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Aggregation and Dissolution of Cationic Dyes with an Anionic Surfactant

Joon Woo Park* and Hesson Chung

Department of Chemistry, Ewha Womans University, Seoul 120, Received October 16, 1985

Spectral behaviors of cationic dyes, methylene blue(MB) and acridine orange(AO), with varying concentrations of sodium dodecylsulfate(SDS) were studied. At low concentration of SDS(<1 mM), these dyes formed insoluble dye-surfactant aggregates. When [SDS] is 4-5 mM, the aggregates were dissolved into mixed micelles of constant composition. At higher concentration of [SDS], the composition of mixed micelles were changed with [SDS], resulting only monomeric form of dyes in micelles. AO-SDS system showed greater aggregating and less dissolving properties, and weaker effect of salt than MB-SDS system did. These were attributed to the greater hydrophobic nature of the former dye. The monomer/dimer ratios of dyes in mixed micelles at given [SDS] were greatest at 20°C, reflecting the dependency of CMC of the surfactant on temperature.

Introduction

It is well known that surfactants exert profound effects on many chemical reactions and interactions. The effects of surfactants arise mainly from changes in the local environments and concentrations of interacting species due to the interaction with surfactant micelles. In order to elucidate the nature of effects of surfactants and to design desirable surfactant systems, it is essential to understand the nature of interactions between molecules and surfactants.

The dye-surfactant systems have attracted considerable amounts of interest. The enhanced energy transfer between dyes in dye-surfactant systems made them good model membrane systems of chloroplast.¹⁻⁴ The peculiar behaviors in both absorption⁵⁻⁷ and fluorescence^{8,9} spectra of dyes in the presence of surfactants of opposite charge were attributed to the formation of a continuum of dye-surfactant aggregates or mixed micelles depending on the surfactant : dye ratio(S/D). The wide range of mixed micelle was also evidenced from hydrolysis kinetic studies of esters of azonaphthol sulfonate dyes in mixed micelles with cationic surfactants.^{10,11}

However, the nature of interactions between dyes and surfactants is not known in detail. In this paper, we compared the interaction properties of methylene blue(MB) and acridine orange(AO) with a common anionic surfactant, sodium dodecylsulfate(SDS).

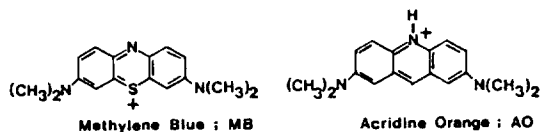
tural similarity as shown, they exhibit large difference in their self-associating properties.¹² It was hoped that such intrinsic difference in the associating properties of these two dyes might also be manifested in the interaction with a surfactant and the results would provide valuable information on the nature of dye-surfactant interactions.

Experimental

Sodium dodecylsulfate(SDS) was obtained from Kanto and was recrystallized from ethanol. Methylene blue(Shinyo Pure Chemicals) was recrystallized from 3:1 ethanol-water twice. Acridine orange was obtained from Sigma and used as received. Solutions of MB and AO containing desired amounts of SDS were prepared and kept in the dark overnight. Prior to spectral measurement, the solutions were centrifuged for 10 minutes at 4000 rpm. Concentrations of dyes were calculated from weight data of dyes used to prepare the stock solutions. Absorption spectra were recorded on a Beckman DU-8B spectrophotometer at 25°C using cells of 1 cm pathlength, unless otherwise specified.

Results and Discussion

Both the position and intensity of absorption spectra of MB and AO solutions were varied sensitively with SDS concentrations as shown in Figure 1 and 2. For example, the absorption spectra of 1×10^{-5} M MB exhibited a peak at 660 nm in the absence of SDS. When concentration of SDS was low(<1 mM), the addition of SDS resulted in decrease of the absorbance without noticeable change in the spectral shape. In the range of 1-3 mM SDS, the increasing concentration of SDS had little effect on the spectra. Further addition of SDS



These dyes were chosen because, despite of their struc-

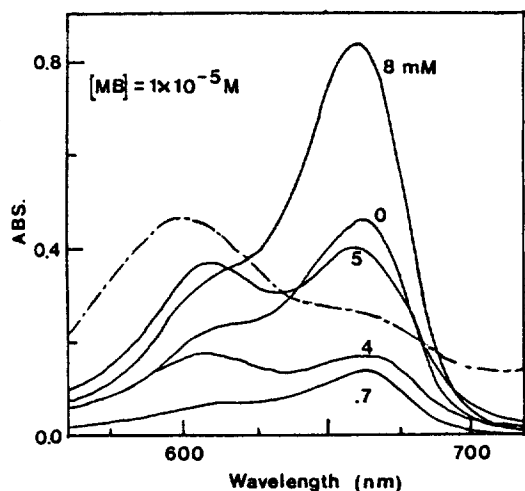


Figure 1. Absorption spectra of 1×10^{-5} M methylene blue solutions at various concentrations of SDS shown. Broken line is a spectrum of uncentrifuged 2×10^{-5} M MB in 4 mM SDS taken by using a 0.5 cm cell.

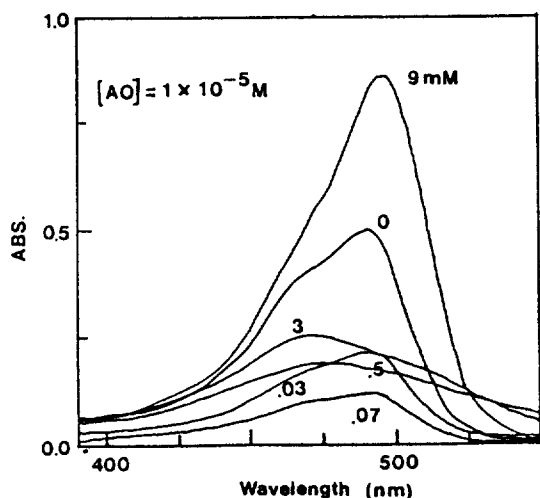


Figure 2. Absorption spectra of 1×10^{-5} M acridine orange solutions at concentrations of SDS shown.

resulted in a new well-defined absorption peak at 610 nm and absorbance values both at 660 and at 610 nm increased with increasing concentration of SDS up to 5 mM SDS. Above this concentration of SDS, further addition of SDS decreased absorbance at 610 nm, while it increased absorbance at 660 nm. Such dependencies of spectral properties of MB on the concentration of SDS could also be noticed from the color of the solutions: the blue color of MB solutions was faded, turned red-violet, and then blue color was deepened as [SDS] increasing.

The spectra of AO solutions were also varied in similar fashion as those of MB with [SDS] as shown in Figure 2. The absorption peak of this dye appeared at 490 nm in the absence of SDS. However, a well-defined peak at 470 nm was appeared in the intermediate concentration of SDS. In contrast to MB, the 470 nm peak, which corresponds to 610 nm peak in MB, was more pronounced than the original 490 nm peak. The variations of absorbance values of MB at 660 nm and of AO at 470 nm were plotted against [SDS] in Figure 3.

The absorption peaks of MB at 660 and 610 nm, and of

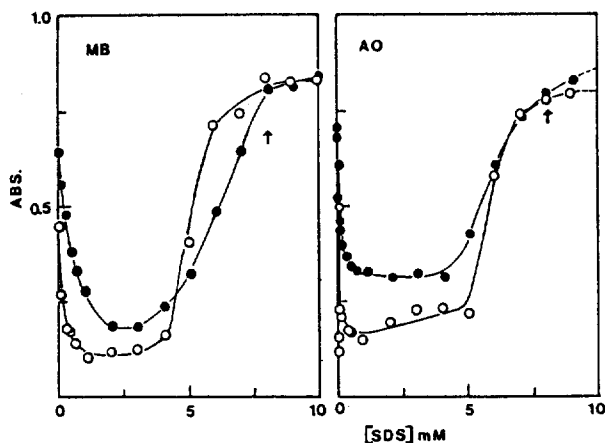
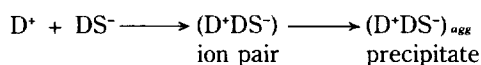


Figure 3. Variations of absorbance values at 660 nm of MB and at 470 nm of AO. Filled circles are data taken in 5 minutes after mixing and open circles are values of centrifuged solutions. Arrows indicate CMC of SDS.

AO at 490 and 470 nm, agree well with α and β bands of the dyes, respectively.^{12,13} These bands are characteristics of all metachromatic dyes and have been attributed to monomeric (α band) and dimeric forms (β band) of the dyes.

At higher concentration of dyes, β band is usually substituted by a third band (γ band) at even shorter wavelength: the positions of γ bands of MB and AO are reported to be 590 and 450 nm respectively.^{12,13} The γ bands belong to the dyes in higher associated forms than the dimer. When the solution was not centrifuged and the concentration of MB was 2×10^{-5} M, we observed a new peak at 598 nm, rather than normal 610 nm in 4–5 mM SDS (Figure 1). This can be interpreted as γ band overlapped with β band. The enhanced absorption near 450 nm in the spectra of AO in 0.5 and 3 mM SDS solutions (Figure 2) may also be attributed to the presence of higher aggregate dye than the dimer.

The decrease of absorbance of dyes by the addition of SDS, when [SDS] < 1 mM, reflects aggregation of dyes with SDS into insoluble salts. The aggregation may be preceded by formation of ion pairs.



The shape of absorption spectra of dye-surfactant mixture was the same as that of free dyes in the concentration range of [SDS] < 1 mM. This can be taken as an evidence that the dye-SDS aggregate is not soluble in water. These results also suggest that the ion pairs exhibit the same spectral characteristics as free dyes. This is in contrast to the charge transfer complexation of MB¹⁴ and Rhodamine 6G¹⁵ with tetraphenylborate anion.

Figure 3 shows that the tendency of aggregation for AO-SDS is much greater than that for MB-SDS. The similar difference was reported in the tendency of self-aggregation of the dyes.¹² AO and MB differ from one another only in substitution of a CH group for a sulfur in the heterocyclic ring. This substitution is expected to have marginal effect on the geometry of the dye aggregates. Rather, the hydrophobic character of a CH group is larger than that of sulfur. Such difference in the polarity of heterocyclic ring seems to be appeared in the difference in solution structure,¹² which is manifested as change in association process. The reported

greater associating tendency of an amphiphatic thiacyanine dye than that of oxacyanine analogue can be interpreted from the same view.⁹ The absorbance increase in the intermediate range of [SDS], 4–5 mM, reflects dissolution of the dye-surfactant aggregates. The dissolution starts at critical concentrations of SDS, 4 mM for MB and 5 mM for AO, which are below critical micelle concentration (CMC) of SDS homomolecule, 8 mM. This result suggests the formation of dye-surfactant mixed micelles during the dissolution process. The higher CMC value of AO-SDS mixed micelle than that of MB-SDS micelle accords well with the greater stability of AO-SDS aggregate as revealed in the aggregation process.

Since the ratio of the absorbance values of monomer and dimer bands of dyes is not changed during the dissolution (see spectra of MB in 4 mM and 5 mM SDS in Figure 1), the composition of the mixed micelle can be assumed to be constant. Several authors^{5–10} observed similar dissolution of dye-surfactant aggregate into mixed micelle, but the constancy of the composition of the mixed micelle was not reported.

To examine the contribution of electrostatic effects on the dye-surfactant interactions, the spectra of dye solutions in 0.1 M NaCl were taken. The absorbance values of monomeric peaks are graphed in Figure 4. This Figure shows that the dye-SDS aggregation occurs at higher concentration of SDS, while the dissolution of the aggregates require lower concentration of SDS, in the presence of added salt. The effect of salt on the aggregation is more pronounced in MB-SDS than in AO-SDS. This implies that the electrostatic interaction between dye and SDS is more important in the former. This conclusion matches well with the important role of hydrophobic factor in the AO-SDS aggregation. Figure 4 also shows that the CMC's of mixed micelles are lowered to ca. 1 mM in the presence of 0.1 M NaCl. This change is parallel to the change of CMC of SDS homomolecule, 1 mM in 0.1 M NaCl from 8 mM in the absence of added salt.

When [SDS] > 6 mM, further addition SDS increased the ratio of monomeric and dimeric forms of dyes. This can be

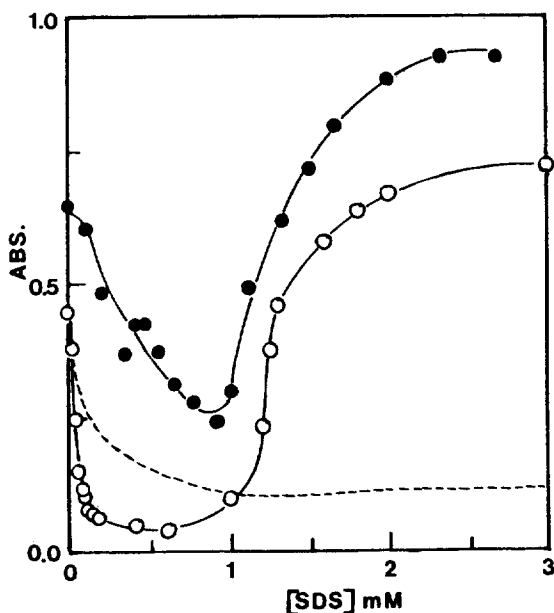


Figure 4. Variations of absorbances of MB at 660 nm (●) and of AO at 490 nm (○) with concentrations of SDS in 0.1 M NaCl. (---) is data of MB taken in the absence of added salt.

explained in terms of equilibrium between these two forms, which reflects the changes in the composition of the mixed micelle at [SDS] > 6 mM.

The changes in the monomer to dimer ratio in mixed micelles were also revealed in the temperature dependencies of the spectra. The variations of absorbance values at monomer and dimer peaks of dye solutions in 6 mM SDS with temperature were plotted in Figure 5. Since the isosbestic points of monomer and dimer absorption of MB and AO are very close to the wavelengths of dimer absorption peaks of the corresponding dyes,^{12,13} the absorbances at dimeric peaks are virtually proportional to the concentrations of total dyes. Figure 5 shows that the concentrations of monomeric form of dyes, *i.e.*, the monomer/dimer ratio, are maximum near 20°C. This can be explained in terms of enthalpy of SDS micellization (ΔH_m): ΔH_m 's of SDS are reported to be 1 kcal/mole at 10°C, 0 at 20°C and -1.1 kcal/mole at higher temperature.¹⁶ Thus, CMC of SDS is minimum at 20°C and the numbers of SDS molecules in micellized state is largest at the temperature. This seems to result in highest monomer concentration of dyes in the micelles. The dye-dye and dye-SDS interaction energy might also affect the monomer-dimer equilibria. Despite of large difference in the enthalpies of dimerization of MB and AO (-5 vs -9 kcal/mole),¹² the temperature dependencies of the equilibria resemble each other very closely. This implies that the dependencies arise mainly from entropic factors. However, the difference in the interaction energy is reflected in the difference in the magnitudes of the equilibrium constants.

The appearance of the dimeric peaks at shorter wavelength region than the corresponding monomeric peaks suggests parallel stacking of dyes in dimer, from exciton theory of interactions between chromophores.^{17,18} The enhanced absorption of dyes in high concentration of SDS (Figures 1 and 2), compared to that in the absence of SDS, arises from the change in the environment of dyes. Kasatani *et al.*¹⁹ recently showed that Rhodamine 6G and methylnindotricarbocyanine dyes are micellized in the region near the surface of SDS micelle. Similar model was suggested for the solubilization site of MB in SDS micelle.⁴ Therefore, it might be concluded that the dyes are sandwiched between SDS molecules in the micellar surface. Such arrangement of dyes reduces the electrostatic repulsion between head groups and result in lower CMC of the mixed micelles than that of homomolecule. In this

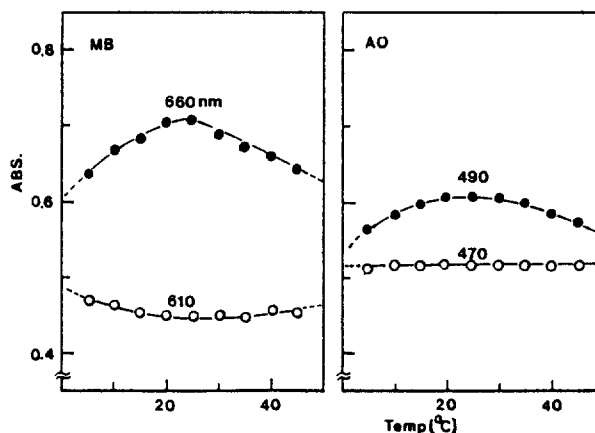


Figure 5. Temperature dependencies of absorbances at monomeric (●) and dimeric (○) peak positions of dyes.

mixed micelles, dyes may not be solubilized randomly, but prefer to occupy a position adjacent to another dye. This preference is determined by the dye-dye interaction energy, which is larger in AO than in MB.

Acknowledgement. This work was supported by a grant (1984) from Korean Research Institute for Better Living of Ewha Womans University.

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Photoreaction of 1,4-Disubstituted-1,3-Butadiyne with Alcohol

Tae Suk Lee and Sang Chul Shim*

Department of Chemistry, Korea Advanced Institute of Science and Technology, P.O. Box 150 Cheongyangni, Seoul 131

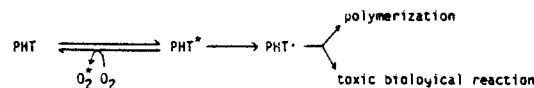
Sung Sik Kim

Department of Chemistry, Chonbuk National University, Chonju 520, Received October 29, 1985

Irradiation of 1,4-diphenyl-1,3-butadiyne and 5,5-dimethyl-1-phenyl-1,3-hexadiyne with methanol yields 1:1 polar addition products, [E]- and [Z]-1,4-diphenyl-1-methoxy-1-buten-3-yne and [E]- and [Z]-5,5-dimethyl-1-methoxy-1-phenyl-1-hexen-3-yne, respectively. These geometrical isomers were converted into each other reaching the photostationary state on irradiation with 300 nm UV light. The photoaddition reaction of 1,4-diphenyl-1,3-butadiyne and 5,5-dimethyl-1-phenyl-1,3-hexadiyne with methanol seems to proceed from the zwitterionic lowest excited state.

Introduction

Certain naturally occurring conjugated polyacetylenes have been reported to be phototoxic to a variety of microorganisms, human skin fibroblasts, mosquito larvae, and Paramecium.¹⁻⁵ The examples are shown in Figure 1. In particular, 1-phenyl-1,3,5-heptatriyne(PHT), a polyacetylenic compound isolated from *Bidens pilosa* L, does not induce cross-links in calf thymus DNA in the presence of UVA in contrast to 8-methoxypsoralen phototoxicity which involves cross-link in DNA.^{1,6-7} Instead, phototoxic poly-yne such as PHT exert their phototoxic action via the viral membrane damage and as a consequence the viral genome, DNA or RNA, is unable to replicate.⁸ A mechanism involving free radical of PHT has been proposed.⁹



PHT by the absorption of photon leads to the formation of the excited state, PHT*, and the subsequent formation of free radical species PHT·. The toxic reaction and the polymerization reaction compete for the species and the excited state of PHT is also quenched by O₂ leading to the lower toxicity of PHT. But this mechanism does not show phototoxic sites and photoadducts of PHT with substrates. Nothing is definitely known yet about the photochemistry of conjugated poly-yne except 1,4-dialkylsubstituted diynes which abstract hydrogen atom when they were irradiated in hydrogen donor solvents (pentane, cyclohexane, methylene dichloride, meth-