Interactions between Sodium Tetradecyl Sulfate and a Series of Homogeneous Polyoxyethyleneglycol-*n*-Dodecyl Ethers

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ABSTRACT

The surface tensions of a mixed system of sodium tetradecyl sulfate (STS) and a series of polyoxyethyleneglycol-*n*-dodecyl ethers (nED) were measured at temperatures of 30 and 40 C, respectively. When the STS concentration was fixed, the surface tension curves of the mixed system showed a flat portion in the range of which the mixed micelles would be formed. With a decrease of the added STS concentration, the length of the flat portion in these curves decreased gradually, and finally disappeared in the presence of 0.05 mM STS. Furthermore, when the concentration of STS was fixed at 1.0 mM, which is below the critical micelle concentration (CMC), the flat portion length in the surface tension curves decreased with decreasing ethylene oxide chain length in nED and with increasing temperature. The influence of increment of temperature was comparable to that for reducing the length of ethylene oxide chain in nED.

INTRODUCTION

Although properties of the mixed system of anionic and nonionic surfactants have been investigated (1-6), the nonionic surfactants used in most previous studies had a Poisson distribution of the ethylene oxide chain. This will make the surface tension measurements of the mixed system less meaningful by selective adsorption of the more hydrophobic portion.

Recently, we have reported the properties of mixed micelles between an anionic surfactant and a series of homogeneous polyoxyethyleneglycol-*n*-alkyl ethers (C_nE_m) having no distribution in the ethylene oxide chain. We found that the mixed micellar region in the bulk solution was confirmed from the appearance of a long plateau on the surface tension curve of nonionic surfactant solution in the presence of sodium dodecyl sulfate (SDS) with a fixed concentration (6.3 mM) and that the length of this plateau was dependent on the ethylene oxide and alkyl chain lengths in the nonionic surfactant molecule (7-10). However, the effect of the alkyl chain length in an anionic surfactant on the plateau region corresponding to the mixed micellar has not been reported.

In this study, the mixed micelle properties for a series of homogeneous polyoxyethyleneglycol-*n*-dodecyl ethers ($C_{12}E_n$: n = 5-8) and sodium tetradecyl sulfate (STS) will be discussed on the basis of experimental results obtained by measuring the surface tensions at 30 and 40 C, respectively.

EXPERIMENTAL PROCEDURES

Materials

Sodium tetradecyl sulfate (STS) and a series of polyoxyethyleneglycol-*n*-dodecyl ethers $C_{12}H_{25}O(CH_2CH_2O)_nH$- (nED; n = 5-8) were supplied by Nikko Chemical Co., Tokyo, Japan.

STS was washed with petroleum ether using Soxhlet extraction for 100 hr. Then, the crude product was purified by repeated recrystallization from ethanol until the minimum in the surface tension vs concentration curve disappeared.

The nonionic surfactants (nED) were highly pure as confirmed by gas liquid chromatography, thin layer chromatography, and surface tension measurements.

Water used in this study was purified by passing through a Milli-Q system (Nihon Millipore Co.) until its specific conductivity fell below $10^{-7}\Omega^{-1}cm^{-1}$.

Measurement

Surface tensions were determined by a modified Wilhelmy-type surface tension meter (Shimazu ST-1). The surface tension of solutions prepared by dilution of the mother liquor was measured at 30.0 and 40.0 ± 0.1 C. The equilibrium value was obtained by repeated measurements at 5 min intervals until it kept a constant surface tension value for 25 min.

RESULTS AND DISCUSSION

Figure 1 shows the surface tension/log C curve of STS as a function of added concentration of 8ED. The fixed concentrations of 8ED were below its critical micelle concentration (CMC) (6.3×10^{-5} M). The surface tension of each curve decreased with increasing the concentration of STS, and then reached a relatively flat portion in the curve. With further increments of the STS concentration, the surface tension began to rise to the value of the STS solution alone. The STS concentration at the lower inflection point of the flat portion in the curve was influenced by the fixed concentration of 8ED, while the higher inflection point appeared in the curve at the concentration near the CMC of STS alone.

Thus, in this diluted concentration of STS, the surface layer comprises nonionic surfactant and some vacant spaces, with no surfactants existing when the concentration of 8ED is below its CMC. Further, STS is adsorbed to this vacancy by increasing the concentration, so the surface tension decreases until the STS concentration reaches the value at the lower inflection point. At this lower inflection point, the surface layer is covered mainly with 8ED and STS molecules. This lower inflection point shifted to lower the concentration of STS with increasing the added concentration of 8ED.

The appearance of the flat portion on the surface tension curves suggests the existence of interaction between STS and 8ED. Further, it is implied that some mixed micelles will be formed in this region as reported previously (7-10). The surface tension of the mixture solution

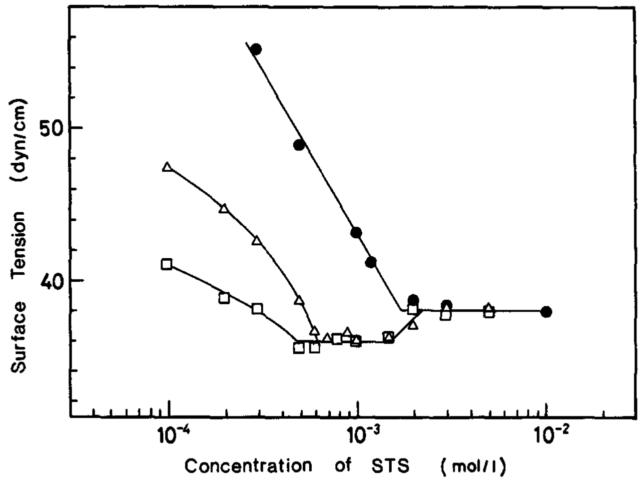

FIG. 1. The surface tension curves of sodium tetradecyl sulfate (STS) as a function of added concentration of octaethyleneglycol-*n*-dodecyl ether (8ED) at 40 C; 8ED conc, (●) 0, (△) 5 × 10^{-6} M, (□) 1 × 10^{-5} M.

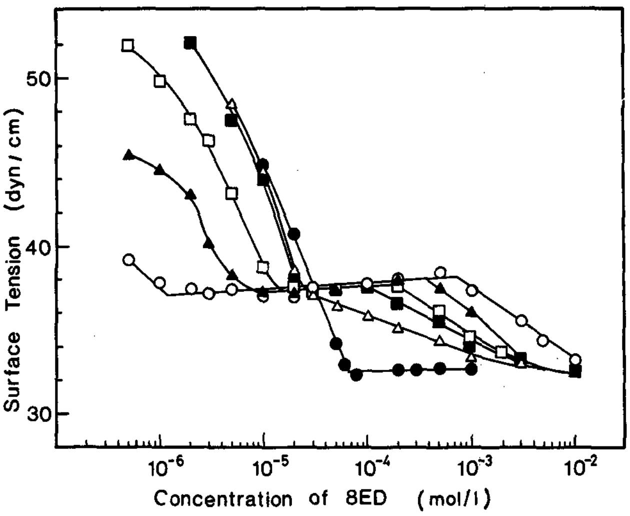

FIG. 3. The surface tension curves of 8ED in the presence of various added concentrations of STS at 40 C; STS conc, (●) 0, (△) 5 × 10^{-5} M, (■) 1 × 10^{-4} M, (□) 2 × 10^{-4} M, (▲) 5 × 10^{-4} M, (○) 1 × 10^{-3} M.

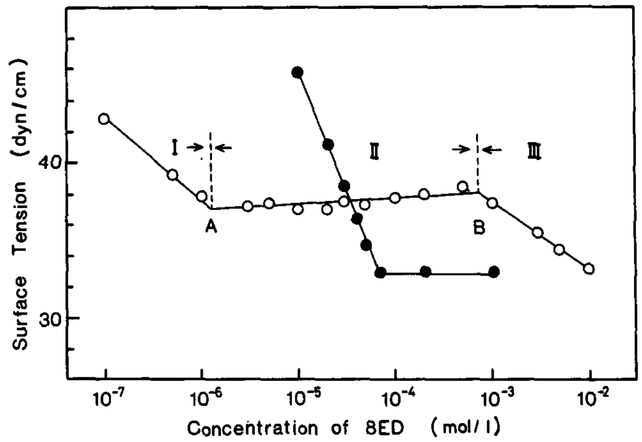

FIG. 2. The surface tension curves of 8ED in the absence (●) and in the presence of 1 × 10^{-3} M STS (○) at 40 C.

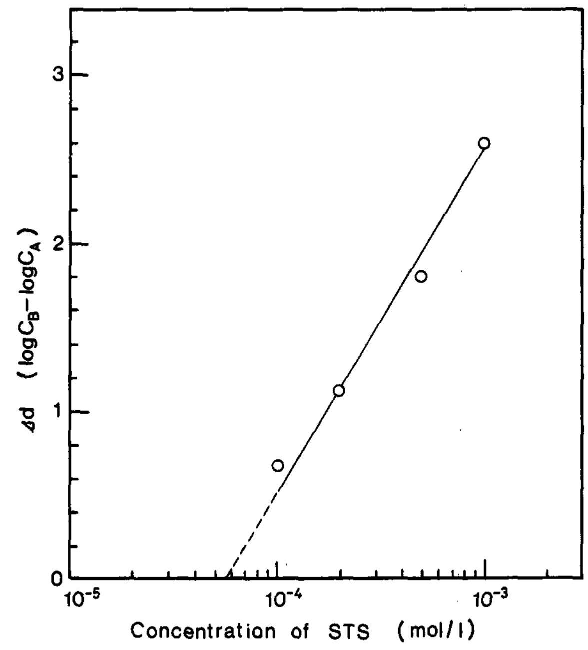

FIG. 4. The length of flat portion (log C$_B$-log C$_A$) vs the added concentration of STS at 40 C.

began to increase near the CMC of STS toward the value of a micellar solution of STS alone. This result is similar to the surface tension behavior of STS containing a certain contaminant, such as a higher alcohol. In this region, the abrupt enhancement of the STS composition occurs in mixed micelles, just like 8ED will be solubilized in STS micelles.

Figure 2 gives the surface tension/log C curve of 8ED in the absence of STS and in the presence of a particular concentration (1.0 mM) corresponding to the higher inflection point in the curve in Figure 1. This curve of 8ED in the presence of 1.0 mM STS has two inflection points at lower and higher concentrations of 8ED, and furthermore, the surface tension between the two inflection points is almost constant. This existence of the flat portion supports an idea that some mixed micelles will be formed between 8ED and STS in this region. The curve shown in Figure 2 can be divided into three parts, denoted I, II and III.

In part I, which is located at a concentration lower than inflection point A, the surface tension decreased gradually to point A by increasing the concentration of 8ED. This means that STS and 8ED adsorb on the surface layer of the mixed solution. In part II, the mixed micelles between STS and 8ED will be formed in the flat portion in the surface tension curve between the point A and the point B. Clint (1), Lange and Beck (3), Schick and Manning (11) have pointed out that the CMC of the mixed micelles is lowered more than that of the single surfactant. In this study, the concentration of 8ED at the point A corresponding to the CMC of the mixed solution was lowered, compared with the CMC of 8ED alone. In part III, the surface tension decreased gradually from the point B. In this region, the mixed micelles with excess 8ED or some single 8ED micelles are formed, which has been confirmed by the TCNQ solubilization methods (8,12,13). Moreover, Ingram (14) has shown that the surface tension/concentration curves for a mixture of ionic and nonionic surfactants can

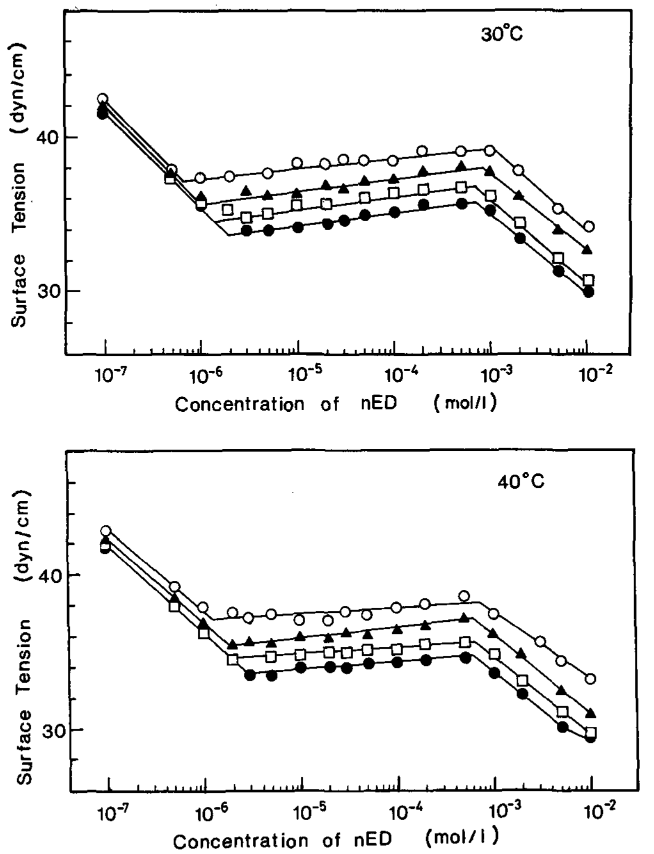

FIG. 5. The surface tension curves of a series of polyoxyethyleneglycol-*n*-dodecyl ether (nED: n = 5–8) in the presence of 1×10^{-3}M STS at 30 and 40 C; (○) 8ED, (▲) 7ED, (□) 6ED, (●) 5ED.

be predicted by using a regular solution model. The pattern seen in Figure 2 is clearly due to an approximately constant β_m (micelle interaction constant) (14).

Figure 3 shows the surface tension/log C curves of 8ED in the presence of various fixed concentrations of STS. With a decrease of added concentration of STS, the length of each flat portion decreased gradually. That is, each first inflection point shifted gradually to the higher concentration, whereas each second inflection point shifted to the lower concentration of 8ED. This shift at the first inflection point coincided with the result of Lange and Beck (3). Finally, at 5×10^{-5}M fixed concentration of STS, this flat portion disappeared in the curve. To make this result clear, the length of each flat portion is plotted against the logarithm of STS concentration shown in Figure 4. Here, the length of the flat portion is defined as the difference between the values of logarithm of concentration at two inflection points. The length of flat portion decreased linearly with reducing the fixed STS concentration. When the fixed STS concentration reaches the vicinity of 5×10^{-5}M, this flat portion length will take zero value, as shown by the dashed line. This indicates that the fixed concentration of STS required for appearance of the flat portion, i.e., the so-called critical fixed concentration, is ca. 5×10^{-5}M of STS.

Figure 5 shows the surface tension/log C curves of a series of nED with an ethylene oxide chain length from 5 to 8 in the presence of 1.0 mM STS at the temperatures of 30 and 40 C. The length of the flat portion decreased with the decrease of ethylene oxide chain length from 8 to 5 in the nonionic surfactant at both temperatures. Thus, the decrease of this flat portion means that the region where the mixed micelles of STS and nED are formed becomes narrow as the ethylene oxide chain length decreases. Furthermore, the length of each flat portion in the curve for the mixture solution with the same ethylene oxide chain length decreased with increasing the temperature from 30 to 40 C. This result provides the same effect as shortening of the ethylene oxide chain length in the nonionic surfactant molecule. A similar behavior has been observed in the system of SDS and nED (10).

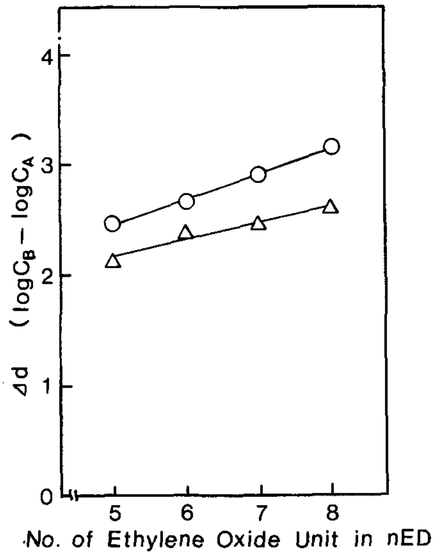

FIG. 6. The length of flat portion ($\log C_B$-$\log C_A$) vs the number of ethylene oxide unit at 30 and 40 C; (○) 30 C, (△) 40 C.

Figure 6 illustrates the difference between the values of the logarithm of the concentration corresponding to both ends of the flat portion ($\log C_B$-$\log C_A$) against the number of ethylene oxide unit in nED at temperatures of 30 and 40 C.

These curves exhibited linear relationships. The difference of the flat portion length between the two temperatures can be related to a degree of the dehydration of the ethylene oxide chain in nED; the dehydration of the ethylene oxide chain in 8ED molecule is larger than that of 5ED molecule in the mixed system.

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