· Technical

Effect of Nonionic Surfactant upon Surface Tension of Anionic Surfactant

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ABSTRACT

The surface tension of sodium dodecyl sulfate was determined in the presence of nonionic surfactant. The nonionic surfactant used was homogeneous pentaethyleneglycol-n-dodecylether which has no poisson distribution of added mole numbers of ethyleneoxide. The concentration of sodium dodecyl sulfate was changed at various fixed concentrations of homogeneous pentaethyleneglycol-n-dodecylether. Two inflection points were observed on each surface tension curve, and the surface tension maintained a constant value between the inflections, regardless of the concentrations of added homogeneous pentaethyleneglycol-n-dodecylether. However, the concentrations of sodium dodecyl sulfate at the inflections were affected at the concentrations of homogeneous pentaethyleneglycol-n-dodecylether, respectively. When the homogeneous pentaethyleneglycol-n-dodecylether concentrations were fixed below the critical micelle concentration, the concentration of sodium dodecyl sulfate at the lower inflection point decreased with increasing concentration of homogeneous pentaethyleneglycol-n-dodecylether, while that of the higher was hardly influenced. If the homogeneous pentaethyleneglycol-n-dodecylether concentrations were fixed above the critical micelle concentration, the sodium dodecyl sulfate concentrations at the two inflections both increased with an increment of homogeneous pentaethyleneglycol-n-dodecylether concentration. These results were interpreted in terms of mixed surface layer and mixed micelles consisting of sodium dodecyl sulfate and homogeneous pentaethyleneglycol-n-dodecylether. Also, the surface tension curves of homogeneous pentaethyleneglycol-n-dodecylether in the presence of sodium dodecyl sulfate, as well as those of sodium dodecyl sulfate with given concentrations of homogeneous pentaethyleneglycol-n-dodecylether, were studied.

INTRODUCTION

Several articles have been published on the properties of the mixture of an anionic surfactant and a nonionic one, and workers have interpreted their results with the aid of mixed micelle formation between the surfactants (1-6). Particularly, the effect of dodecyl-hexaethyleneglycol monoether on the micellization of sodium dodecyl sulphonate has been investigated by Corkill, et al. (4). Nevertheless, studies of surface properties of the mixture consisting of an anionic surfactant and a nonionic one have been left uninvestigated. This may be partly because of the distribution of ethyleneoxide in the nonionic surfactant used in most previous studies. Poisson distribution of chain length will make the surface studies of the mixture less meaningful by selective adsorption of the more hydrophobic portion. Recently, Lange and Beck (7) have determined the critical concentration of mixed micelle formation between anionic surfactants and homogeneous nonionic ones by surface tension measurements (7). They showed that the surfactants were mixed nonideally in the mixed micelle. Therefore, certain interactions between an anionic surfactant and a nonionic surfactant also are expected in the surface layer. We have attempted to obtain more detailed information on surface properties of the mixture by surface tension measurements, using the well defined system consisting of sodium dodecyl sulfate (SDS), homogeneous pentaethyleneglycol-n-dodecylether (5ED), and distilled water. The results will be of use in reviewing bulk properties of a mixture of an anionic surfactant and a nonionic one from a standpoint of a surface property.

EXPERIMENTAL PROCEDURES

Materials

The anionic surfactant used here was SDS synthesized according to the modified method of Dreger, et al. (8). Instead of using acetic acid as a solvent for dodecanol, chloroform was used. The crude product was purified by five recrystallizations from either ethanol or isopropanol-water mixed solutions followed by extraction with ethylether. The purity of this sample was confirmed by surface tension.

The nonionic surfactant used was 5ED supplied from Nikko Chemicals Co., Tokyo, Japan, and its purity had been tested with gas liquid chromatography (GLC), thin layer chromatography (TLC) and surface tension.

The water used in this experiment was purified by passing through an ion exchange column followed by distillation from alkaline permanganate solution.

Measurements

The surface tension was determined by a modified Wilhelmy type self-recording surface tensiometer, Shimazu ST-1. The measurements were made at 25 ± 0.2 C until the values agreed with each other within 0.1 dyne/cm for 1/2 hr, and the closely agreeing values were incorporated into our data. The time needed for attaining this steady state was usually ca. 2 hr.

RESULTS AND DISCUSSION

The surface tension-log C curves of SDS are shown in Figures 1 and 2 as a function of added concentrations of 5ED. The concentrations of nonionic surfactant are below its critical micelle concentration (cmc) (5.6×10^{-5} mole/liter) in Figure 1 and above the cmc in Figure 2. When the concentrations of 5ED were fixed below the cmc, each of the curves started from the surface tension values of pure single 5ED solutions of the same fixed concentrations, respectively (Fig. 1). Surface tensions decreased with increasing concentration of SDS and reached relatively flat portions of the curves. With further increments of the SDS

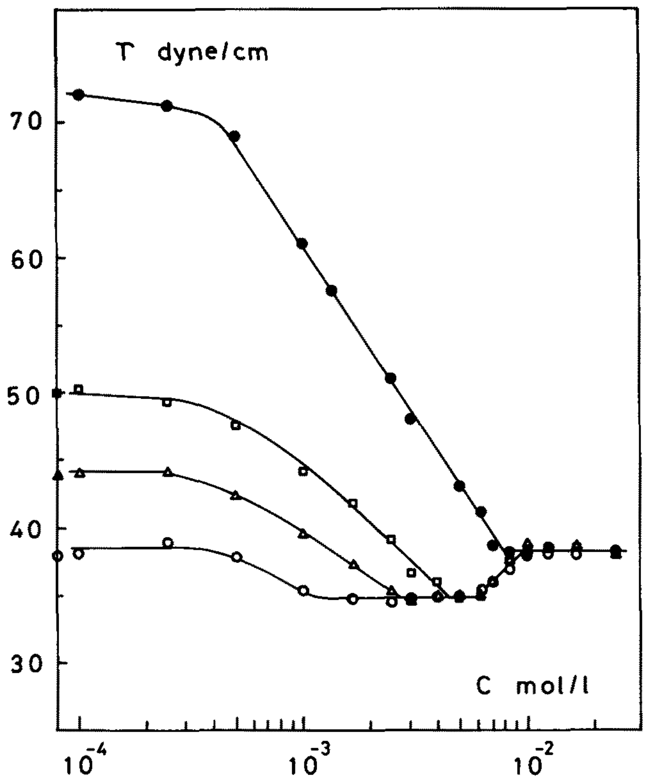

FIG. 1. The surface tension of sodium dodecyl sulfate as a function of pentaethyleneglycol-n-dodecylether (5ED) additive concentration below critical micelle concentration. The values on the vertical axis refer to the surface tension values of just 5ED in solution at the fixed concentration, respectively. Additive concentration of 5ED (mole/liter): –●–=o, –□– = 5.0 x 10^{-6}, –△– = 1.0 x 10^{-5}, and –○– = 2.0 x 10^{-5}.

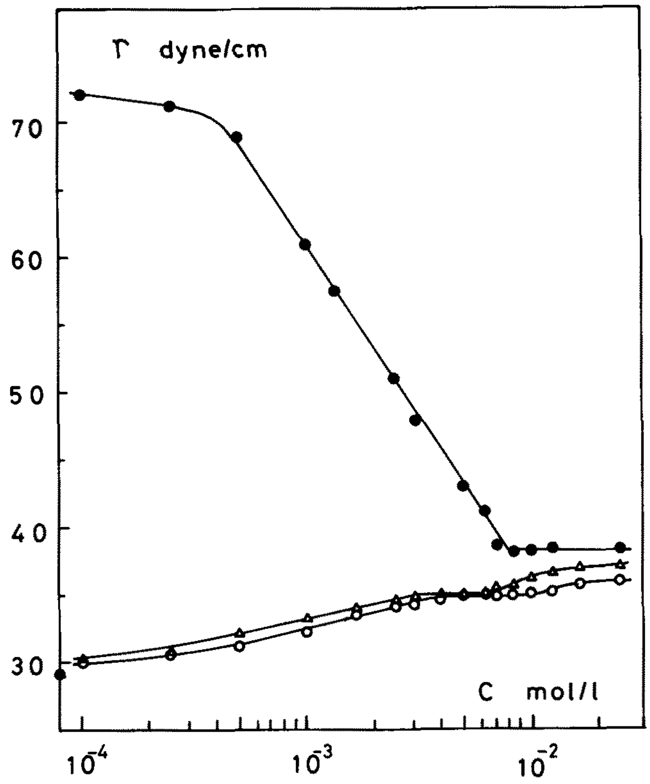

FIG. 2. The surface tension of sodium dodecyl sulfate as a function of pentaethyleneglycol-n-dodecylether (5ED) additive concentration above critical micelle concentration. The values on the vertical axis refer to the surface tension values of just 5ED in solution at the fixed concentration, respectively. Additive concentration of 5ED (mole/liter): –●– = o, –△– = 2.5 x 10^{-4}, –○– = 1.0 x 10^{-3}.

concentration passing through the flat portion, surface tensions began to rise to the value of the micellar solution of SDS alone. The SDS concentration at the lower end of this flat portion was influenced by the concentration of 5ED added, while the higher end was hardly influenced at all.

The surface tension agreement between the mixture and the unmixed 5ED solution of the same fixed concentration in the low concentration region of SDS is to be noted. This result shows that 5ED keeps its surface activity with or without existence of SDS; in other words, 5ED and SDS do not interact in sufficiently diluted solution. This fact and the decreasing trend of the surface tension in the lower concentration region of SDS lead us to presume that, when the concentration of added 5ED is fixed below its cmc, some vacant space having no surfactant has been left in the surface layer. It will be to this surface space that SDS adsorbs initially with an increment of its concentration in 5ED solution. The surface tension decrement caused in this way ceases at a certain concentration of SDS, where the surface layer is covered mostly with 5ED and SDS. The downward tendency of the curves and the migration trend of the lower inflection points with increasing concentration of 5ED both support the above presumption. The more the concentration of added 5ED increases, the larger the surface area occupied by 5ED becomes, and a lesser concentration of SDS is required to cover the vacant surface space.

Appearance of the flat portion on the surface tension curves is an interesting result. This clearly shows certain interactions between SDS and 5ED. Several authors (9-11) have reported interactions between anionic surfactants and nonionic polymers. Especially for aqueous mixtures of SDS and polyethyleneoxide, which can be regarded as a terminal member of the 5ED series, Jones (9) found a short plateau on the surface tension curve of SDS plotted as a function of additive concentration of polyethyleneoxide. This plateau was interpreted in terms of polymer-surfactant complex and their micelles. Further, some reports concerning the interaction between anionic surfactants and nonionic ones have been published (1-6). Among them, Nakagawa and Inoue (1) showed the existence of mixed micelles in aqueous solutions of SDS and polyoxyethylene lauryl ether. The appearance of the flat portion in our results also will be attributable to mixed micelle formation. However, the surface tension of the mixture begins to increase near the cmc of SDS (7.7 x 10^{-3} mole/liter) toward the value of a micellar solution of single SDS. This result is similar to the surface tension behavior of SDS containing a certain contaminant, such as dodecanol, i.e., the higher inflection point refers to the SDS concentration where abrupt enhancement of the SDS composition occurs to mixed micelles, just as 5ED is solubilized in SDS micelles at cmc. Therefore, SDS seems to be dominant in mixed micelles above the higher inflection point.

When SDS was added to 5ED solutions of certain concentrations above the cmc, the curves showed unusual behavior (Fig. 2). The surface tensions of the mixtures coincided with each other in the low concentration region of SDS. However, they were slightly higher than the surface tension of a single 5ED micellar solution, even at the lowest SDS concentration measured. This positive deviation increased with increasing concentration of SDS, leading to a plateau and then to another increment near the cmc of SDS. The plateau had almost the same surface tension as the flat portion in Figure 1, regardless of an additive amount of 5ED, while the SDS concentrations at the lower and the higher inflection points of the plateau both increased with increasing 5ED concentration.

The cloud point of the pure single 5ED solution (1.0 x

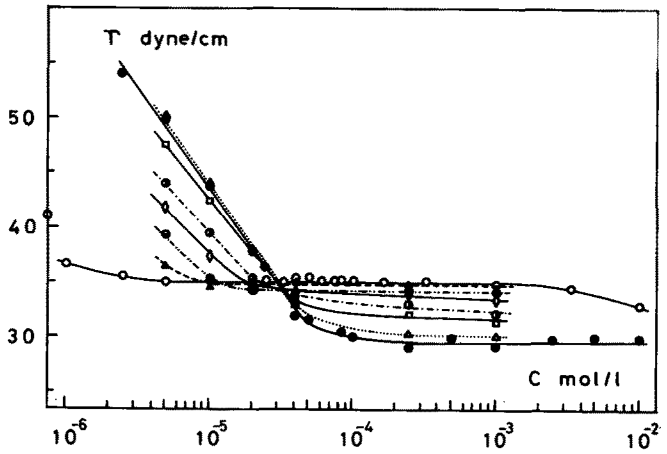

FIG. 3. The surface tension of pentaethyleneglycol-n-dodecylether as a function of sodium dodecyl sulfate (SDS) additive concentration below cirtical micelle concentration. Additive concentration of SDS (mole/liter): —●— = o, ·········△········· = 1.0 x 10^{-4}, —□— = 5.0 x 10^{-4}, —·—·—●—·—·— = 1.0 x 10^{-3}, —◇— = 1.7 x 10^{-3}, —··—··●—··— = 2.5 x 10^{-3}, ————▲———— = 3.3 x 10^{-3}, and ——○—— = 6.3 x 10^{-3}.

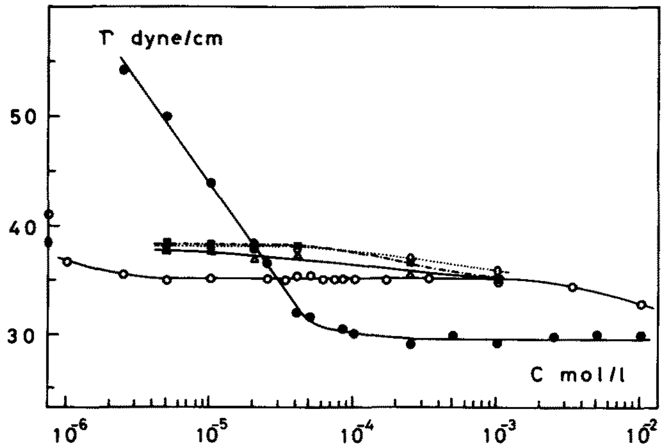

FIG. 4. The surface tension of pentaethyleneglycol-n-dodecylether as a function of sodium dodecyl sulfate (SDS) additive concentration above critical micelle concentration. Additive concentration of SDS (mole/liter): —●— = o, —○— = 6.3 x 10^{-3}, —△— = 8.3 x 10^{-3}, —□— = 1.3 x 10^{-2}, and —0— = 2.5 x 10^{-2}.

10^{-3} mole/liter) was 30.0 C; however it could not be observed in the mixture (1.0 x 10^{-3} mole/liter 5ED and 1.0 x 10^{-4} mole/liter SDS). A significant additive effect of a small amount of anionic surfactant upon cloud points of nonionic ones has been published. The elevation of cloud point was interpreted in terms of mixed micelle formation (12, 13). In the present case, the results also are due to mixed micelles formed by penetration of SDS monomers into 5ED micelle. The penetration continues to progress with increasing SDS concentration, and 5ED may lose its dominance in mixed micelles at the lower inflection point. As the mixed micelle progresses in its SDS/5ED ratio, the surface tension increases gradually. The positive deviation of the surface tension from the value of the single 5ED micellar solution indicates desorption of 5ED from the surface layer, probably accompanied by compensatory adsorption of SDS.

Between the lower and the higher inflection points, a mixed surface layer seems to be relatively stable, i.e. the surface composition change is rather moderate in this region compared with the other. Above the higher inflection point, the surface tension of the mixture approaches the value shown by the micellar solution of SDS. Therefore, the relatively stable mixed surface layer should change into an SDS dominant one at the higher inflection point.

Figures 3 and 4 show the surface tension curves of 5ED in the presence of SDS. Among them, the curves of 5ED with 6.3 x 10^{-3} mole/liter SDS and without existence of SDS were measured to confirm the reproducibility of the results shown in Figures 1 and 2. With increasing concentrations of added SDS, the surface tension decreased in the low concentration region of 5ED, while it increased in the high concentration region (Fig. 3). A knick point was observed on each surface tension curve. The concentration of 5ED at the knick, which will be regarded as the critical concentration of mixed micelle formation between 5ED and SDS, decreased with increasing concentration of SDS. This decreasing tendency of critical mixed micelle concentration coincided with the result of Lange and Beck (7). When the additive concentration of SDS was fixed between ca 3 x 10^{-3} mole/liter and 7 x 10^{-3} mole/liter, the surface tension of 5ED was buffered significantly to make a long plateau on the curve. Since this plateau has the same surface tension as that of the flat portion in Figure 1, the long plateau can be explained in terms of a relatively stable mixed surface layer and mixed micelle mentioned above.

In Figure 4, where additive concentrations of SDS are kept constant above the cmc, the surface tensions decreased gently with increasing concentration of 5ED. This decrement may be attributed to replacement of SDS monomers being adsorbed on the surface by 5ED monomers. The replacement is accompanied by a gradual change of SDS dominant mixed micelles to relatively stable mixed ones and then to 5ED dominant ones in the bulk phase.

From all the above discussion and provided that the mixed surface layer and the mixed micelles reach an equilibrium, properties of the mixture consisting of SDS and 5ED can be clasified into four regions: (A) mixed surface layer without existence of micelles, (B) 5ED dominant mixed surface layer and mixed micelle, (C) relatively stable mixed surface layer and mixed micelle, and (D) SDS dominant mixed surface layer and mixed micelle.

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[Received March 18, 1974]