Interaction of Cationic Dye and Anionic Detergent above and below the Critical Micelle Concentration as Revealed by Fluorescence Characteristics[1)]

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(Received June 15, 1983)

The interaction of 3,3′-diethylthiacarbocyanine iodide, a cationic dye, with sodium dodecyl sulfate (SDS), an anionic detergent, was studied as a function of the concentration of SDS ([SDS]) above and below the critical micelle concentration (cmc). The [SDS]-dependent fluorescence spectra, quantum yield and decay measurements revealed the deaggregation of the dye above the cmc and the formation of the dye–SDS aggregate below the cmc.

The photophysical and photochemical behavior of organic molecules in organized assemblies such as micelles[2,3)] has been receiving current attention from several viewpoints, such as (1) the influence of the micellar environment on the very fast photophysical process like rotational diffusion,[4)] (2) the photophysical study in relation to finding a good lasing system,[5,6)] (3) the measurement of the aggregation number of micelles,[7)] and (4) the construction of a model membrane system to mimic a biological system like chloroplasts, with special emphasis on the enhancement of the energy transfer and electron transfer efficiencies.[8–20)] The study of the spectroscopic properties of organic molecules in micellar media provides us with the basic properties of such a system which are useful in understanding many specific features of the system as mentioned above.

Many peculiarities have been noted for the spectroscopic properties of the dye with a detergent with the opposite charge around the critical micelle concentration (cmc). Pinacyanol, a cyanine dye, has been used in the "spectral change method" to determine the cmc of many detergents.[21)] Mataga and Koizumi[22,23)] studied the variation in absorption spectra and fluorescence quenching of the Rhodamine 6G (Rh-6G)–sodium dodecyl sulfate (SDS) system, which was dependent on the concentration of SDS ([SDS]), around the cmc. Mukerjee and Mysels[24)] studied absorption spectra of the pinacyanol–SDS system as a function of [SDS], and examined critically the "spectral change method" mentioned above. Lohoczki and Hevesi[9)] studied the variation of absorption spectra of the thionine–SDS system especially below the cmc (*i.e.* in the premicellar region). From further investigation of these peculiarities in the absorption and fluorescence spectra along with the fluorescence lifetime and quantum yield, detailed picture on the nature of dye–detergent interaction can be obtained.

In the present paper, the [SDS]-dependent variation in absorption and fluorescence spectra, quantum yield, and decay characteristics of 3,3′-diethylthiacarbocyanine iodide (DTC)–SDS system was studied, and the nature of the dye–detergent interaction was discussed. The structural formula of DTC is given in Fig. 1.

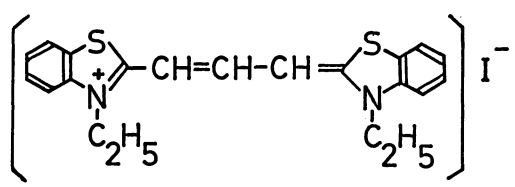

Fig. 1. Structural formula of 3,3′-diethylthiacarbocyanine iodide.

Experimental

Materials. DTC (Dojin Kagaku), Rhodamine B (Eastman-Kodak), and Rhodamine 101 (Exciton) were used without further purification. The purity of these dyes was checked by thin-layer chromatography. SDS (Nakarai, protein research grade), quinine sulfate (Wako), *m*-dimethylaminonitrobenzene, and 4-dimethylamino-4′-nitrostilbene (Nakarai) were used as received. Water was distilled twice. Sulfuric acid, benzene, hexane, *o*-dichlorobenzene, and ethylene glycol were of G. R. grade of Wako or Nakarai and were used as received.

Absorption and Fluorescence Spectra. Absorption spectra were measured by a Shimadzu UV-200 recording spectrophotometer. Fluorescence spectra were measured by a Hitachi 650-10S spectrofluorimeter with a Hamamatsu R928 photomultiplier (sensitive to 930 nm). Measurements were made at room temperature for aerated solutions.

Fluorescence Decay. In the measurement of fluorescence decay curves, the dye solution in a quartz spectrofluorimeter cell was pumped with the second harmonic of a Nd^{3+}: YAG laser. Fluorescence decay was measured with a Hamamatsu C979 streak camera, using a Nihon-shinkukogaku interference filter (579 nm), or a Toshiba VO56 or 57 cut-off filter. The time-scale of the streak camera was fully calibrated. All measurements were made at room temperature for aerated solutions. The results of three to nine shots on the same sample were averaged.

Quantum Yield Measurements. The fluorescence quantum yield (ϕ) of the dye solution was measured with reference to that of quinine sulfate standard solution (1×10^{-6} M† in 0.5 M H_2SO_4), $\phi_{st}=0.55$,[25)] using the formula[26)]

$$\frac{\phi}{\phi_{st}}=\frac{F}{F_{st}}\cdot\frac{A_{st}}{A}\cdot\frac{E_{st}}{E}\cdot\frac{n^2}{n_{st}^2}, \quad (1)$$

where F, A, E, and n are the integrated area under the fluorescence spectrum (corrected for the response function of the spectrofluorimeter), the absorbance/cm at the exciting wavelength, the intensity of the exciting light measured by a photocell (Hamamatsu S1133-01) corrected for its response function, and the refractive index of the sample solution, respectively. F_{st}, A_{st}, E_{st}, and n_{st} are the corresponding quantities of the

† 1 M=1 mol dm^{-3}, 1 mM=1×10^{-3} mol dm^{-3} in this paper.

standard solution. The exciting wavelength was 365 and 520 nm for quinine sulfate and DTC, respectively. All measurements were made at room temperature (25±2 °C) for aerated solutions. The relation $n \approx n_{st}$ was assumed. The response function of the spectrofluorimeter was measured using *m*-dimethylaminonitrobenzene (1×10^{-5} M in benzene–hexane mixture (30 : 70 in volume)) and 4-dimethylamino-4′-nitrostilbene (1×10^{-5} M in *o*-dichlorobenzene).[27,28] That of the photocell was measured using the solution of Rhodamine B in ethylene glycol. In order to check the accuracy of the present method of quantum-yield determination, the quantum yield of Rhodamine-101 was measured. The quantum yield of this dye has been known to be 1.0.[6,29] The quantum yield of Rhodamine 101 (6×10^{-6} M in ethanol) measured by the present method was 1.04—1.06. The accuracy (within *ca.* 10%) of the present method was thus proved.

Cmc Measurements. The cmc of SDS was determined conductometrically. The electrodes of the conductivity cell were platinum plates without platinum black. The temperature of the cell was kept at 25.0±0.1 °C. The bridge used was a Yanaco MY-8 Conductivity Outfit or a Yokogawa Hewlett-Packard 4255 A Universal Bridge. The cmc determined was 7.4±0.1 mM, in good agreement with the generally accepted published value (8.1 mM).[30]

Results

Absorption and Fluorescence Spectra of DTC and DTC–SDS. The absorption spectra of the aqueous solutions of DTC are shown in Fig. 3. For [DTC]$\lesssim 2.0 \times 10^{-5}$ M, the shape of the absorption band remained essentially the same and was quite similar to that of the methanol solution. The dye is present essentially as a monomer in these solutions. The dimer band at 510 nm became apparent for [DTC]$\gtrsim 5.0 \times 10^{-5}$ M. The ratio of the absorbance at 510 nm to that at 556 nm (A_{510}/A_{556}) increased with the concentration of the dye, while the corresponding ratio was essentially constant in methanol (See Fig. 3). The fluorescence maximum which appeared around 580 nm is due to the monomer of the dye. The absorption spectra of DTC–SDS solutions are shown in Fig. 4. The ratio A_{510}/A_{560} (the dimer band was found at 510 nm, and the monomer band at 560 nm) increased and then decreased with [SDS] for [SDS]<cmc, and decreased with [SDS] for [SDS]>cmc, as shown in Fig. 5. Comparison of Figs. 3 and 5 reveals two opposite action of SDS on DTC, *i.e.*, the aggregation of the dye below the cmc, and the deaggregation of the dye above the cmc. The fluorescence spectra of the DTC–SDS solutions are shown in Fig. 6. The fluorescence peak shifted to 594 nm. The shift of ≈14 nm compared with the aqueous solution is due to the micellar environment. It is to be noticed that the 594 nm peak appeared even at [SDS]=6.0 mM, *i.e.*, in the *premicellar* region. This shows the presence of some aggregate which provides the micelle-like

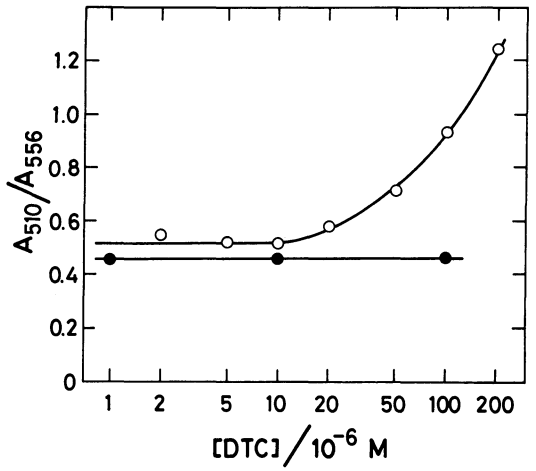

Fig. 3. The ratio of the absorbance of the 510 nm band to that of the 556 nm band.
○ In water, ● the corresponding ratio in methanol (In methanol, the peak and shoulder moved to 558 and 525 nm, respectively.).

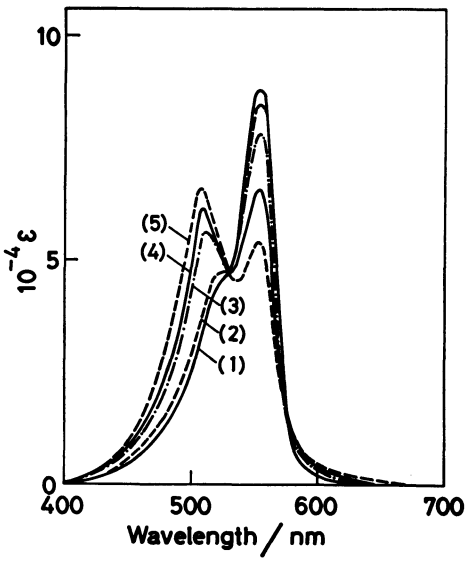

Fig. 2. Absorption spectra of DTC in aqueous solutions. (1) [DTC]=2×10^{-6} M—1×10^{-5} M, (2) 2×10^{-5} M, (3) 5×10^{-5} M, (4) 1×10^{-4} M, (5) 2×10^{-4} M.

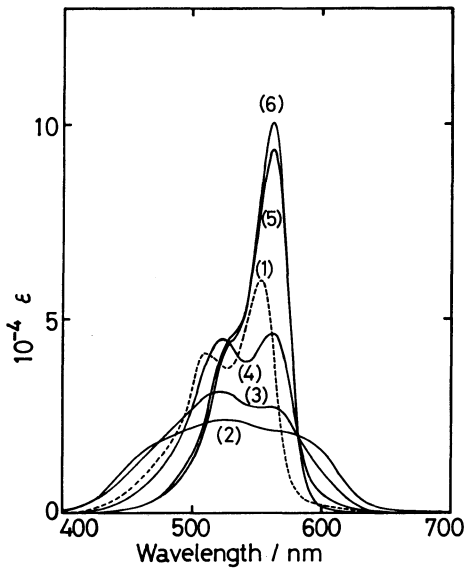

Fig. 4. Absorption spectra of DTC–SDS solutions. [DTC]=5×10^{-5} M, (1) [SDS]=0, (2) 3.0, (3) 4.0, (4) 5.0, (5) 8.0, (6) 10.0 mM.

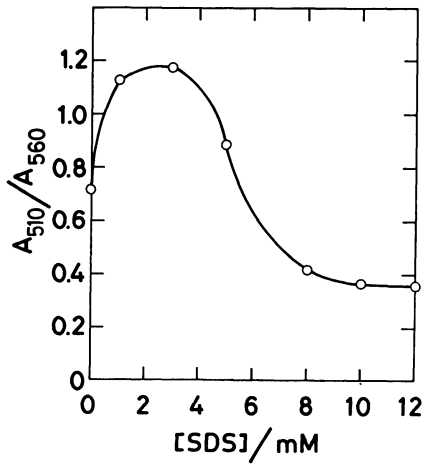

Fig. 5. The ratio of the absorbance of the 510 nm band to that of the 560 nm band.
[DTC]$=5.0\times10^{-5}$ M.

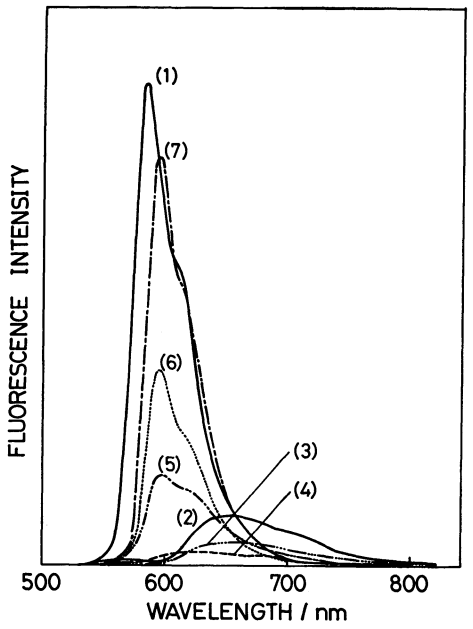

Fig. 6. Fluorescence spectra of DTC–SDS solutions.
[DTC]$=5.0\times10^{-5}$ M, (1) [SDS]$=0$, (2) 1.0, (3) 4.0, (4) 5.0, (5) 6.0, (6) 8.0, (7) 10.0 mM. The intensities are 10 times larger as shown for (6) and (7).

environment in this [SDS] region.

For [SDS]$=1$—4 mM, the absorption spectra are characterized with broad bands to the shorter wavelength of the dimer band and to the longer wavelength of the monomer band, as shown in Fig. 4. Fluorescence band in this [SDS] region appeared as a broad band with a peak around 655 nm, as shown in Fig. 6. Fine precipitate appeared around [SDS]$\cong1$ mM when the dye concentration was high.

Fluorescence Quantum Yield. The variation of fluorescence quantum yield (ϕ) of DTC as a function of [SDS] is shown in Fig. 7. The obtained value $\phi=0.03$ in water is comparable with the reported values $\phi=$ 0.048 in ethanol,[31] or 0.042 in water–methanol (9 : 1).[32] Fluorescence quenching which is evident in the pre-

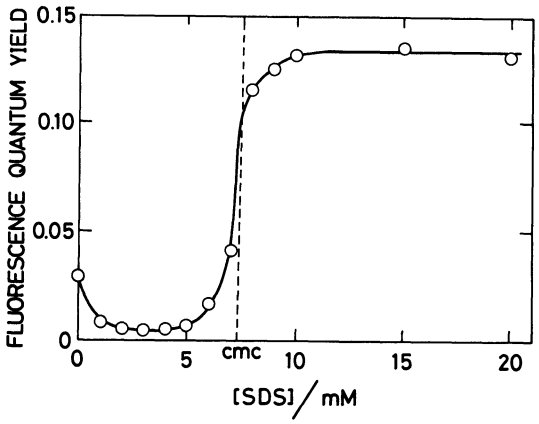

Fig. 7. Variation of fluorescence quantum yield of DTC as a function of [SDS], [DTC]$=2.0\times10^{-5}$ M.

micellar region must be the results of static and dynamic quenching of the monomer fluorescence by the presence of dimer and dye–SDS aggregate. The fluorescence quantum yield as compared with that in the aqueous solution is drastically enhanced by the addition of SDS above the cmc. This must be partly due to the deaggregation action of SDS micelles on the dye. However, this action alone cannot fully explain the observed enhancement of the fluorescence, because DTC molecules in the aqueous solution exist essentially as monomers at this [DTC] (2×10^{-5} M), as mentioned above in relation to the absorption spectra.

Fluorescence Decay. The nature of dye–detergent interaction is revealed most clearly in the fluorescence decay characteristics. The fluorescence decay curves for the aqueous solution ($\lambda_{max}=580$ nm) and SDS solutions ($\lambda_{max}=594$ nm) of DTC ([DTC]$=5.0\times10^{-5}$ M and 2.0×10^{-6} M) are shown in Figs. 8(a) and (b). An exponential decay with a lifetime of 100 ps was observed for the aqueous solution. The same decay behavior was observed over the whole concentration range studied (1.0×10^{-4}—2.0×10^{-6} M). It is comparable with that predicted by Roth and Craig[31] for methanol solution (150 ps). The observed decay is apparently that of the monomer, and the quenching by the dimer did not occur in these concentrations.

The decay behavior of the DTC (5.0×10^{-5} M)–SDS solutions (Fig. 8(a)) was found to depend largely on [SDS]. Such a large variation in the fluorescence decay behavior with [SDS] can be explained by comparison with the absorption and fluorescence spectra and by referring to the other cationic dye–SDS solutions (*e.g.* pinacyanol–SDS[12,14,24]). The fluorescence decay for [SDS]$=1.0\times10^{-2}$ M was exponential. Its lifetime, 410 ps, was much longer than that of the monomer in the aqueous solution (100 ps) mentioned above. Therefore, the decay behavior cannot be explained by the deaggregation effect alone.

For [SDS]$=8.0$ mM, the nonexponential decay behavior can be attributed to the presence of P_3, P_4, $\cdots$ micelles besides P_1 and P_2 micelles (P_1, P_2, $\cdots$ micelles are the micelles which incorporate one, two, $\cdots$, dye molecules). The distribution of dyes among micelles is usually treated in terms of Poisson statistics.[33] The

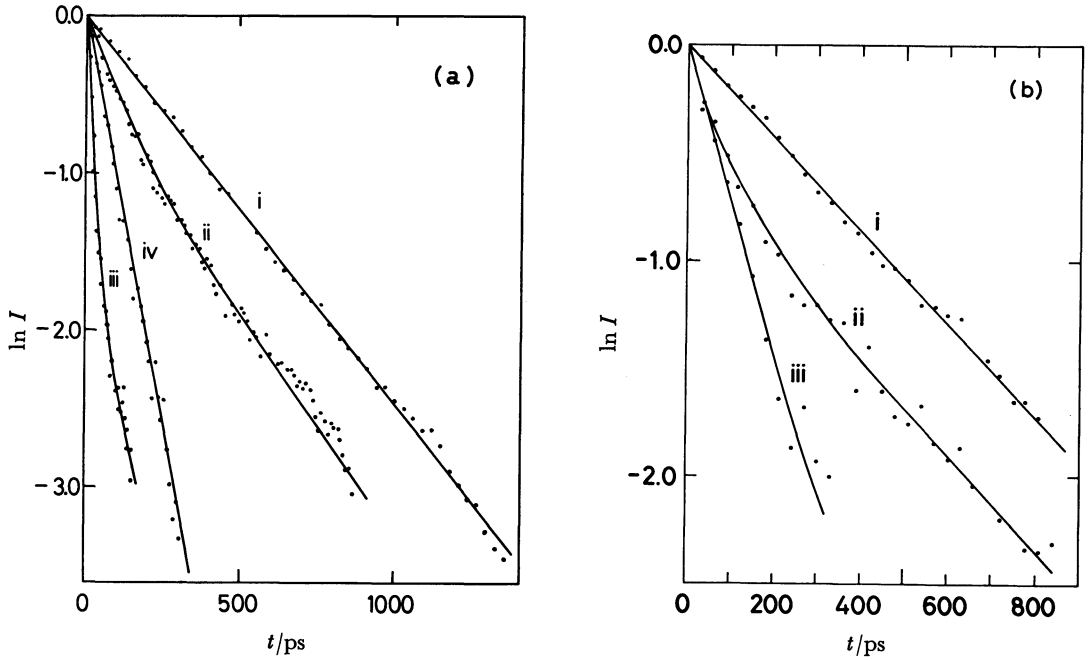

Fig. 8. Flourescence decay curves of DTC–SDS solutions.
(a) [DTC]$=5.0\times10^{-5}$ M, (i) [SDS]$=1.0\times10^{-2}$ M, (ii) 8.0×10^{-3} M, (iii) 5.0×10^{-3} M, (iv) 0 M; (b) [DTC]$=2.0\times10^{-6}$ M, (i) [SDS]$=1.0\times10^{-2}$ M, (ii) 5.0×10^{-3} M, (iii) 1.0×10^{-3} M. At [SDS]$=8.0\times10^{-3}$ M (not shown), the decay was almost identical to (i).

dye molecules in P_1 and P_2 micelles follow the monomer decay. Those in P_3, P_4, ··· micelles are, however, influenced by the quenching by dimers. The observed decay is the sum of the decays in P_1, P_2, P_3, ··· micelles and hence nonexponential.

For [SDS]$=5.0$ mM, the observed decay was very fast. Since the fluorescence band is a superposition of 594 and 655 nm fluorescence, where the latter seems to be enhanced by the energy transfer from the former, the decay must be composed of (1) that of the 594 nm fluorescence due to the dye molecules in the micelle-like environment (affected by the energy transfer mentioned above) plus (2) that of the 655 nm fluorescence. Apparently, the observed fast decay reflects only the decay of the component (1), since the component (2) is very weak compared with (1).

A similar [SDS]-dependent variation of fluorescence decays was observed for [DTC]$=2.0\times10^{-6}$ M (Fig. 8(b)). However, in this case each decay pattern appeared at the smaller [SDS] compared with the case of [SDS]$=5.0\times10^{-5}$ M. The slow decay with the lifetime $\approx$450 ps appeared at [SDS]$=10.0$ mM. An exponential decay with almost the same lifetime was observed at [SDS]$=8.0$ mM. The nonexponential decay (which is similar to the case of [DTC]$=5\times10^{-5}$ M and [SDS]$=8$ mM) appeared at [SDS]$=5$ mM. At [SDS]$=1$ mM the decay was very fast, as was observed for [DTC]$=5\times10^{-5}$ M and [SDS]$=5$ mM. A similar decay pattern which is dependent on both of [dye] and [SDS] has been reported for the acridine orange–SDS system.[12,34]

Discussion

The Effect of SDS on the Aggregation State of the Dye. The characteristics of the absorption and fluorescence spectra, fluorescence intensity and quantum yield of the dye–detergent systems as mentioned above reveal two opposite effects of SDS on the aggregation state of the dye, aggregation below the cmc and deaggregation above the cmc.

Dye–SDS Aggregate Formation in the Lower Premicellar Region. In the lower premicellar region ([SDS]$=$ 1—4 mM), the very broad absorption band and the weak, long-wavelength fluorescence band at 655 nm show the presence of some aggregated state of the dye.

Two types of higher aggregate of cyanine dyes, H-aggregate and J-aggregate are known.[35] The former is characterized with an absorption band to the shorter wavelength of the dimer band, while the latter with the absorption band to the longer wavelength of the monomer band. Resonance fluorescence is peculiar to the J-aggregate. The H- and J-aggregate have different stack structure, head-to-head and head-to-tail, respectively. While some *meso*-substituted or benzo-fused derivatives of DTC show the strong tendency to form H- and J-aggregates,[36–38] DTC itself does not. This is evident from the absorption spectra (Fig. 2) which are composed of only monomer and dimer bands to the limit of highest concentration limited by the solubility of the dye in water.

Contrary to this behavior in aqueous solutions, DTC forms higher aggregate in SDS solutions in the lower premicellar region, as shown by the presence of broad

absorption bands to the shorter and longer wavelengths of the monomer and dimer bands (Fig. 4). Clearly, the aggregates in this case are composed of the dye and SDS, *i.e.* the DTC–SDS aggregates. Then, what is their composition like? How are they related to the H- and/or J-aggregate in the aqueous solution of the related compound?

For some dye–detergent systems with the opposite charge, *e.g.*, pinacyanol–SDS[12,14,24] and Acridine Orange–SDS,[34] the dye–detergent aggregate forms a large particle and precipitates from the solution around [SDS]≈1—2 mM. This is due to the 1 : 1 complex of the cationic dye (D^+) and the dodecyl sulfate anion (S^-), $(D^+S^-)_n$.[24] In the DTC–SDS system presently studied, very minute particles appeared in the solution when [DTC] was high (*e.g.* 1.0×10^{-5} and 5.0×10^{-5} M) and [SDS] was around 1 mM.[39] These must be due to the $(D^+S^-)_n$ type aggregate. The DTC–SDS aggregate characterized with the very broad absorption band and the 655 nm fluorescence will also be due to the essentially 1 : 1 complexes dispersed and stabilized in the aqueous solution by the addition of slight excess of SDS molecules.[24]

The emission spectra of the related dye, 3,3′-diethyl-9-methylthiacarbocyanine iodide, at 78 K in EPA matrix were studied by Cooper and Liebert.[40] To the longer wavelength of the monomer fluorescence peak at 562 nm, a group of three emission peaks was observed in the 580—760 nm region. A sharp band at 594 nm was assigned to the dimer emission, a broad low-intensity band at about 648 nm to the excimer emission, and a sharp band near 680 nm to the triplet—singlet transition (phosphorescence). By referring to this observation, the broad structureless emission band of the DTC–SDS solution in the lower premicellar region ([SDS]≈1—4 mM) can be most reasonably assigned to the excimer fluorescence of the dye molecule in the DTC–SDS aggregate.

Resonance Raman spectra of DTC–SDS solutions give further information on the structure of the DTC–SDS aggregate.[39] The relative intensities of Raman bands varied as a function of [SDS]. For [DTC]= 1×10^{-5} M, the relative band intensities at [SDS]= 2.5 mM were very similar to those of solid DTC (KBr disk). DTC molecules in the DTC–SDS aggregate must be in the aggregation state like that of the dye in the solid state.

Not only the electrostatic attraction between the dye cation (D^+) and the dodecyl sulfate anion (S^-), but also the hydrophobic interaction between the dye molecules and detergent molecules must be working in the stabilization of the DTC–SDS aggregate in the lower premicellar region. When the electrostatic interaction becomes dominant (at the lower [SDS] edge of this [SDS] region), the precipitation of $(D^+S^-)_n$ occurs. The hydrophobic interaction becomes increasingly dominant with [SDS]. DTC–SDS aggregates change into dye-rich induced micelles and then into the ordinary micelles with increasing [SDS], as will be discussed later.

Deaggregation and Immobilization of the Dye above the cmc. The deaggregation of the dye, an effect of SDS which is opposite to that in the lower premicellar region, is evident above the cmc by monomer-type absorption spectra. The deaggregation is apparently due to the distribution of the molecules among micelles. However, the fluorescence intensity much enhanced, the quantum yield much larger, and the fluorescence lifetime much longer than in the aqueous solution cannot be explained by the deaggregation effect alone, because the enhancement occurred even for [DTC] at which the dye is present essentially as a monomer in the aqueous solution.

The enhancement of fluorescence intensity compared with the aqueous solution was explained as due to the environmental change (the hydrophobic environment) and/or to the immobilization of dye molecules in the miceller media.[1] The enhancement of a similar nature has been reported in a recent communication by Humphry-Baker *et al.*[41] for a cyanine dye–SDS solution, and by Nakashima and Kunitake[42] for some cyanine dyes bound to synthetic bilayer membranes. The enhancement in these systems were attributed to the inhibition of the radiationless decay by the micellar environment which immobilize the cyanine dyes to some extent.

The immobilization effect of micelles on dyes is revealed in the rotational diffusion. This was studied by transient absorption by Lessing and von Jena.[4] They obtained the rotational relaxation time (τ_R) of a few nanoseconds in the micellar media, in contrast to that of a few hundred picoseconds in solvents of low viscosity.[43–45] Humphry-Baker *et al.*[41] examined the rotational motion in excited states by fluorescence polarization measurements, and calculated the rotational rate about one order of magnitude smaller in the micellar than in alcoholic solutions. The prevention of rotational motion is more evident in the bilayer system of Nakashima and Kunitake.[42] The values of τ_R were obtained for the aqueous and SDS ([SDS]=15 mM) solutions of DTC from the fluorescence polarization to be 380 ps and 1.9 ns, respectively.

Such an effect of micelles on the movement of dye molecules has sometimes been expressed in terms of the "microviscosity (or, microscopic viscosity)." For example, the microviscosities of SDS or hexadecyltrimethylammonium bromide (HTAB) micelles measured near room temperature are reported to be about 15—30 cP.[3] The dependence of fluorescence intensity of the dyes on the viscosity of solvents has been extensively studied.[46–54] This effect is especially evident for cyanine dyes.[49–54] It is known that cyanine dyes undergo photochemical cis-trans isomerization at the central methine chain.[50,54–58] This photoisomerization process is one of the important nonradiative decay channels in cyanine dyes. The suppression of this process in the micellar media can explain the observed large fluorescence enhancement of cyanine dyes.

Formation of Dye-rich Induced Micelles in the Higher Premicellar Region. It is to be noticed that this fluorescence enhancement effect was not limited to the region above the cmc. It was found even in the *higher* premicellar region (*i.e.*, [SDS]=*ca.* 4 mM-cmc). This is clearly due to the presence of the chemical entity which provides the dyes with a micelle-like environment.

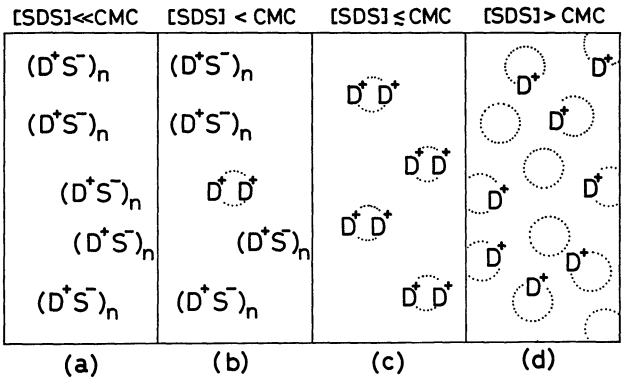

Fig. 9. A schematic model of the dye–detergent system with the opposite charge. See text for explanation.

In this [SDS] region the $(D^+ \cdot S^-)_n$-type 1 : 1 complex changes gradually with the [SDS] into the ordinary micelles above the cmc. The complex is successively diluted with SDS in this region. The presence of dye-rich induced micelles which incorporate a few dye molecules in the micelle-like aggregate in this [SDS] region has been proved by Mukerjee and Mysels for the pinacyanol–SDS system.[24] The energy-transfer efficiency between Rh-6G (donor) and DTC (acceptor) showed a maximum in this [SDS] region.[10] The fluorescence decay of the donor cannot be interpreted if the donor and acceptor are uniformly distributed in the solution, although [SDS] is *below* the cmc. Donor and acceptor molecules must be locally concentrated in dye-rich induced micelles.[11] The appearence of the maximum in the energy-transfer efficiency was found also in the Rh-6G–pinacyanol system,[12,14] for which the participation of dye-rich induced micelles in the energy transfer process is proved by the comparison with the absorption spectra. The maximum of electron-transfer efficiency also appeared in the premicellar region.[13,18]

Nature of Dye–Detergent Interaction. A schematic model of the dye–detergent system with the opposite charge is given in Fig. 9. In the lower premicellar region ([SDS]≅1—4 mM, (a) in the figure) the dye–detergent aggregate (with an essentially 1 : 1 composition, stabilized and dispersed in the aqueous solution by the addition of a slight excess of SDS) is formed. This aggregate is depicted as $(D^+S^-)_n$ in the figure for simplicity. This aggregate is successively diluted with SDS and changes into the dye-rich induced micelles in the higher premicellar region ([SDS]≅4 mM-cmc, (b) and (c) in the figure). The dye-rich induced micelles change into ordinary micelles above the cmc through further dilution with SDS ((d) in the figure).

Someone may argue that the presence of dye-rich induced micelles *below* the cmc is contradictory statement, and that the cmc itself must be lowered. However, the cmc is usually determined by the break of some *macroscopic* physical quantity like electrical conductivity. The addition of dye molecules to the SDS solution causes only a slight shift (*e.g.* by 0.1—0.4 mM) to the lower SDS region, as shown for Rh-6G–DTC–SDS,[10] acridine orange–SDS[34] or Rh-6G–pinacyanol–SDS.[14] The spectroscopic evidences for the presence of dye-rich induced micelles, *i.e.*, the absorption and fluorescence bands appearing at the wavelengths indicating micellar environment and the enhancement of the energy-[10–12,14] or electron-[13] transfer efficiency, are observed for [SDS] much lower the cmc thus newly determined for the dye–SDS system.

The presence of premicellar aggregates has been reported also for some metal complex cation-anionic detergent systems.[13,17–19,59–61] Ozeki *et al.*[61] carried out the measurements of surface tension and light scattering experiments for the $[Fe(phen)_3](ClO_4)_2$–SDS system (phen=1,10-phenanthroline), and clarified that (1) the shift of the cmc is rather small (7.6 mM to 7 mM) even in the presence of $[Fe(phen)_3](ClO_4)_2$ (5.0×10^{-5} M), and that (2) there is a threshold detergent concentration (C_{pre}) at which the formation of the premicellar aggregate starts far below the cmc (0.35 mM by the surface tension measurement). They stated that the hydrophobic interaction plays a very important part in the formation and stabilization of the premicellar aggregate. A similar mechanism of formation and stabilization by hydrophobic interaction must be present in our premicellar aggregates, *i.e.*, the essentially 1 : 1 complexes dispersed and stabilized in the aqueous solution by the addition of slight excess of SDS molecules which appeared in the lower premicellar region, and dye-rich induced micelles which appeared in the higher premicellar region.

The present authors are grateful to Dr. Yoshihumi Kusumoto of Kagoshima University for his cooperation in the earlier stage of this work. They are also grateful to Mr. Nobukazu Hata for his assistance in the quantum yield measurements. They are also grateful to Professor Shoichi Ikeda of Nagoya University for helpful discussions. This work is supported partly by the Joint Studies Program (1980—81) of the Institute for Molecular Science, and by the Grant-in-Aid No. 447006 from the Ministry of Education, Science and Culture.

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