New Amphoteric Surfactants Containing a 2-Hydroxyalkyl Group. V.

Interaction of an Amphoteric Surfactant with Sodium Dodecylbenzenesulfonate in Mixed Micelles

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The interaction mode of amphoteric surfactant, N-(2-hydroxydodecyl)-N-(2-hydroxyethyl)-β-alanine (C12-HAA) with sodium dodecylbenzenesulfonate (LAS) was studied using ultraviolet and fluorescence spectroscopy, and turbidity measurement. Anormality of fluorescence peak intensity was revealed in the higher range above the cmc, depending on the occupied ratio of the components in the binary system, whereas there was no indication of an extra increment in the increase of fluorescence intensity of the LAS component with concentration covering the lower range below the cmc of each binary system. Besides, a great enhancement of turbidity appeared particularly in the neutral region, exhibiting a sharp break at considerably higher concentration. The obvious change of molar extinction for the LAS component in the mixed system is observed in the neighborhood of the base dissociation constant (pK2) of C12-HAA. Hence, the interaction is dependent on pH value. We may conclude that the COO⁻ of C12-HAA and the SO₃⁻ of LAS must interact mutually through counterions association in the alkaline region and that a complex formation occurs between the -NH⁺ of C12-HAA and the SO₃⁻ of LAS by the Coulomb attraction in the neutral region.

1 Introduction

So far we have studied the preparation and the basic physicochemical properties of new amphoteric surfactant, N-(2-hydroxyalkyl)-N-(2-hydroxyethyl)-β-alanine (C12-HAA) with sodium dodecylbenzenesulfonate (LAS) was studied using ultraviolet and fluorescence spectroscopy, and turbidity measurement. Anormality of fluorescence peak intensity was revealed in the higher range above the cmc, depending on the occupied ratio of the components in the binary system, whereas there was no indication of an extra increment in the increase of fluorescence intensity of the LAS component with concentration covering the lower range below the cmc of each binary system. Besides, a great enhancement of turbidity appeared particularly in the neutral region, exhibiting a sharp break at considerably higher concentration. The obvious change of molar extinction for the LAS component in the mixed system is observed in the neighborhood of the base dissociation constant (pK2) of C12-HAA. Hence, the interaction is dependent on pH value. We may conclude that the COO⁻ of C12-HAA and the SO₃⁻ of LAS must interact mutually through counterions association in the alkaline region and that a complex formation occurs between the -NH⁺ of C12-HAA and the SO₃⁻ of LAS by the Coulomb attraction in the neutral region.

Synergisms and improved effects in a binary system are observed for surface tension, foaming power, detergency, dye solubilization, and other surface activities. Various binary combinations with C12-HAA and other surfactants such as anionic, cationic, and nonionic surfactants or soap have been available in practical use. A few papers, however, have hitherto been published with regard to the interaction of an amphoteric surfactants. The fundamental workings of a mixed micelle structure and photochemical function are available as a biomembrane model of energy transform mechanism as reported by Nagamura et al.

In this report, the interaction of C12-HAA with LAS in the mixed micelle solution is studied by both the measurement of ultraviolet absorption (UV) and the measurement of the fluorescence emission spectra for the phenylene group in the LAS molecule.

2 Experimental

The amphoteric surfactant C12-HAA was prepared and purified in the same manner as described in the previous paper. The anionic surfactant LAS, obtained from the Tokyo Kasei Co., Ltd. was purified according to a conventional recrystallization method. The surface tension was measured by the Wilhelmy's vertical plate method with a Shimazu ST-1 tensiometer.
The surface tension ($\gamma$) vs. concentration ($C$) plot for a single surfactant system has a sharp break point. However, the plot for the mixed system has a downward convex curve having a broad minimum. Therefore, the cmc value is determined from the intersection point of the approximate linear line of the dilute solution in the $\gamma$ vs. $C$ plot and the line of $\gamma = \text{minimum}^{10-12}$. UV spectra were recorded with a Shimazu UV-200 spectrophotometer. To correct the influence of pH, the aqueous solution in a reference cell was adjusted to the pH value of the sample solution measured. Fluorescence spectra were recorded on a Hitachi MPF-4 fluorescence spectrophotometer. The turbidity of the solutions was measured with a Nippon Precision Optical Instrument Co., SEP-PT-501 turbidimeter. Acidity and alkalinity were controlled by adding 2 N HCl or 2 N NaOH solution and pH values were measured with a Hitachi-Horiba F-5 pH meter.

3 Results and Discussion

A mixture of two surfactants usually form mixed micelles in an aqueous solution, and the cmc of a mixture is known to lie always between those of the individual components\(^ {12-14} \). Fig. 1 shows the relationship between the cmc value and the component ratio of C\textsubscript{12}-HAA/LAS at pH 6.7 and 11.0.

Fig. 1 shows the relationship between the cmc and the component ratio of C\textsubscript{12}-HAA/LAS at pH 6.7 and 11.0, respectively. The cmc of C\textsubscript{12}-HAA itself was observed to be about 2 mM. The cmc of the mixed system decreased abruptly by the addition of a slight amount of LAS, and then gradually decreased with the decrease of the C\textsubscript{12}-HAA/LAS component ratio. The cmc at pH 11.0 is lower than that at pH 6.7. In the UV spectra for the C\textsubscript{12}-HAA/LAS binary system, the absorption peak occurred at 261 and 253 nm. These were attributed to the $\pi-\pi^*$ transition of benzene ring in the LAS molecule. Therefore, fluorescence spectra were recorded in accordance with the excitation frequency of 255 nm, revealing a maximum emission at ca. 290 nm.

Fig. 2 shows the dependence of the molar absorption coefficient ($\varepsilon$) on the pH value for the C\textsubscript{12}-HAA/LAS (1.6 mM/0.4 mM) binary system and the pure LAS (0.4 mM) system. In general an amphoteric surfactant tends to be compatible with anionic, cationic, or nonionic surfactant in any ratio. The compatibility of C\textsubscript{12}-HAA and LAS was evaluated by the turbidity measurement. There was no indication of any enhancement in the turbidity of the mixed systems which covered the alkaline side above ca. pH 6.7. The solutions, however, suddenly became turbid on the acidic side below pH 6, to give a flocculent precipitate. The positive charge of the ammonium group in C\textsubscript{12}-HAA interacts with the negative group of the LAS molecule by the Coulomb force to form an insoluble complex without formation of an ionic pair. Therefore, the measurements of spectra were extended to the overall pH range above 6.5. The actual $\varepsilon$ of LAS itself exhibited a constant value of ca. 470. The $\varepsilon$ of the C\textsubscript{12}-HAA/LAS mixed system gave ca. 430 in the
pH range of 6.5~8.5, and increased steeply with pH, reaching ca. 500. The mutual transformation among cationic, zwitterionic, and anionic forms for C_{12}-HAA with the change of pH was pursued by a potentiometric titration method as previously reported. The base dissociation constant (pK_a) is 8.45 and the isoelectric point (pI) is 6.80. The anionic structure (COO^-) is completely formed in the alkaline solution of pH above 8.45. The pI is the point where the net charge is just nil and the groups of opposite characteristics such as -NH_2^+ and -COO^- are well-balanced. Although the -NH_2^+ group gradually changes to -NH^- group in the pH range from pI to pK_a, the amphoteric structure still exist from the result of differential titration method. An anomalous increment of ε at ca. pH 9 appearing close to pK_a may be caused by the distinction between (1) the interaction of C_{12}-HAA in a zwitterionic form with LAS and (2) the interaction of C_{12}-HAA in an anionic form with LAS. This finding was in agreement with our previous results, in which the difference of ε between the mixed system and the pure LAS system was negative at pH 6.7 and positive at pH 11.0.

Fig.-3 (a) shows the relationship between the ε and C_{12}-HAA concentration at a given LAS concentration of 2 mM at pH 6.7 and 11.0, respectively. Fig.-3 (b) shows the relationship between arbitrary emission intensity of fluorescence and C_{12}-HAA concentration at a given LAS concentration of 2 mM. The ε and the emission intensity of fluorescence for the system at pH 11.0 were hardly changed with the increase of C_{12}-HAA concentration. On the contrary, the ε at pH 6.7 decreased and fluorescence intensity at pH 6.7 increased, preserving the LAS concentration at a given level with C_{12}-HAA concentration. These results in the neutral region reveal the interaction between a zwitterionic form of C_{12}-HAA and an anionic form of LAS. The interaction in the C_{12}-HAA/LAS system is affected by the component ratio and the concentration in the system, as shown in Fig.-2 and Fig.-3 (a).

Fig.-4 shows the relationship between the fluorescence intensity and the concentration of C_{12}-HAA/LAS (1/1 molar ratio) binary system, taking the concentration of pure LAS system as a standard at pH 11.0 and 6.7, respectively. Therefore, the intensity of the binary system was normalized by LAS concentration of the system. Further, the turbidity of the former system had also to be measured, because the influence of high turbidity on a quenching of fluorescence had to be corrected, particularly in high concentration. There is no indication of enhancement in turbidity for the alkaline region, but the binary system in the neutral side becomes turbid at concentration above C_{12}-HAA/LAS (5 mM/5 mM).

When the binary system was compared with the pure LAS, the curve of fluorescence intensity was the same at concentration below the cmc (ca. 0.6 mM), as shown in Fig.-1. Since each molecule was presumed to be monomeric in a solution, no interaction occurred between C_{12}-HAA and LAS. On the other hand, the fluorescence intensity increased in the alkaline region, showing that the interaction between C_{12}-HAA and LAS became more significant at high pH. This finding was in agreement with our previous results, in which the difference of ε between the mixed system and the pure LAS system was negative at pH 6.7 and positive at pH 11.0.
The presence intensity of the mixed system at concentration above the cmc was higher than that of pure LAS. The result revealed an appreciable interaction between C12-HAA and LAS. The maximum peak of fluorescence intensity for both the mixed system and the pure LAS system at relatively high concentration is assumed to be due to a "concentration-quenching" or a reabsorption.

UV and NMR spectra were run in detail to identify a complex formation of the mixed micelle. LAS displays four absorption bands; 255.5 nm, 261.5 nm (λmax), 268 nm, and 272.5 nm. These bands originate from the π→π* transition of phenylene group. No shift of these bands for pure LAS (e.g. 0.5 mM) was observed irrespective of pH change (pH 5 to 11). These bands were not shifted in the mixed system of C11-HAA/LAS (5 mM/0.5 mM) at pH 11.0. On the other hand, these bands at pH 6.7 were shifted toward the long wavelength region in the above same mixed system. For example, the λmax 261.5 nm for the C11-HAA/LAS (5 mM/0.5 mM) system at pH 6.7 was shifted to 263 nm. The electron attractive force of -SO3 group in LAS molecule is weakened by -NH+ group in HAA molecule. Therefore, the absorption peak is shifted to a longer wavelength.

The complexing structure of the mixed micelle was also examined from the ring current effect of the benzene ring by NMR method. The NMR peak (δ 7.4~7.9 ppm) of benzene protons for pure LAS was independent of pH change. The peak for the C11-HAA/LAS (200 mM/200 mM) mixed system at pH 11.0 was, however, shifted slightly downfield (about 3.6 Hz). The measurement for the above same system at pH 6.7 was impossible because of gelification and the spectrum at low concentration in the neighborhood of the cmc was not detectable owing to poor sensitivity of NMR.

\[ \text{pH} \geq 8.5 \]

\[ 8.5 \leq \text{pH} \leq 6.5 \]

**Fig.-4** Relationship between intensity or turbidity and LAS concentration.

**Fig.-5** Model of interaction between C11-HAA and LAS in mixed micelle.
Models of mutual interaction indicated by the above results are illustrated in Fig.-5. The complex in the region of 6.5~8.5 is thought to be formed between the anionic group of sulfonate in LAS molecule and the cationic group in the zwitterionic structure of C_{12}-HAA. In the alkaline above pH 8.5, the charged head groups and the relatively small sodium counterions are located in the Stern layer. Further, most of the counterions are located outside the shear surface in the Gouy-Chapman electrical double layer. The net charge on the micelle is reduced by the counterions in the Stern layer. Therefore, the electrical repulsion between the \(-\text{COO}^-\) group of HAA and the \(-\text{SO}_3^-\) group of LAS is weakened by the counterions association for the negative charged groups to facilitate the formation of the mixed micelle.

Acknowledgements

Financial support of this work provided by Meisei University is gratefully acknowledged. The authors thank Mr. Y. Takahashi and Mr. M. Yoshino for their technical assistance.

(Received Nov. 16, 1981)

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