ORIGINAL ARTICLE

# Synthesis and Surface Active Properties of a Novel Linear Dodecyl Diphenyl Ether Sulfonate Gemini Surfactant

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Received: 13 June 2011/Accepted: 16 March 2012/Published online: 7 April 2012 © AOCS 2012

Abstract The linear dodecyl diphenyl ether sulfonate gemini surfactant ( $C_{12}$ -DLADS) has been synthesized by a new route from lauric acid according to a five-step reaction sequence consisting of acidification, Friedel-Crafts acylation, Clemmensen reduction, sulfonation and a neutralization reaction. The surfactant and intermediates were characterized by <sup>1</sup>H-NMR, HPLC/MS and elemental analysis. The properties have been studied by surface tension  $(\gamma_{CMC})$  and conductivity measurements. The thermodynamic parameters of micellization were calculated. The test results show that C12-DLADS has lower critical micelle concentration (CMC) and better capability for lowering the  $\gamma_{\rm CMC}$ . The  $\gamma_{\rm CMC}$  and CMC are 36.04 mN/m and 6.03  $\times$  $10^{-4}$  mol/L respectively at 45 °C. Moreover, with the increase in temperature, the conductivity of C12-DLADS increased, while the counterion binding  $K_0$  decreased. The thermodynamic data show that the micellization process for the surfactant C<sub>12</sub>-DLADS is entropy driven.

**Keywords** Gemini surfactant · Synthesis · Surface tension · Conductivity · Thermodynamic data

# Introduction

Gemini surfactants, which have two hydrophobic groups, two hydrophilic groups, and a rigid or flexible spacer group

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C. Dandan e-mail: rabbit19820925@hotmail.com in the molecule, are a recent family of compounds [1-3]. In the past decades, gemini surfactants have attracted considerable interest because of their unique physicochemical properties such as lower critical micelle concentration (CMC), higher efficiency in reducing surface tension and lowering the Krafft temperature than conventional monomeric surfactants [3-5]. Alkyl diphenyl ether sulfonate gemini surfactants, which have been reported elsewhere [6, 7], are one kind of gemini surfactant. Their intermediates have been obtained from diphenyl oxide and alkylate reagent via the Friedel-Crafts alkylation reaction. However, the synthetic method has many shortcomings, for example the alkylate has many isomers, i.e., it is a mixture of linear and branched chain species. These shortcomings have caused a bottleneck in the scientific research. In order to study the relationship between structure and properties of alkyl diphenyl ether sulfonate gemini surfactants, single and highly purified model compounds must be synthesized. Our new linear dodecyl diphenyl ether sulfonate gemini surfactant (C12-DLADS) has been obtained from lauric acid as the raw material in a five-step sequence of reactions, according to Scheme 1.

#### **Experimental Procedures**

#### Materials

Lauric acid, diphenyl ether and chlorosulfonic acid of chemically pure grade were obtained from Sinopharm Chemical Reagent China. Thionyl chloride, anhydrous aluminium chloride, hydrochloric acid and zinc dust of analytical grade obtained from Sinopharm Chemical Reagent China. Mercuric chloride of analytical grade obtained from Tongren Chemicals China. Scheme 1 Synthesis procedures of C12-DLADS



# Synthesis Procedure

#### Synthesis of 4,4'-Di(lauroyl) Diphenyl Ether [1]

Lauryl chloride was synthesized by reacting lauric acid and thionyl chloride under refluxing. Diphenyl ether (0.088 mol) in nitromethane (30 mL) was placed in a dried, 250-mL, three-necked, round-bottomed flask equipped with mechanical stirrer, a condenser closed with a calcium chloride drying tube and a dropping funnel. Then anhydrous aluminium chloride (0.30 mol) was added. The mixture was stirred and cooled to below room temperature by an iced salt bath.

Then the lauroyl chloride (0.22 mol) was added dropwise for 0.5 h under stirring. After this addition, external heating was applied and stirring was continued for 24 h. The reaction continued for 20 min in ice bath, 24 h at room temperature and 6 h at 70 °C successively. Then, it was dumped in ice water that contained a small amount of hydrochloric acid, stirred until the ice dissolved and laid aside overnight. A white powdery solid of 95.6 % yield was obtained by filtration, washing ordered with distilled water and ethanol until a pH of around 7, and vacuum drying.

Synthesis of 4,4'-Di(Linear Dodecyl) Diphenyl Ether [2]

4,4'-Di(lauroyl) diphenyl ether (10 g) and hydrochloric acid (30 g) were placed in a dried, 100-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, a condenser and an addition funnel. Then, the prepared zinc amalgam was quickly added, and then external heating was applied and refluxing was continued for 8 h. Moreover, the appropriate hydrochloric acid was added after 1 h interval. The resulting complex was poured into hot water (333 K), and two layers separated. The aqueous solution was extracted three times with mineral ether. The mineral ether extracts were all combined and washed successively with saturated sodium carbonate solution, deionized water, and then dried over anhydrous calcium chloride. A light yellow crude product was obtained by filtering and recovering the mineral ether. 4,4'-di(linear dodecy) diphenyl ether separated by column chromatography is a white crystalline species. The structures were confirmed by <sup>1</sup>H-NMR spectroscopy and elemental analysis. <sup>1</sup>H MNR (Bruker Avance 500 400 MHz CDCl<sub>3</sub>, TMS) for di(4,4'-linear chain dodecy) diphenyl ether:  $\delta$ : 0.862–0.879 [t, 6H, 2CH<sub>3</sub>CH<sub>2</sub>], δ: 1.256–1.300 [m, 40H, 2CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>], δ: 2.546– 2.585 [t, 4H, 2Ph $CH_2$ ],  $\delta$ : 6.893–6.914 [m, 3, 3', 5, 5'-4H at benzene ring], δ: 7.103–7.124 [m, 2, 2', 6, 6'-4H at benzene ring]. Found %: C 85.25, H 11.60. Theory%: C 85.37, H 11.46. M.p. 35.2–36.0 °C.

J Surfact Deterg (2012) 15:703-707

Synthesis of 4,4'-Di(linear dodecyl) Diphenyl Ether Disulfoacid [3]

4,4'-Di(linear dodecyl) diphenyl ether (2 g) dissolved in 15 mL of chloroform was placed in a dried, 100-mL, threenecked, round-bottomed flask equipped with a magnetic stirrer, a condenser closed with a calcium chloride drying tube and an addition funnel. Then, chlorosulfonic acid was added. After 6 h of reaction, deionized water was added. The resulting complex was poured into a separatory funnel and two layers separated. The aqueous solution was extracted three times with chloroform. The chloroform extractions were all combined and concentrated. The 4,4'-di(linear dodecyl) diphenyl ether disulfoacid separated by column chromatography is a light yellow powder. The structures were initially confirmed by elemental analysis. Found %: C 64.98, H 8.66, S 9.74. Theory%: C 64.86, H 8.71, S 9.61.

Synthesis of C<sub>12</sub>-DLADS [4]

First 3 g of the appropriate 4,4'-di(linear dodecy) diphenyl ether disulfoacid dissolved in 5 mL of water was placed in a dried, 100-mL, three-necked, round-bottomed flask equipped with a magnetic stirrer, a condenser and an addition funnel. The acids were neutralized with a sodium hydroxide solution. Then, the sample solution was dried to constant weight to attain the desired products. The surfactant was characterized by high performance liquid chromatography (HPLC) and mass spectrometry. HPLC indicated that the mass fraction of C12-DLADS is 98.2 %. ESI-MS(negative): *m*/*z* 332.18: [M-2Na]<sup>2–</sup>, 687.36: [M-Na]<sup>–</sup>.

#### Surface-Active Properties

#### Measurements of Surface Tension

The surface tension of the surfactant solutions was measured using the drop-volume technique at  $318.0 \pm 0.1$  K [8]. The surface tension of pure water was measured as being 68.8 mN/m at 318.0 K.

#### Measurements of Electric Conductivity

The electric conductivity of the surfactant solutions  $\kappa$  was measured using a DDS-11 digital conductivity meter (Shanghai Tiancheng instrument company, Shanghai, P. R.China) at 298.0  $\pm$  0.1, 308.0  $\pm$  0.1 and 318.0  $\pm$  0.1 K respectively.

#### **Results and Discussion**

Surface Tension of C12-DLADS in Aqueous Solution

In general, the critical micelle concentration (CMC) and the surface tension at CMC ( $\gamma_{CMC}$ ), which is usually taken as the minimum surface tension achievable by a surfactant, are the most important parameters to characterize the surface activity of a surfactant [9].

The surface tensions of aqueous solutions of  $C_{12}$ -DLADS was measured at 318.0 K with drop-volume technique. We can see from Fig. 1 that the surface tension of a  $C_{12}$ -DLADS solution exhibits a sharp break corresponding to the CMC at  $6.03 \times 10^{-4}$  mol/L at 318.0 K, which indicates that this new gemini-type surfactants had very high surface activity.

Electric Conductivity of C<sub>12</sub>-DLADS in Aqueous Solutions [10]

The electric conductivity  $\kappa$  of the surfactant solutions was measured at 298.0  $\pm$  0.1, 308.0  $\pm$  0.1 and 318.0  $\pm$  0.1 K respectively.

Then the conductivity was plotted versus the surfactant concentration in Fig. 2.

An anion gemini surfactant can associate into micelles according to the following equilibrium

$$n\mathbf{S}^{2-} + 2n\mathbf{X}^+ \leftrightarrow \left(\mathbf{S}_n\mathbf{X}_{2n-2p}\right)^{2p-} + 2p\mathbf{X}^+ \tag{1}$$

where  $S^{2-}$  are surfactant anions,  $X^+$  are its counter ion, *n* is aggregation number an $(S_n X_{2n-2p})^{2p-}$  is the 2n - 2p counterion, which is on the micelle surface.

Electric conductivity of the micelle surface is a = p/n. In practice, *a* is defined by using the ratio of the slope before and after the CMC.

$$a = S_2 / S_1 \tag{2}$$

where  $S_1$  is a straight slope under the CMC and  $S_2$  is a straight slope above it. Thus, the counter ion binding  $K_0 = 1 - a$ .

Table 1 indicates that with the increase in temperature, the conductivity and CMC of  $C_{12}$ -DLADS increases, while the counterion binding  $K_0$  decreases.

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

For C<sub>12</sub>-DLADS, the thermodynamic parameters of micellization, such as free energy ( $\Delta G_m^0$ ), enthalpy ( $\Delta H_m^0$ ), and



Fig. 1 Surface tension of C12-DLADS water solutions at 45 °C



Fig. 2 Plots of conductivit  $y(\kappa)$  versus surfactant concentration (c)

<b>Table 1</b> Effects of temperature (1) on critical micelle concentration
(CMC) and properties of C <sub>12</sub> -DLADS solutions

	C <sub>12</sub> -DLADS		
T (K)	298	308	318
$10^{-4}$ CMC (mol L <sup>-1</sup> )	2.899	3.179	4.986
S <sub>1</sub>	210.2	225.9	225.0
$S_2$	62.1	72.4	83.2
a	0.30	0.32	0.37
<i>K</i> <sub>0</sub>	0.70	0.68	0.63

entropy  $(\Delta S_m^0)$  can be calculated from following equation [10]:

$$\Delta G \approx \operatorname{RT}\{[1 + (i/j)K_0] \ln \operatorname{CMC} + (i/j)K_0 \ln(i/j)\}$$
(3)

for gemini surfactants, i/j = 2; in the presence of excess electrolytes,  $K_0 = 1$ . In the opposite case,  $K_0$  values are measured by the conductivity method.

$$\Delta H_{\rm m}^0 = -T^2 \partial \left( \Delta G_{\rm m}^0 / T \right) / \partial T$$
  
= -RT<sup>2</sup>(1 + 2K<sub>0</sub>) \delta \ln CMC / \delta T. (4)

In order to calculate the enthalpy, CMC value can be fitted by the following polynomials.

$$\ln \text{CMC} = a + b T + c T^2 + d T^3$$
(5)

where a, b, c, d are matched coefficient of the enthalpy that can be calculated by simultaneous equations (4) and (5).

$$\Delta H_{\rm m}^0 = -\mathrm{RT}^2 (1+2K_0)(b+2c\,T+3d\,T^2) \tag{6}$$

$$\Delta S_{\rm m}^0 = \frac{\left(\Delta H_{\rm m}^0 - \Delta G_{\rm m}^0\right)}{T}.\tag{7}$$

The thermodynamic parameters of micellization for  $C_{12}$ -DLADS, at various temperature are shown in Table 2.

As show in Table 2, the values of  $\Delta G_m^0$ , and  $\Delta H_m^0$ , are all negative at the tested temperatures, indicating that the formation of micelles is spontaneous and exothermic. The entropy of micellization  $\Delta S_m^0$  reflects the changes in disorder due to the formation of micelles. The values of  $\Delta S_m^0$ are all positive, which means the surfactant molecules are likely to spontaneously associate into micelles. The reason is that in aqueous solution, water molecules can form an ordered area called the "iceberg model" around surfactant molecules. With the formation of micelles, the "iceberg

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

T (K)	$\frac{\Delta G_{\rm m}^0}{(\rm kJ\ mol^{-1})}$	$\frac{\Delta H_{\rm m}^0}{\rm (kJ\ mol^{-1)}}$	$ \Delta S_{\rm m}^0 \ (\rm kJ\ mol^{-1}\ K^{-1}) $	$-T\Delta S_{\rm m}^0$ (kJ mol <sup>-1</sup> )
298.15	-43.26	-13.13	0.094	-28.03
308.15	-40.46	-16.49	0.078	-24.04
318.15	-39.73	-20.30	0.061	-19.41

model" around surfactant molecules collapses, and the disorder of the system is enhanced [11].

The values of  $\Delta S_m^0$  decreases with the increase of temperature. Therefore, the micelle formation process of this system is a thermodynamically spontaneous process driven by the entropy [12].

# Conclusions

We proposed a new method to synthesize a linear gemini anionic surfactant and characterized its properties, which were found to be unusual. The CMC was about one order of magnitude lower than those of conventional alkyl benzene sulfonates, and lower than similar branched chain anionic gemini surfactants [6]. Moreover, with the increase in temperature, the conductivity of the C<sub>12</sub>-DLADS solution increased, while the counterion binding  $K_0$  decreased. The thermodynamic data show that the micellization process for the surfactant C<sub>12</sub>-DLADS is entropy driven.

**Acknowledgments** We would like to thank the Jiangnan University key basic research program and the Geological and Scientific Research Institute of the Shengli Oilfield for financial support.

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