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SYNTHESIS AND PROPERTIES OF A SPIN LABELED SODIUM DODECYL SULFATE

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A nitroxide spin labeled surfactant, N-oxyl-4',4'-dimethyl-oxazolidine derivative of sodium 10-oxododecyl sulfate, was synthesized from decanedioic acid. The ESR spectrum of the compound showed a typical pattern for nitroxide radical and the critical micelle concentration was 21.6 mmol/kg at 25.0 ± 0.1°C.

Recently, the dynamic properties of micellar solution have been studied by using the spin label or spin probe method. However, most of the studies have been performed with micellar solutions containing a simple nitroxide compound.[1] In order to obtain the detailed information on the dynamic properties of micelle, it is desirable to use the sample consisted of the labeled molecules only. In this study, a stable nitroxide radical was introduced into the hydrocarbon chain of sodium dodecyl sulfate (SDS) and some properties of the labeled compound were examined.

The spin labeled surfactant, N-oxyl-4',4'-dimethyloxazolidine derivative of sodium 10-oxododecyl sulfate (SL-SDS), was synthesized by the scheme as shown in Fig.1. The processes (a)-(e) were carried out by the usual ways.[2)-5)] Since the radical is unstable for reduction and sulfation, the processes (f) and (g) were accomplished as follows: 10 ml anhydrous ether solution containing 17.5 mg (0.46 mmol) of $LiAlH_4$ was cautiously added to 20 ml anhydrous ether solution of 144 mg (0.46 mmol) of N-oxyl-4',4'- dimethyloxazolidine derivative of methyl 10-oxododecanoate at -15 ~ -20°C and the mixed solution was allowed to stand for 30 min at 0°C. Then, to the solution were carefully added 5 ml of cold water and 10 ml of 5% sulfuric acid at -15 ~ -5°C. The ether extract was dried over anhydrous sodium sulfate. After removing ether, a yellow oil was eluted with hexane-ether (1:1) through a column of activated alumina. The nitroxide alcohol, N-oxyl-4',4'- dimethyloxazolidine derivative of 10-oxododecyl alcohol, was obtained in 70% yield.

Sulfur trioxide-pyridine, 55.5 mg (0.35 mmol), was portionwise added over a period of 5 - 10 min to the solution containing 100 mg (0.35 mmol) of the nitroxide alcohol, 1 ml of anhydrous dioxane and 0.02 ml of anhydrous pyridine at 20 - 25°C. Thereafter, the mixture was allowed to stand for 24 h with stirring at 30 - 40°C. The mixture was then cooled, neutralized with 10% sodium hydroxide and poured into 10 ml of cold methanol. After filtration, solvents were vaporized under reduced pressure. A paste like residue was purified by washing with ether and SL-SDS was obtained in 25% yield. It was a pale yellow solid and stable for a few months in aqueous solution at room temperature. The composition was supported by the elementary analysis.

Figure 2 shows the X-band ESR spectra of SL-SDS (0.1 mmol/kg) in water and aqueous SDS (1 mol/kg) solution. The ESR spectrum of SL-SDS in water consists of three sharp lines with a hyperfine coupling constant of 15.6 G, while that in 1 mol/kg aqueous SDS solution has three broader lines due to the restricted motion of the labeled surfactant.

From the inflection point of conductivity vs. concentration plot, the critical micelle concentration (CMC) of SL-SDS was determined as 21.6 mmol/kg at 25.0 ± 0.1°C. It lies between those of SDS (8.3 mmol/kg) and sodium decyl sulfate (33.2 mmol/kg). The results of ESR spectra and conductivities of SL-SDS indicate that the micelle is an aggregation formed by a small number of surfactant ions. The increase of CMC and the decrease of micellar aggregation number of SL-SDS compared with those of SDS may be ascribed to the decrease in the hydrophobicity of surfactant and the steric hindrance due to oxazolidine ring in the micelle formation.[6]

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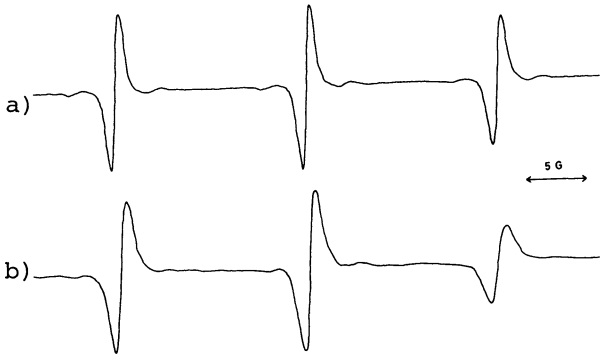

Fig.2. ESR spectra of SL-SDS (0.1 mmol/kg) at 25 ± 1°C in a) water and b) 1 mol/kg SDS solution.

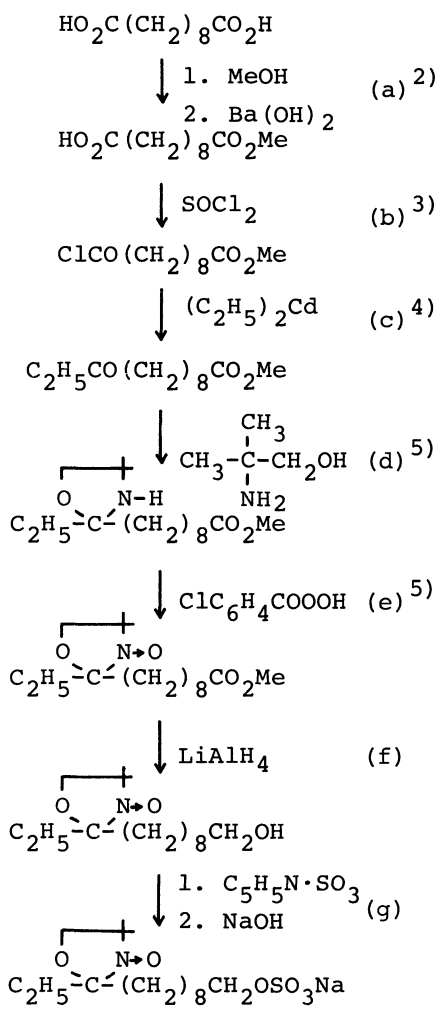

Fig.1. Overall scheme for synthesis of SL-SDS.

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