



Synthesis and Characterization of Sodium N,N'-dioctyl-ethylenediamine Diacyl Propionate

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Abstract

Sodium N,N'-dioctyl-ethylenediamine diacyl propionate, an anionic gemini surfactant, was synthesized by ethylenediamine with n-octyl bromide, followed by reaction with succinic anhydride, cesium hydroxide and triethylamine as catalyst, through N-alkylation and N-acylation. Structure of the intermediate and final product was characterized by infrared spectrometer and nuclear magnetic resonance apparatus. The influences of material ratio and reaction time on the N-alkylation product yield were investigated. Experimental results showed that the yield of the N-alkylation product reached up to 64% under the optimum reaction conditions, the yield of the N-acylation product was 39%.

Keyword: Gemini surfactants, Characterization, Alkylation, Acylation

1. Introduction

Gemini surfactants, a new type of surfactant, are made up of two amphiphilic moieties connected at the level of the head groups or very close to the head groups by a spacer group [Zana R, 2002, p205-253]. Compared to traditional surfactants, gemini surfactants have many excellent performances for its special structure. Surface tension of water can be reduced effectively because of the low critical micelle concentration; and excellent synergistic effect can be performed when remixed with other surfactants [Menger F M, 2000, p1906-1920.]. At present the cationic Gemini surfactants are more reported in the literature [Yang Y., 2005, p67-77; Yu, L., 2008, p59-62.], while the anionic Gemini surfactants reported in the literature less [Skoog D A, 1992.].

Nowadays, the main problem hindering their applications in commerce is their complicated synthesis and purification processes. In this paper, the intermediate of the Gemini, N,N'-dioctyl ethylenediamine, was synthesized by

ethylenediamine with n-octyl bromide at room temperature through N-alkylation firstly. And then, an anionic gemini surfactant, Sodium N,N'-dioctyl-ethylenediamine diacyl propionate, was synthesized by the reaction of the intermediate with succinic anhydride. The influences of material ratio and reaction time on the N-alkylation product yield were investigated. The cmc and γ_{CMC} of the Gemini were measured.

2. Experimental

2.1 Materials and main instruments

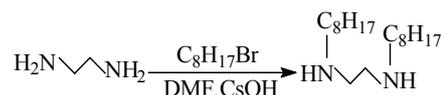
Materials: ethylenediamine, octyl bromide, MF, CsOH, NaOH, tetrahydrofuran, succinic anhydride, triethylamine.

Main instruments: rotary evaporator; fourier transform infrared spectrometer; nuclear magnetic resonance apparatus; surface tension instrument.

2.2 Synthesis method

2.2.1 Synthesis and purification of N, N'-dioctyl ethylenediamine

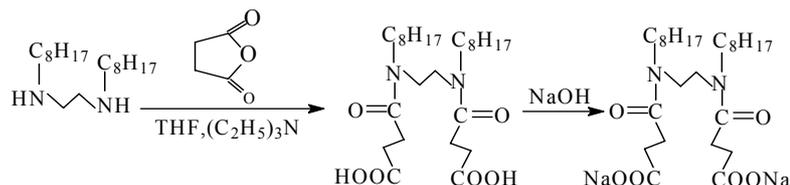
The reaction mechanism is as follows:



A certain mole ratio of ethylenediamine and n-octyl bromide was added to a certain amount of DMF containing CsOH. The mixture was stirred for several hours at room temperature. White solid was obtained after filtration. The solid was washed with NaOH aqueous solution and distilled water several times, and then dried under reduced pressure and 50°C for 5-6 hours [Salvatore R N, 2002, p674-683].

2.2.2 Synthesis and purification of Sodium N, N'-dioctyl-ethylenediamine diacyl propionate [Yoshimura T, 2005, p2682-2688].

The reaction mechanism is as follows:



A certain amount of intermediate and an excess of succinic anhydride were added to tetrahydrofuran containing triethylamine. The reaction mixture was refluxed for several hours under stirring. After being cooled to room temperature, the solution was filtered to remove insoluble materials. The filtrate was evaporated under reduced pressure, the solid was washed with ethanol and distilled water for several times, dried under reduced pressure, and then turned into sodium salt after neutralization. The yield was 39%.

3. Results and Discussion

3.1 The effect of the material ratio on the N-alkylation product yield

DMF 20ml, CsOH 0.15g, ethylenediamine 0.01mol, reaction time was 24h, The material ratio was variable factor. The experimental results were shown in Figure 1. The yield of the intermediate was increased with the increasing of n-octyl bromide. When the material ratio was more than 2.75, the yield decreased slowly. This was mainly because the intermediate transformed into tertiary amine. The optimum molar ratio was determined at 2.75.

3.2 The effect of reaction time on the N-alkylation product yield

Making the reaction time as variable factor, molar ratio 2.75:1, other reaction conditions were the same as 2.1. The results were shown in Figure 2. We can see that reaction time has great influence. The yield was increased with the prolonging of reaction time at the initial reaction stage, while reduced with the prolonging of reaction time. The reason may be as the prolonging of reaction time, the intermediate transformed into tertiary amine. The optimum reaction time was chose as 28h.

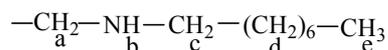
3.3 FT-IR of the intermediate and the Gemini

The FT-IR spectra of the intermediate were showed in Figure 3. The absorption peak of 3247.11 cm^{-1} was the stretching vibration of N-H. The absorption peaks of 2804.97 cm^{-1} to 2957.72 cm^{-1} were the stretching vibration of methyl and methylene groups. The peak of 752.99 cm^{-1} was the bending vibration of N-H. The absorption peaks of 1496.20 cm^{-1} and 1384.38 cm^{-1} were the symmetric and asymmetric bending vibration of methyl. The peak of 1133.08 cm^{-1} was the stretching vibration of C-N.

The FT-IR spectra of the Gemini were shown in Figure 4. It could be find out that the FT-IR spectra of final product don't had the vibration of N-H. The absorption peak of 1729.68cm^{-1} was the stretching vibration of carbonyl group.

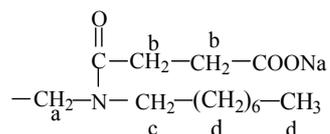
3.4 ¹H-NMR spectra of intermediate and the Gemini

¹H-NMR spectra (CDCl_3) of intermediate were shown in Figure5. The constitutional formula of intermediate was as follows:



The data were shown in Figure5. The peak of chloroform proton was at the point of 7.28. The displacements of the other protons were a (2.73 ppm), b (1.62 ppm), c (2.60 ppm), d (1.29-1.51 ppm), e (0.89 ppm), consistent with theoretical value.

¹H-NMR spectra (D_2O) of Gemini were shown in Figure 6. The constitutional formula of Gemini was as follows:



The data were shown in Figure6. The peak of D_2O proton was at the point of 4.70. The displacements of the other protons were a (3.94-4.01 ppm), b (2.44-2.46 ppm), c (3.02 ppm), d (1.03-1.12 ppm), consistent with target products.

4. Conclusions

An anionic gemini surfactant was synthesized, its surface activity was investigated. Optimum condition of N-alkylation was: DMF 20ml; ethylenediamine 0.01mol; n-octyl bromide 0.0275mol; CsOH 0.15g, reaction time was 28h. Experimental results showed that the yield of the N-alkylation product reached up to 64% under the optimum reaction condition, the yield of the N-acylation product was 39%.

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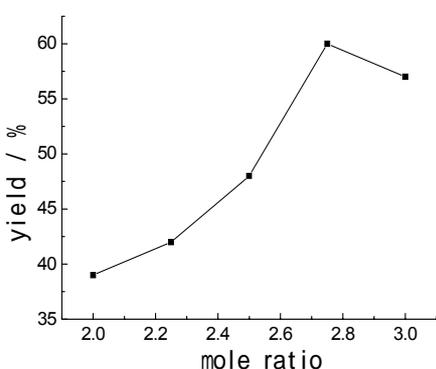


Figure 1. The effect of the material ratio on the N-alkylation product yield

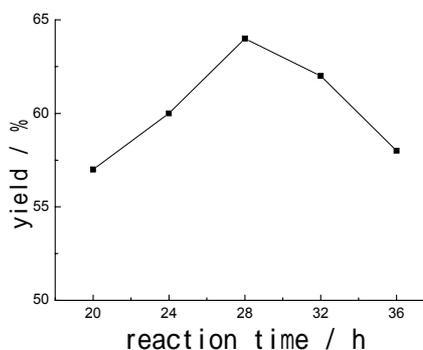


Figure 2. The effect of reaction time on the N-alkylation product yield

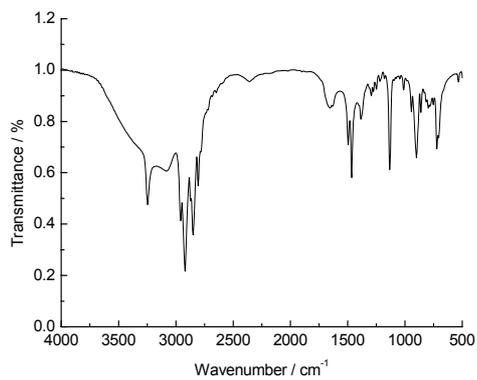


Figure 3. FT-IR spectra of the intermediate

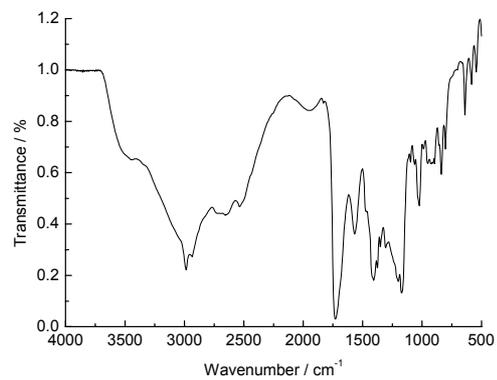


Figure 4. FT-IR spectra of the Gemini

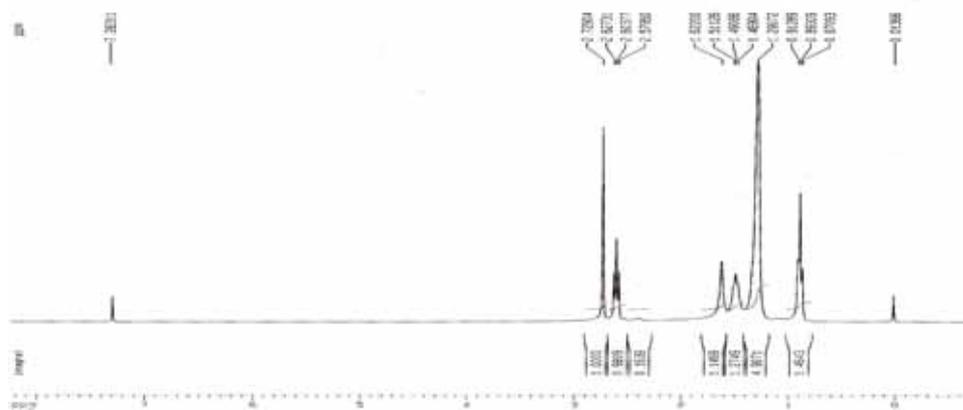


Figure 5. ¹H-NMR spectra of intermediate

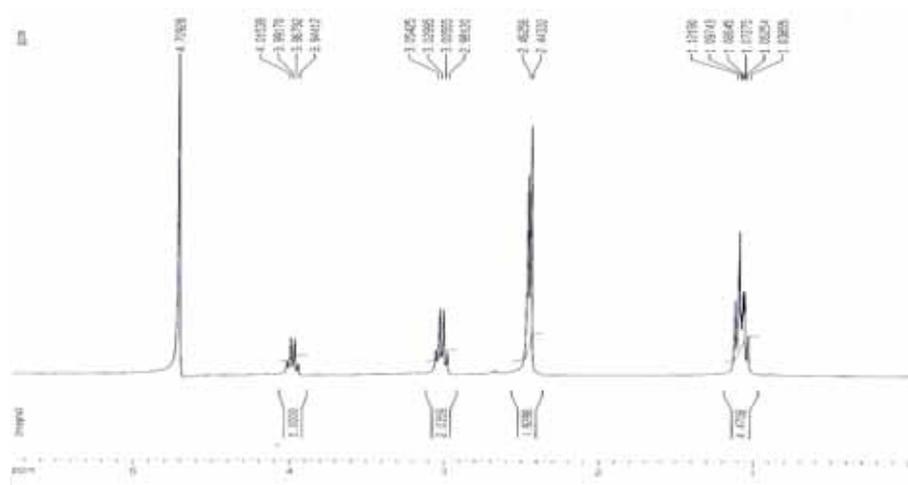


Figure 6. ¹H-NMR spectra of Gemini