

Synthesis and Physicochemical Investigation of Long Alkylchain Betaine Zwitterionic Surfactant

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Abstract An effective and economic two-step route was developed to synthesize the long alkyl chain betaine zwitterionic surfactant directly from natural fatty acids. The optimal processing conditions for synthesizing the intermediate and final product were probed and the yields of 96.4% and 88.3% were obtained for each step, respectively. The surface active behavior of the synthesized decylbetaine surfactant was investigated using the surface tension method. The related thermodynamic parameters were calculated and discussed. The fluorescence probe technology was applied to determine the micropolarity of decylbetaine micelles.

Keywords Synthesis · Zwitterionic surfactant · Long alkyl chain betaine · Surface tension · Critical micelle concentration · Fluorescence probe

Introduction

Zwitterionic surfactants are increasingly attracting the interest of researchers both in industrial applications and within academic fields owing to their unique properties [1–5], such as excellent water solubility, insensitivity to the presence of salts and to temperature, good biodegradability, biological safety due to their mildness to the skin and eyes, high foam stability, and a synergistic effect with a wide variety of ionic and nonionic surfactants [6, 7]. Many zwitterionic surfactants have been synthesized [8] and the increasing demand for this kind of surfactant has already enabled them to achieve well above average growth. However, in comparison with other classes of surfactants, the production cost of zwitterionic surfactants is high and thus limits their more wide industrial uses. Recently the synthesis and the study on the applications and properties of zwitterionic surfactants has become a scientific topic [9–11]. Nevertheless, little attention has been paid to the economic factor of preparation of the zwitterionic surfactants.

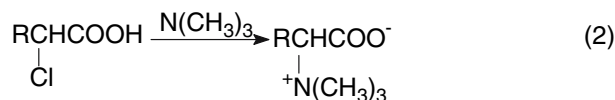
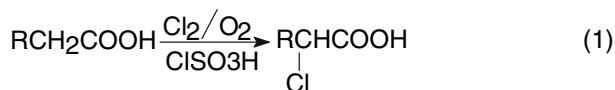
Alkylbetaines and their derivatives represent a class of zwitterionic surfactants with a positive charge on the nitrogen atom and a negative charge on the carboxyl group, which exists as electro-neutral internal salts within a wide pH range [12]. In this work, an attempt was made to prepare a long-chain alkylbetaine surfactant from natural fatty acids by an economic pathway. The synthesis involved a two-step procedure. First, carboxylic acid was selectively chlorinated at the alpha position with molecular chlorine to afford the product α -chlorocarboxylic acid. This intermediate was then reacted with trimethylamine in a hermetic reactor and the product was obtained (Scheme 1). This synthesis route is a desirable one due to the great decrease in the cost of the alkylbetaine surfactants.

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Scheme 1

The decylbetaine surfactant was prepared according to Scheme 1 in the present study. The surface active behavior of the surfactant and the micropolarity of its micelles were investigated by surface tension and fluorescence probe technology, respectively.

Experimental Procedures

Materials and Equipment Setup

Dodecanoic acid and chlorosulfuric acid were obtained commercially (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China), both were 99% pure and used as received. The fluorescence probe pyrene, 99% pure, from Sigma, was also used without further treatment. The synthesis of intermediate α -chlorododecanoic acid was carried out in a cylindrical glass reactor (RAT-5D, Shanghai Shenshun Bio-tech Co.) equipped with a stirrer. The temperature was controlled by circulating oil in the external jacket vessel. The ammonolysis reaction was performed in a 1-L reaction kettle (WHF-1, Weihai Automatically-controlled Reaction Kettle Co. Ltd., Peoples Republic of China).

Synthesis and Analysis

Preparation of α -Chlorododecanoic Acid

The intermediate α -chlorododecanoic acid was synthesized according to the pathway shown in Scheme 1(1). A weighed amount (1,000 g, 5 mol) of melted dodecanoic acid was added to the 1.5-L cylindrical glass reactor equipped with a stirrer. Chlorosulfuric acid was added dropwise with stirring and the temperature was increased gradually to a given temperature. The mixture of chlorine and oxygen in a molar ratio of 2:1 was bubbled into the liquid through a glass sinter. Oxygen acted as a radical scavenger in the reaction system. The flow rates of both gases were controlled and metered by means of rotameters. After the reaction, chlorine was removed by introducing nitrogen and the product was cooled to room temperature. The samples of the product were methylated with trifluoro

boron–methanol and then analyzed by gas chromatograph (FULI 9790, Fuli Analytical Instrument Co., Ltd) equipped with an SE54 capillary column and FID detection. The catalyst in the product was separated through extraction with water. Then the upper liquid was dried in a vacuum system for future use.

Preparation of Decylbetaine Surfactant

The intermediate α -chlorododecanoic acid (234.5 g, 1 mol) was highly dispersed in aqueous solution in a 1-L hermetic reactor which was equipped with a stirrer, cooling coil, and thermocouple temperature controller. And then three times of the amount of (calculated by molar ratio, i.e. 3 mol) trimethylammonium gas were added and the reaction continued for 8 h at 80 °C. A yield of 88.3% of decylbetaine was achieved. After the reaction, trimethylamine was driven from the solution by boiling. The residual α -chlorododecanoic acid was extracted with ethyl acetate and the salt was removed by mini electro dialysis equipment. The dried crude product was obtained by evaporation of the water. A colorless crystal was obtained by recrystallization of the crude product from acetone several times. The structure and purity of the final product was confirmed by IR (FTLA 2000-104, ABB Inc., Canada), elemental analysis (Vario EL III, Elementar Co., Germany, about 4.5 mg sample was examined each time) and ¹H NMR (Bruker ARX-300 NMR spectrometer, Switzerland, 300.13 MHz. All agents were dissolved by D₂O, using D₂O ($\delta = 4.70$ ppm) as an internal reference.).

Surface Tension Method

Surface tension (γ) was measured at constant ionic strength (0.1 M NaCl) and at 25 ± 0.02 °C by the drop volume method [13]. The measurement error for surface tension is within ± 0.1 mJ m⁻².

Steady-State Fluorescence Measurements

All the fluorescence spectra of Pyrene (Py) were measured on an RF-5301 PC spectrofluorometer (SCHIMADZU, Japan). Emission spectra of Py were obtained by exciting the samples at 335 nm. About 2 mL of the sample solution was placed in a 4-mL quartz cell, which was temperature-controlled at 30 °C. The pyrene spectrum was scanned at wavelengths from 350 to 450 nm. Intensities of the first vibronic band I_1 and the third vibronic band I_3 were taken from the emission intensities at 373 and 384 nm, respectively.

Results and Discussion

Optimizing the Reaction Conditions

The α -chlorocarboxylic acid is a potential intermediate in the fine chemical industry due to its high reactivity, which is based on the charge shift caused by the electronegative chlorine atom in the alpha position. The carbon atom attached to chlorine gets a partially positive charge and it readily reacts with a nucleophile. The synthesis of α -chlorocarboxylic acids catalyzed by strong acidic agents was developed in a previous work [14]. Nevertheless, a large amount of catalyst (mol fraction $y_{\text{ClSO}_3\text{H}} = 0.0670$) is needed to obtain high yields in a reasonable reaction time owing to the relative low activity of long alkyl chain carboxylic acid. The conditions for preparing long chain α -chlorocarboxylic acid were not yet developed for industrial practice. The present work was carried out in order to develop practical reaction conditions. Temperature, the dosage of catalyst and the ratio of the amount of oxygen to chlorine were found to be the key factors influencing the yield of α -chlorododecanoic acid. The lowest fraction of catalyst chlorosulfonic acid is $y_{\text{ClSO}_3\text{H}} = 0.0343$ to guarantee a high yield of the product. A yield of 96.4% of α -chlorododecanoic acid was obtained in 3 h under the following optimized conditions: temperature 120 °C; Cl_2 feed 40 L/h; O_2 feed 20 L/h; amount of catalyst added $y_{\text{ClSO}_3\text{H}} = 0.0343$; stirring rate 1,000 rpm (see Fig. 1).

Although α -alkylchain betaine surfactants have been successfully synthesized by α -bromo-fatty acids [15], the

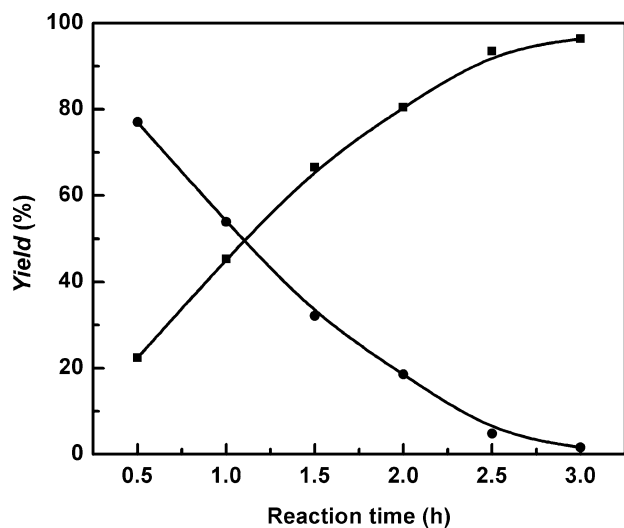


Fig. 1 Changes in the concentration of dodecanoic acid (filled circles) and α -chlorododecanoic acid (filled squares) with reaction time at optimal condition: temperature 120 °C; Cl_2 feed 40 L/h; O_2 feed 20 L/h; amount of catalyst added $y_{\text{ClSO}_3\text{H}} = 0.0343$; stirring rate 1,000 rpm

study has drawn little attention because of its high cost and low yield. In this study, a simple route of synthesizing long alkyl chain betaine surfactant is explored by the substitute reaction of α -chloro-fatty acid with trimethylamine. The synthesis of decylbetaine was carried out in a hermetic reactor to prevent the volatilization of trimethylammonia. The effects of the molar ratio of the reactants, concentration and temperature on the yield of long alkyl betaine were studied. Experimental results show that the reaction can give a good yield (ca. 88.3%) as the molar ratio of trimethylammonia to α -chlorododecanoic acid is ca. 3:1 at 80 °C for 8 h (Fig. 2).

The structural characterization and purity were studied in detail. The infrared spectrum of decylbetaine showed a carbonyl band of carboxylate at $1,640\text{ cm}^{-1}$ and a weak C–N stretching vibration bond of the quaternary ammonium salt at 960 cm^{-1} while the infrared spectrum of the reactant α -chlorododecanoic acid showed a carbonyl band of a carboxyl group at $1,726\text{ cm}^{-1}$. The derived $^1\text{H-NMR}$ spectrum was analysed and assigned as follows: 0.73 (triplet, 3H, $-\text{CH}_3$); 1.23–1.60 [multiplet, 16H, $-(\text{CH}_2)_8-$]; 1.72 [multiplet, 2H, $-\text{CH}_2-\text{CH}-\text{N}^+(\text{CH}_3)_3$]; 3.08 [single, 9H, $-\text{N}^+(\text{CH}_3)_3$]; 3.48–3.52 (multiplet, 1H, $\alpha\text{-H}-\text{CH}_2-\text{CH}-\text{N}^+(\text{CH}_3)_3$). The $\alpha\text{-H}$ chemical shift of the product is obviously different with 4.25 of the α -chloroalkyl acid [14], and the value of the chemical shift of decylbetaine is similar to that of the *N*-dodecyl betaine reported in reference [16]. Analysis results and physical properties of compounds found in this work are summarized in Table 1.

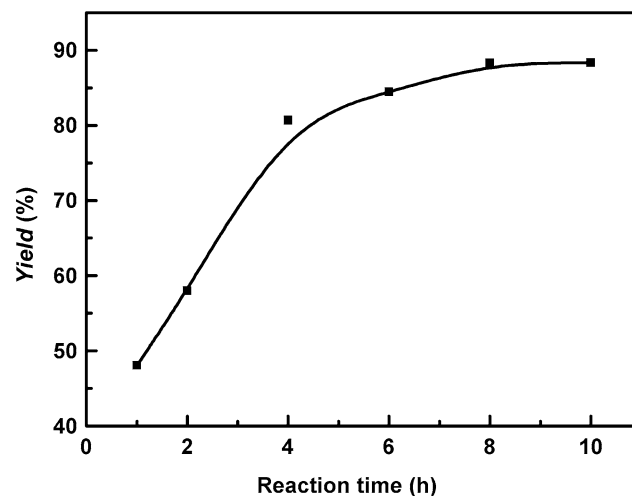


Fig. 2 Changes in the yield of decylbetaine with reaction time at optimal condition: temperature 80 °C; the molar ratio of trimethylammonia to α -chlorododecanoic acid 3:1

Table 1 The yield and physical properties for α -chlorododecanoic acid and decylbetaine surfactant

Compound	Yield (%)	$T_{KP}(^{\circ}C)$	m.p. ($^{\circ}C$)	IR $\nu_{C=O}(cm^{-1})$	1H NMR(α -H) (δ)	Anal found(calc'd)
α -Chlorododecanoic acid	96.4	–	36.5–37	1,726	4.25	–
Decylbetaine surfactant	88.3	<0	182	1,640	3.52	C:69.86(69.99) H:12.03 (12.10) N:5.22(5.44)

Surface-active Properties

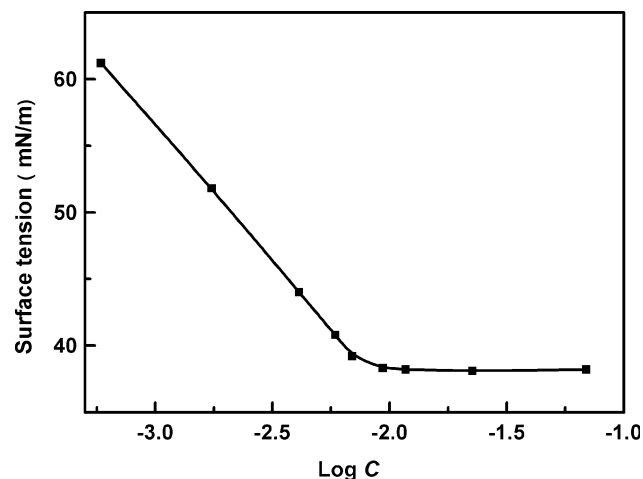
Plots of surface tension versus concentration for decylbetaine are shown in Fig. 3. From the plot we obtained the critical micelle concentration (cmc) and the minimum surface tension γ_{cmc} of decylbetaine surfactant as 8.1×10^{-3} mol/L and 38.2 mN/m, respectively.

Using cmc and γ_{cmc} , the maximum surface excess, the area per molecule and the standard free energy of micellization in aqueous solution are calculated by Gibbs adsorption equation [17]

$$\Gamma_{max} = -\frac{1}{2.303nRT} \left(\frac{d\gamma}{d \log C} \right) T \quad (1)$$

$$A_m = (\Gamma_{max} N_a)^{-1} \quad (2)$$

$$\Delta G_{mic}^{\circ} = nRT \ln(Q \cdot C_{cmc}) \quad (3)$$

**Fig. 3** Variation of surface tension with the concentration of decylbetaine surfactant

where R is the gas constant, N_a is the Avogadro constant and Q is the stoichiometric parameter for a salt. Most researchers deal with the zwitterionic surfactants as the nonionic ones [17–19] for their formally neutral structure and this was also the case in this study, that is, $n = 1$ and $Q = 1$. The results obtained are listed in Table 2, where the values of typical anionic, cationic and nonionic surfactants with the same chain length are also included in order to compare their properties with that of decylbetaine.

Table 2 shows that the minimum area per molecule of decylbetaine, A_{min} , is slightly smaller than that of $C_{10}H_{21}SO_4Na$, along with a larger surface excess adsorption amount Γ_{max} . This can be attributed to the argument that the zwitterionic surfactant with a formally net charge results in smaller intermolecular repulsions and thus a more closely packed adsorption layer at the aqueous-air interface is formed. The detected increasing order of cmc and the standard Gibbs energy of micellization ΔG_{mic}° is $C_{10}H_{21}N^+(CH_3)_3Br^- > C_{10}H_{21}SO_4^-Na^+ > C_{10}H_{21}CH N^+(CH_3)_3(COO^-) > C_{10}H_{21}O(C_2H_4)_8OH$ for the four surfactants containing equivalent hydrophobic groups. The results may be due to the intramolecular repulsive interaction between the headgroups with the same charge for ionic surfactants at the micelle interface. And thus zwitterionic and nonionic surfactants with the neutral headgroup tend to form micelles at lower concentrations than ionic surfactants accompanied by the decreasing ΔG_{mic}° .

The fluorescence probe technology is applied to investigate the micropolarity of decylbetaine surfactant micelles based on the sensitivity of the ratio I_1/I_3 of Py to its environmental polarity [22]. The results are shown in Fig. 4.

As can be seen in Fig. 4, the value of I_3/I_1 increases with the surfactant concentration and an abrupt change occurs in

Table 2 Some thermodynamic parameters for decylbetaine determined in this work and other types of surfactants with the same carbon chain at 25 $^{\circ}C$ from references [20, 21]

Surfactant	cmc mmol L $^{-1}$)	γ_{cmc} (mN m $^{-1}$)	$10^6 \Gamma_{max}$ (mol.m $^{-2}$)	$10^{20} A_{min}$ (m 2)	ΔG_{mic}° (kJ mol $^{-1}$)
$C_{10}H_{21}CH N^+(CH_3)_3(COO^-)$	6.9	38.2	3.1	53	–22.3
$C_{10}H_{21}N^+(CH_3)_3Br^-$	67	40	–	–	–13
$C_{10}H_{21}SO_4^-Na^+$	33	40	3.0	56	–17
$C_{10}H_{21}O(C_2H_4)_8OH$	1.0	–	2.3	70	–27

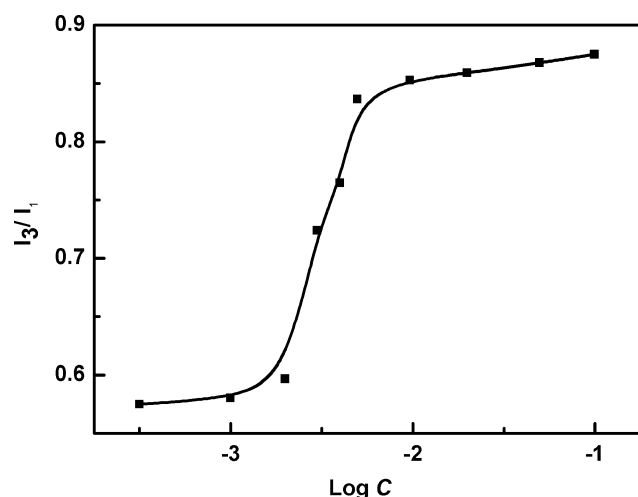


Fig. 4 Changes in the fluorescence characteristics of pyrene, I_3/I_1 as a function of decylbetaine concentration

the vicinity of cmc. Then the plateau value 0.875 is reached. This value is equivalent to the micropolarity of ethanol reported in Ref. [23], which is much larger than that of water (0.53). This indicates that although decylbetaine has good solubility in water, the micropolarity of its micelle is much smaller than in an aqueous environment.

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