants but few about anionic gemini surfactants which have a better surfaceactive properties and a lower CMC [1–7]. The CMCs of anionic gemini surfactants are the same as those of cationic gemini surfactants, ten to twenty times lower than the CMCs found in the corresponding monomeric surfactants [8–10].

A new kind of anionic gemini surfactant ( $C_{12}$ -DSDM) was synthesized with diphenylmethane as raw material in four-step reaction sequence including a Friedel–Crafts acylation, a Clemmensen reduction, a sulfonation and a neutralization. Scheme 1 shows the whole process to attain the new gemini surfactant.

#### **Experimental Procedures**

#### Materials

Lauric acid of chemically pure grade was obtained from Sinopharm Chemical Reagent China, diphenylmethane of industrial grade (98 % purity) from Jintan City Fine Chemical Plant of China, and aluminium chloride, chlorosulfonic acid of chemically pure grade from Sinopharm Chemical Reagent China were used as received. Sodium chloride of analytical grade from Sinopharm Chemical Reagent China was baked at 773 K for 5 h before use. Other chemicals used were all of analytical grade.

Synthetic Procedure

Synthesis of 4,4'-di(Linear Lauroyl) Diphenylmethane(1a)

Diphenylmethane (11.53 g) and nitromethane (27.18 g) were placed in a 250-ml, three-necked, round-bottomed flask equipped with a mechanical stirrer, a dropping funnel and a condenser with a calcium chloride drying tube which was connected to a gas absorption device. The mixture was stirred with the flask sitting in an iced salt bath, and then anhydrous aluminium chloride (25.59 g) was added. After

X. Hujun  $\cdot$  G. Hui  $\cdot$  K. Peng  $\cdot$  C. Dandan ( $\boxtimes$ ) School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, People's Republic of China e-mail: rabbit19820925@hotmail.com



the catalyst was completely dissolved, lauroyl chloride (30 g) was added dropwise over about 0.5 h. Twenty minutes after the addition, the reaction proceeded at room temperature for 24 h. Then the reaction mixture was heated to 70 °C for another 6 h until no more gas was given off. The solution was decanted into iced water which contained a small amount of hydrochloric acid, and stirred until the ice melted. The product was then put it aside, washed with water and filtered several times until the pH was around 7. After that, ethanol was used to wash the product. The product was constantly stirred while being washed with ethanol, heated to slightly boiling, then cooled to room temperature, and filtered. Repeating the whole process three times was sufficient. The product was dried to constant weight with a yield of 91.1 %.

### Synthesis of 4,4'-di-Linear Alkylated Diphenylmethane(2a)

Water (69.52 ml), hydrochloric acid (3.48 ml) and mercuric chloride (9.62 g) were placed in a 500-mL, threenecked, round-bottom flask equipped with magnetic stirring device. After the mixture had completely dissolved, zinc powder (34.76 g) was added slowly. The mixture was filtered 10 min later, and then the zinc amalgam was set aside.

4,4'-Di(lauroyl) diphenylmethane (28.3 g) was placed in a 5500-mL, three-necked, round-bottom flask equipped with mechanical stirrer and a condenser. Then hydrochloric acid (96.91 g) and the previously prepared zinc amalgam were added. External heating was applied and refluxing was continued for 8 h. The upper level of the mixture was 4,4'-di-linear alkylated diphenylmethane, and the zinc amalgam was at the lower level. The product was dried and purified by silica gel chromatography. The fixed phase was 200–300 eye silica gel, and the eluting agent was a mixture of benzene and ethyl acetate with a volume ratio of 180:1. The drops were collected in a beaker, the eluting agent was dried out, and the pure product was obtained. The structure was confirmed by <sup>1</sup>H-NMR spectroscopy. <sup>1</sup>H NMR (Bruker Avance 500 400 MHz CDCl<sub>3</sub>, TMS) for 4,4'-di-linear alkylated diphenylmethane:  $\delta$ : 0.88 [t, 6H, 2<u>CH<sub>3</sub>CH<sub>2</sub></u>],  $\delta$ : 1.57 [dd, 4H, 2CH<sub>3</sub><u>CH<sub>2</sub></u>(CH<sub>2</sub>)<sub>9</sub>CH<sub>2</sub>],  $\delta$ : 1.28 [br, 36H, 2CH<sub>3</sub>CH<sub>2</sub>(<u>CH<sub>2</sub></u>)<sub>9</sub>CH<sub>2</sub>],  $\delta$ : 2.56 [t, 4H, 2Ph<u>CH<sub>2</sub></u>],  $\delta$ : 7.08 [m, 8H, at benzene ring],  $\delta$ : 3.91 [s, 2H, Ph<u>CH<sub>2</sub></u>].

# Synthesis of $C_{12}$ -DSDM(3a)

4,4'-Di-linear alkylated diphenylmethane (20 g) and chloroform (50 g) were placed in a dry, 250-mL, three-necked, round-bottom flask equipped with a mechanical stirrer, a dropping funnel and a condenser with a calcium chloride drying tube which was connected to a gas absorption device. Chlorosulfonic acid (11.55 g) was added dropwise, and after that the reaction proceeded at room temperature for 6 h. The product yield was 90 %. Adequate 15 % sodium hydroxide was added until the pH was 9–10. The chloroform and water were extracted in a rotary evaporator, and the product was dried to constant weight.

The mass spectrum (Fig. 1) shows a molecular ion peak at m/z 685.4 (C<sub>37</sub>H<sub>58</sub>S<sub>2</sub>O<sub>6</sub>Na). The other salient peaks are indicated in Scheme 2.

## Measurements of Surface Tension

The surface tension at various temperatures and salt concentration can be measured by using the drop-volume technique. The surface adsorption  $\Gamma_{\text{max}}$  and the minimum area of each molecule  $A_{\text{min}}$  can be calculated using the following equations. [11–12]

$$\Gamma_{\text{Max}} = \frac{-1}{2.303 n R T} \left( \frac{\partial \gamma}{\partial \lg c_{\text{Max}}} \right)_T \tag{1}$$

$$A_{\rm Min} = \left(N_A \Gamma_{\rm Max}\right)^{-1} \times 10^{14} \tag{2}$$

where  $\gamma$  is the surface tension in mN/, *c* is the concentration of C<sub>12</sub>-DSDM in mol/L. *T* is the thermodynamic



 $m/e708(M_0^+)$ ;685.4(M-Na);597( $M-C_8H_{17}$ );589.4(685.4 $-C_9H_{19}$ ) 331.2(346.2 $-CH_3$ );261.1(331.2 $-C_5H_{10}$ )

temperature in K, *R* the gas constant 8.31 J mol<sup>-1</sup> K<sup>-1</sup>,  $N_A$  is the Avogadro number.

# Thermodynamic Parameters of Micellization of $C_{12}$ -DSDM in Aqueous Solutions

The thermodynamic parameters of micellization can be calculated by the following equations. [13-16]

$$\Delta G_m^0 \approx RT\{(1 + (i/j)K_0) \ln CMC + (i/j)K_0 \ln(i/j)\}$$
(3)

For gemini surfactants i/j = 2 in the presence of excess electrolytes,  $K_0 = 1$ 

$$\Delta H_m^0 = -T^2 \partial \frac{\left(\Delta G_m^0/T\right)}{\partial T} = -3RT^2 \frac{\partial \ln CMC}{\partial T}$$
(4)

$$\Delta S_m^0 = \frac{1}{T} \left( \Delta H_m^0 - \Delta G_m^0 \right) \tag{5}$$

where  $\Delta G_m^0$ ,  $\Delta H_m^0$ , and  $\Delta S_m^0$  are the free energy, enthalpy and entropy of micellization.

#### **Results and Discussion**

Surface Chemical Properties of C<sub>12</sub>-DSDM in Aqueous Solutions

The surface chemical properties of  $C_{12}$ -DSDM are listed in Table 1. As shown in Table 1, the CMC and  $\gamma_{\rm CMC}$  of  $C_{12}$ -DSDM in aqueous solution are 1.452 mmol  $L^{-1}$  and 38.49 mN m $^{-1}$  at 298 K, indicating that this new geminitype surfactant has a very high surface activity.

As shown in Table 1, under certain concentrations of sodium chloride, the CMC gradually increases with increasing temperature. The reason is that the structure formed by water molecules around the hydrophobic groups is destroyed by the increase in temperature, which is stops the formation of micelles.

At a specific temperature, the CMC gradually decreases with the increase in the concentration of sodium chloride, and the reason is the electrostatic repulsion between

c(NaCl)/ mol L <sup>-1</sup>	T/K	$CMC/mmol L^{-1}$	$\gamma_{\rm CMC}/{\rm mN}~{\rm m}^{-1}$	$\Gamma_{max}/\mu mol m^{-2}$	$A_{min}/nm^2$	C <sub>20</sub>	pC <sub>20</sub>
0	298.0	1.452	38.49	1.86	0.89	6.1385	3.21
	303.0	2.363	38.36	1.86	0.89	6.1392	3.21
	308.0	3.551	38.28	1.84	0.90	6.1543	3.21
	313.0	3.972	38.20	1.84	0.90	6.2631	3.20
0.10	298.0	0.635	36.68	1.86	0.89	7.1326	3.15
	303.0	0.659	36.54	1.86	0.89	7.1485	3.15
	308.0	0.681	36.21	1.77	0.94	7.2145	3.14
	313.0	0.701	36.14	1.77	0.94	7.3267	3.14
0.20	298.0	0.215	36.19	1.77	0.94	7.1248	3.15
	303.0	0.232	35.68	1.74	0.95	7.2261	3.14
	308.0	0.251	35.63	1.71	0.97	7.2418	3.14
	313.0	0.261	35.59	1.63	1.02	7.3109	3.14

 Table 1 Surface chemical properties of C<sub>12</sub>-DSDM

**Table 2**  $\Delta G_m^0$ ,  $\Delta H_m^0$ ,  $\Delta S_m^0$  and  $T\Delta S_m^0$  of micellization of C<sub>12</sub>-DSDM surfactants in aqueous solutions

c(NaCl)/ mol L <sup>-1</sup>	T/K	$CMC/mol L^{-1}$	$\Delta G_m^0$ kJ mol <sup>-1</sup>	$\Delta H_m^0$ kJ mol <sup>-1</sup>	$\Delta S_m^0 \text{ kJ mol}^{-1} \text{ K}^{-1}$	$-T\Delta S_m^0$ kJ mol <sup>-1</sup>
0.10	298.0	$0.635 \times 10^{-3}$	-51.28	-16.24	0.1176	-35.04
	303.0	$0.659 \times 10^{-3}$	-51.86	-15.52	0.1199	-36.33
	308.0	$0.681 \times 10^{-3}$	-52.47	-14.98	0.1217	-37.48
	313.0	$0.701 \times 10^{-3}$	-53.09	-12.61	0.1293	-40.47
0.20	298.0	$0.215 \times 10^{-3}$	-59.33	-34.47	0.0834	-24.85
	303.0	$0.232 \times 10^{-3}$	-59.75	-36.92	0.0753	-22.82
	308.0	$0.251 \times 10^{-3}$	-60.14	-28.88	0.1014	-31.23
	313.0	$0.273 \times 10^{-3}$	-60.46	-24.23	0.1158	-36.25

surfactant ions is weakened due to the presence of large quantity of counterions, which greatly suppresses the electric double layer, and make the monolayer more compact and the micelles much easier to form.

Thermodynamic Parameters of Micellization of C<sub>12</sub>-DSDM in Aqueous Solutions

The thermodynamic parameters of micellization of  $C_{12}$ -DSDM in aqueous solutions at various temperatures are shown in Table 2. It can be seen that the values of  $\Delta G_m^0$  and  $\Delta H_m^0$  are all negative at various temperatures [8], which indicates the formation of micelles is spontaneous and exothermic [9]. The entropy of micellization ( $\Delta S_m^0$ ) which reflects the disorder of the system due to the formation of micelles is always positive, which means the C<sub>12</sub>-DSDM molecules are easy associated into the micelles. As shown in Table 2, the values of  $\Delta S_m^0$  decrease with the increase in temperature. This is probably because with the increase of temperature, the thermal motion of molecule increases, and at some level destroys the "iceberg model" formed by water molecules which surround the surfactant molecules. Then the surfactant molecules enter into the micelles and reduce the entropy. Therefore, the micelle formation of this system is a thermodynamically spontaneous process driven by the entropy.

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#### **Author Biographies**

Xu Hujun is a Ph.D. graduate at the Wuxi Institute of Light Industry and Nanjing University of Science & Technology. He has been involved in surfactant and detergent science and technology for the past 20 years.

**Geng Hui** graduated from Jiangnan University. He is currently involved in research on gemini surfactant applications and synthesis as a postgraduate at Jiangnan University.

**Kang Peng** graduated from Jiangnan University. He is currently involved in research on gemini surfactant applications and synthesis as a postgraduate at Jiangnan University.

**Chen Dandan** graduated from Jiangnan University. He is currently involved in research on gemini surfactant applications and synthesis as a postgraduate at Jiangnan University.