February, 1983] © 1983 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 56, 627—628 (1983) 627

Study of the Mixed Solutions of an Anionic and a Nonionic Surfactant by Using the Azo-hydrazone Tautomerism of an Acidic Dye

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(Received June 11, 1982)

Synopsis. The absorbances of the azo-hydrazone tautomer of sodium 4-(*p*-sulfonatophenylazo)-1-naphthol-2-sulfonate dissolved in an aqueous solution of polyethylene glycol octyl dodecyl ether (8ED) were measured in the presence of various concentrations of sodium dodecyl sulfate (SDS). The existence of a mixed micellar region of SDS and 8ED in the bulk solution was confirmed by this azo-hydrazone tautomer method.

The present authors have previously reported the properties of mixed micelles between an anionic surfactant and a series of homogeneous polyethylene glycol dodecyl ethers (*n*ED) with no Poisson distribution and their dependence on the oxyethylenechain length.[1–4] The existence of a mixed micellar region in the bulk solution has been suggested from the finding that a long plateau appears on the surface-tension curve of nonionic surfactants in the presence of sodium dodecyl sulfate (SDS) at a constant concentration. Further, the authors have determined the cmc of mixed solutions of SDS and 7ED by the charge-transfer-solubilization method.

Recently, the cmc of nonionic surfactants has been determined spectroscopically by using the keto-enol tautomer of benzoylacetone or benzoylacetoanilide.[5,6] This method might also be used to elucidate the properties of mixed micelles. In this work, the properties of mixed micelles of SDS and polyethylene glycol octyl ether (8ED) were investigated by using an azo-hydrazone tautomer of sodium 4-(*p*-sulfonatophenylazo)-1-naphthol-2-sulfonate (PNDS) as one of the tautomers.

PNDS was prepared in the following way: Sulfanilic acid ($NH_2C_6H_4SO_3H$) was diazotized and coupled with potassium 1-naphthol-2-sulfonate ($HOC_{10}H_6SO_3K$). The PNDS thus obtained was purified by chromatography on Wakogel C-200, using a mixture of 1-butanol, acetic acid, and water as the eluent. The PNDS was dried at 100 °C under a vacuum. A homogeneous nonionic surfactant, polyethylene glycol octyl dodecyl ether (8ED) was supplied by the Nikko Chemicals Co., Ltd. This 8ED was highly pure, as was confirmed by gas-liquid chromatography, thin-layer chromatography, and cloud-point and surface-tension measurements. SDS as an anionic surfactant was synthesized by a modification of the method of Dreger *et al.*,[7] and subsequently purified by repeated recrystallizations from ethanol. The purity of SDS was confirmed by the absence of any minimum in the surface-tension diagram. The water used in all the experiments was purified by passing it through the MILL-Q Reagent–Grade Water System (Millipore, Ltd.) until its specific conductivity fell below $10^{-7}\ \Omega^{-1}/\text{cm}$. 2.5×10^{-5} mol dm^{-3} of PNDS in an aqueous solution was prepared, and then the surfactant solutions with various concentrations were prepared by dissolving a certain quantity of each surfactant into the PNDS aqueous solution in order to keep the concentration of PNDS constant. After the temperature of the samples had attained 25 °C, the absorption spectra of the samples were measured in a 1.0-cm quartz cell by means of a spectrophotometer (Model Hitachi ESP-3T).

It is well known that PNDS exists mostly in the hydrazone form in water and is tautomerised to the azo form in polar organic solvents.[8] To confirm this behavior, the absorption spectra of PNDS dissolved in water–ethanol mixtures were measured. It was seen that the spectrum of PNDS in water had an absorption band at 490 nm, where PNDS exists in the hydrazone form, while on the other hand, the spectrum in ethanol provides an absorption band at 410 nm which is attributed to the azo form. The absorbance of the hydrazone form decreased with an increase in the content of ethanol in the mixtures. Furthermore, an isobestic point was clearly observed at 435 nm. The above results support the idea that the azo-hydrazone tautomerism of PNDS exists in water–ethanol mixtures.

It is important to check whether or not an aggregation of PNDS exists in an aqueous solution, because dyes usually form aggregates, such as dimers, trimers, and higher oligomers.[9] When the absorbance of PNDS was plotted against the concentration of PNDS, the absorbances of PNDS in an aqueous solution and in ethanol both strictly obeyed Beer's law. This means that an aggregation, if any, of PNDS would occur to only a negligible extent in these solutions.

As the next step, the azo-hydrazone tautomerism of PNDS was examined in aqueous surfactant solutions.

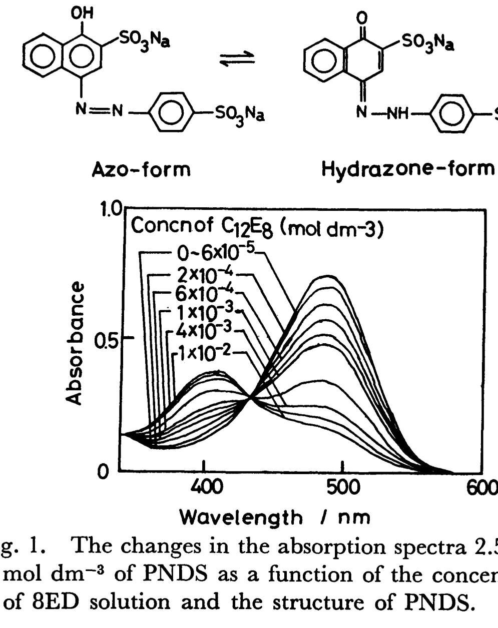

Fig. 1. The changes in the absorption spectra 2.5×10^{-5} mol dm^{-3} of PNDS as a function of the concentration of 8ED solution and the structure of PNDS.

The spectra of PNDS dissolved in surfactant solutions are expected to be different from those in water alone due to the interaction of the PNDS-surfactant. The changes in the absorption spectra of 2.5×10^{-5} mol dm^{-3} of PNDS as a function of the concentration of the 8ED solution and the structure of PNDS are shown in Fig. 1. The absorbance of the hydrazone form was constant until 7.0×10^{-5} mol dm^{-3}; thereafter, it decreased gradually with an increase in the concentration of 8ED. On the other hand, the absorbance of the azo form did not change until 6.5×10^{-5} mol dm^{-3} and then increased with an increase in the concentration of 8ED. Much as in the water–ethanol system, a sharp isobetic point was observed at 435 nm. Thus, the tautomerism from the hydrazone form to the azo form also proceeded in aqueous surfactant solutions. Further, it was found that the absorbances of the hydrazone form and of the azo form began to change near the cmc of 8ED.[10] This fact suggests that the tautomerism from the hydrazone form to azo form is related to a micellar phenomenon, since the absorbances of neither form changes below the cmc.

On the contrary, in the PNDS–SDS system, the absorbance of the hydrazone form decreased negligibly with an increase in the concentration of SDS from 0 to 20 mmol dm^{-3}, while the azo form in the spectrum did not appear at all in this concentration range. Since the cmc of SDS is 8 mmol dm^{-3}, the above result suggests that PNDS molecules are not solubilized into SDS micelles because, presumably, of an electric repulsion between PNDS anion molecules and SDS micelles. Thus, the properties of the mixed surfactant solutions of 8ED and SDS can be estimated by the utilization of the phenomenon that the azo-hydrazone tautomerism is not observed in an aqueous SDS solution, but only in an aqueous 8ED solution.

Figure 2 depicts the absorbances of PNDS *vs.* the concentration of 8ED in the presence of various concentrations of SDS. The concentration of 8ED at which the absorbance of the hydrazone form begins to decline is shifted to a higher concentration of 8ED with an increase in the concentration of SDS present in the mixtures. Similar behavior was observed in the change of the absorbance of the azo form in the mixtures of 8ED and SDS. This result can be interpreted as follows. The PNDS-anion molecules solubilized in 8ED micelles are expelled by the penetration of SDS into 8ED micelles due to electric repulsion; as a result, the mixed micelles of 8ED and SDS are formed. The present authors have previously reported[1,4] that the surface-tension curves of 8ED in the presence of SDS have a long plateau over a wide range of concentrations of 8ED and exhibit two break-points at lower and higher concentrations of 8ED. Further, they have pointed out[1,4] that the first break-points on the surface tension curves correspond to the cmc of mixed micelles of SDS and 8ED, while the second break-points indicate the existence of mixed micelles with excess 8ED. In general, the cmc of mixed micelles is well known to be lowered more than that of each single surfactant.[11–13] Although the present PNDS method does not provide the cmc values of mixed micelles of SDS and 8ED, it seems that the concentration region between the cmc of 8ED alone and the concentration of 8ED corresponding to that point at which the absorbance of the hydrazone form or the azo form begins to change is related, at least, to the presence of a mixed micelle of SDS and 8ED. The length of this region is extended with an increase in the concentration of SDS present in the mixtures. With further increase in the concentration of 8ED in the mixtures, the absorbance of the azo form or the hydrazone form begins to change. Since the concentration of 8ED corresponding to that at point which the absorbance of the azo form or the hydrazone form begins to change is correlated with the second break-point on the surface tension, PNDS might be solubilized into mixed micelles with excess 8ED in this concentration range.

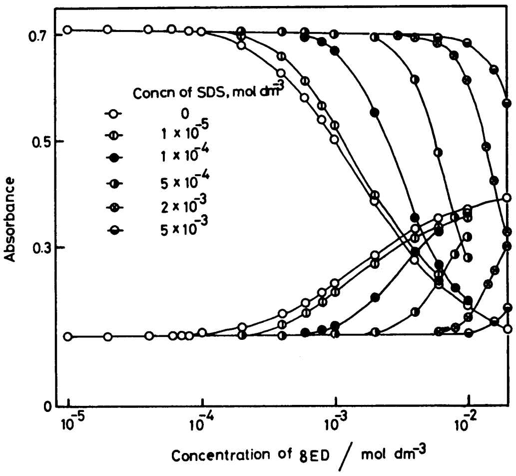

Fig. 2. The absorbances of PNDS *vs.* the concentration of 8ED in the presence of various concentrations of SDS.

Accordingly, the PNDS tautomer is a useful probe for elucidating the properties of mixed micelles of an anionic surfactant and a nonionic surfactant.

References

1) H. Akasu, M. Ueno, and K. Meguro, *J. Am. Oil Chem. Soc.*, **51**, 519 (1974).

2) K. Meguro, H. Akasu, and M. Ueno, *J. Am. Oil Chem. Soc.*, **53**, 145 (1976).

3) H. Akasu, A. Nishii, M. Ueno, and K. Meguro, *J. Colloid Interface Sci.*, **54**, 278 (1976).

4) Y. Takasawa, M. Ueno, and K. Meguro, *J. Colloid Interface Sci.*, **78**, 207 (1980).

5) N. Shoji, M. Ueno, and K. Meguro, *J. Am. Oil Chem. Soc.*, **53**, 165 (1976).

6) N. Shoji, M. Ueno, and K. Meguro, *J. Am. Oil Chem. Soc.*, **55**, 297 (1978).

7) E. E. Dreger, G. I. Keim, G. A. Miles, L. Shedlovsky, and J. Ross, *Ind. Eng. Chem.*, **36**, 610 (1944).

8) R. L. Reeves and R. S. Kaiser, *J. Org. Chem.*, **35**, 3670 (1970).

9) Y. Tanizaki and A. Ando, *Nippon Kagaku Zasshi*, **78**, 343 (1957).

10) K. Deguchi and K. Meguro, *J. Colloid Interface Sci.*, **38**, 596 (1972).

11) M. J. Schick and D. J. Manning, *J. Am. Oil Chem. Soc.*, **43**, 133 (1966).

12) H. Lange and K. H. Beck, *Kolloid Z. Z. Polym.*, **251**, 424 (1973).

13) J. H. Clint, *J. Chem. Soc., Faraday Trans. 1*, **71**, 1327 (1975).