NOTE

Interaction of Sodium 3-[Dodecyloxypoly(oxyethylene)]-1-propanesulfonates with an ESR Spin Probe in the Vicinity of the CMC

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Interaction of sodium 3-[dodecyloxypoly(oxyethylene)]-1-propanesulfonates (LPS's) with an ESR spin probe was investigated in the vicinity of the cmc determined by electric conductance. In contrast to sodium dodecylpoly(oxyethylene) sulfates (LES's), the aforementioned surfactants could interact with the ESR spin probe even below the cmc. This may be explained by the formation of ESR spinprobe-induced micelles.

Moreover, these characteristic features of LPS's could not be recognized in a buffer solution. Therefore, the structure of the solvated hydrophilic and hydrophobic parts of the LPS's appear essential to the formation of the ESR spinprobe-induced micelles in distilled water and to be significantly influenced by electrolytes.

1 Introduction

It is widely known that there is no appreciable aggregation of surfactant below the critical micellization concentration (cmc) and that micelle formation begins abruptly at the cmc. Although no interaction with an ESR spin probe is generally observed below the cmc, it was found that sodium 3-[dodecyloxy poly(oxyethylene)]-1-propanesulfonates (LPS's) could interact with an ESR spin probe below the cmc in a distilled water but not in a buffer solution. We will report the solution properties of LPS's, in comparison with sodium dodecylpoly(oxyethylene) sulfates (LES's).

2 Experimental

2.1 Materials

LPS was prepared from the corresponding homogeneous nonionic surfactant and propane sulfone in the presence of equimolar NaOH

Fig.-1 Synthetic route for LPS and LES.

under reduced pressure¹⁾. Nonionic surfactants were purchased from Nikko Chemicals Co. Ltd., Tokyo. These samples were confirmed as having a homogeneous poly(oxyethylene) chain length. LES was prepared by the reaction of these nonionic surfactants and SO₃-dioxane complexes. Products obtained were used after purification by repeated recrystallization from acetone solution. The number of the poly(oxyethylene) chain length is represented as the symbol "p". Fig.-1 shows schematic routes of the reaction.

2.2 Method

The cmc's were determined by the electric conductivity based on the measurement of their electrical resistance vs. concentration of each surfactant solution.

ESR spectra were recorded using a JES-1X spectrometer at 30°C. A spin probe used was 2-(14-carboxytetradecyl)-2-ethyl-4,4-dimethyl-3-oxazolidyloxyl (16 NS), which was purchased from Sigma Chemical Company. The concentration of the probe was always on the order of 10⁻⁵ M.

3 Results and Discussion

16 NS molecules in an aqueous solution give rise to three symmetric resonance lines based on a fast isotropic motion of a doxyl group.

When 16 NS molecules are dissolved in a micellar system, the line width of a peak-to-peak becomes larger than that in the aqueous phase because the tumbling motion of the doxyl group is so restricted. However, each line still remains symmetric. That is, as illustrated in **Fig.-2**, well below the cmc as in the case of (A) and well above the cmc as in the case of (B), the line shape is symmetric. [Only the higher magnetic field lines ($W=-1$) are illustrated]. However, a spectrum measured in an ESR tube having two capillaries, one containing (A) and the other (B), was not symmetric. This spectrum is evidently composed of superposed spectra of 16 NS localized at the two different levels.

When 16 NS is dissolved in 3 mM LES ($p=7$) solution, the spectrum obtained is asymmetric. The symbols h_u and h_d in **Fig.-2** are the peak heights of the left and right hand

The concentration of 16 NS was kept to be 1×10^{-5} M. Only the higher magnetic field lines ($w=-1$) are illustrated.

Fig.-2 Spectra ($w=-1$) of 16 NS in LES ($p=7$) solution.

Fig.-3 Deviation from unity in the ratio of h_u/h_d for LES.

peaks at the higher magnetic field, respectively. The ratio of h_u/h_d is 0.8. This means that 16 NS molecules are localized at two different levels; one is in micelle and the other in the aqueous phase. Hence, the lack of symmetry indicates the partitioning of 16 NS molecules between two different environments.

Fig.-3 shows the deviation of the ratio of h_u/h_d for LES's in the vicinity of each cmc. The arrow shows the cmc of each surfactant determined by electric conductance. The concentration of 16 NS is kept to be 1×10^{-5} M. The deviation of the ratio from unity is first noticed near the cmc in each case. We found that a fraction of the total 16 NS molecules population exists in the bulk phase even above the cmc, because its ratio has not returned to unity even at the cmc. This indicates that all the 16 NS molecules did not distribute themselves only in a micelle phase near above the cmc.

Fig.-4 shows that, for LPS's, the deviation from unity started far below the cmc. Especially in the case of $p=5$ and 7, this tendency is remarkable. This means the interaction between 16 NS and LPS molecule exists below the cmc determined by electric conductance. At the cmc, almost all 16 NS molecules must exist in the micelle phase because the ratio has already returned to unity. Thus, LPS, different from LES, has a characteristic feature of interacting with a third component such as 16 NS even at a low concentration of LPS. This may be attributed to the formation of 16 NS-induced micelles. Such an observation is familiar in dye-detergent systems²⁾. The tendency in interacting with 16 NS at a low concentra-

Fig.-4 Deviation from unity in the ratio of h_u/h_d for LPS.

Fig.-5 Deviation from unity in the ratio of h_u/h_d for LPS ($p=5$). An arrow shows the cmc determined by electric conductance.

Fig.-6 Effect of electrolytes on the foam volume.

Open symbols : distilled water

Closed symbols : ionic strength 0.03, pH 11

tion of LPS is remarkable compared with LES. This may be caused by its unique structure, having a hydrophobic part between a hydrophilic ethyleneoxide chain and a sulfonate group.

Furthermore, we investigated the effect of electrolytes on the interaction of 16 NS with LPS ($p=5$). **Fig.-5** shows that the deviation from unity began below the cmc in distilled water, however, in a buffer solution the deviation from unity became clear from the cmc. This indicates that the solution properties of LPS ($p=5$) is significantly influenced by adding electrolytes.

Fig.-6 shows the effect of electrolytes on the foam volume of surfactant solutions vs. time. The foam stability may reflect the molecular packing of LPS at the air-water interface. Shaking a LES or LPS solution produced a

stable foam in distilled water. On the other hand, LPS ($p=3$ and 5) formed an unstable foam in a buffer solution, although LES formed a stable foam even in a buffer solution. In the case of LPS ($p=1$), the difference in the stability of the foam was not so largely changed in distilled water or in a buffer solution.

We conclude that such characteristic features of LPS's may be a result of its unique structure mentioned above. The structure of the solvated hydrophilic and hydrophobic parts of LPS ($p=3, 5$, and 7) appears to play an important role in the formation of 16 NS-induced micelles in distilled water and to be significantly influenced by electrolytes.

(Received Sept. 13, 1986)

References

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cmc 近傍における 3-ドデシルオキシ
ポリオキシエチレン-1-プロパン
スルホン酸ナトリウムと ESR
スピンプローブとの相互作用

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電気伝導度から求めた cmc 近傍において、3-[ドデシルオキシポリ (オキシエチレン)]-1-プロパンスルホン酸ナトリウムと ESR スピンプローブの相互作用が調べられた。硫酸ドデシルポリオキシエチレン=ナトリウムとは異なって、先の界面活性剤は ESR スピンプローブと、cmc 以下の濃度で相互作用した。これは ESR スピンプローブが誘起するミセルの生成によって説明できる。

さらに、これらの特徴的性質は、緩衝液中では、認められなかった。従って、界面活性剤の溶媒和された親水、疎水部分の構造が、ESR スピンプローブによって誘起されるミセルの生成に重要な役割を果たし、またその構造は電解質によって大きく影響を受けるものと思われる。