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FLUORESCENCE DECAY OF 3,3'-DIETHYLTHIACARBOCYANINE IODIDE - SODIUM LAURYL SULFATE SYSTEM: DEAGGREGATION OF THE DYE AND DYE-DETERGENT AGGREGATE FORMATION ABOVE AND BELOW THE CRITICAL MICELLE CONCENTRATION

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Fluorescence decay of 3,3'-diethylthiacarbocyanine iodide was studied in aqueous solutions of sodium lauryl sulfate. The large change in decay behavior is attributed to the deaggregation of the dye and the formation of the dye-detergent aggregate above and below the critical micelle concentration, respectively.

Many peculiarities are found in the spectroscopic properties (e.g., change in absorption spectra and fluorescence quenching) of dyes with a detergent of opposite charge around the critical micelle concentration (cmc). For pinacyanol1) and thionine2) with an anionic detergent sodium lauryl sulfate (SLS), the absorption bands which are not found in aqueous solutions appeared. For Rhodamine 6G (Rh-6G) with SLS3), a large change in the intensity ratio among absorption bands and an extensive quenching of fluorescence were observed. The study of the fluorescence decay in these systems seems to be very important to clarify the nature of the interactions between the dye and detergent.

In the present paper, the fluorescence decays of aqueous solutions of 3,3'-diethylthiacarbocyanine iodide (DTC) and DTC-SLS were studied by a picosecond laser-streak camera technique. DTC ("Dotite" reagent from Dojindo) and SLS (Nakarai, protein research grage) were used as received. Water was distilled twice. Excitation was made by the second harmonic of a Nd:YAG laser (532 nm). The fluorescence decay was measured with a Hamamatsu C 979 streak camera. Steady-state fluorescence and absorption measurements were made by a Hitachi 650-10S fluorescence spectrophotometer and a Cary 14 spectrophotometer. All measurements were made at room temperature for aerated solutions.

In the aqueous solutions of DTC, the shape of the absorption band at 556 nm remained approximately the same for $[DTC] \lesssim 2.0 \times 10^{-5}$ M†. The dimer band at 510 nm

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† $1\ M = 1\ mol/dm^3$, $1\ mM = 1 \times 10^{-3}\ mol/dm^3$ in this paper.

became apparent for [DTC] $\gtrsim 5.0 \times 10^{-5}$ M. The fluorescence maximum appeared around 580 nm. This fluorescence band corresponds to the absorption band at 556 nm, and is attributed to the monomeric dye.

The fluorescence decays of aqueous solutions of DTC were found to be exponential. The lifetime, found to be 100 ps, was constant within the experimental error over the whole concentration range studied (1.0×10^{-4} M - 2.0×10^{-6} M). It is comparable with that predicted by Roth and Craig4) for methanol solution (150ps). The observed decay is apparently that of the monomer. The quenching by the dimer did not occur apparently. This seems to be reasonable in view of the low concentrations of the monomer and dimer.

The observed fluorescence decay curves of DTC (5.0×10^{-5} M)-SLS solutions are shown in Fig. 1. A Nihon Shinku Kogaku interference filter (579 nm) was used for i and iv. A cut-off filter V056 was used in its stead for ii and iii. The decay behavior was found to depend largely on [SLS]. The origin for such a large variation in the fluorescence decay behavior with [SLS] was studied by measuring absorption and fluorescence spectra of DTC-SLS solutions. Cmc of SLS was measured conductometrically and found to be 7.5×10^{-3} M (at 25 ± 0.1 °C), in good agreement with the published value (8.1×10^{-3} M).5)

The fluorescence spectra (λ_{ex}: 520 nm) are shown in Fig. 2. The shape of the fluorescence band for [SLS] > 5.0×10^{-3} M was found to be similar to the monomeric fluorescence in aqueous solutions apart from a small shift to the longer wavelength ($\lambda^{F}_{max} \sim 594$ nm), and can be attributed to the monomeric dye. A weak fluorescence band appeared around 655 nm for 5.0×10^{-4} M $\lesssim$ [SLS] $\lesssim 4.0 \times 10^{-3}$ M.6) Both of these components were observed for [SLS] = 5.0×10^{-3} M. In Fig. 3 is plotted the quantity $I_F A_{520}^{-1}$, where I_F and A_{520} are respectively the peak height of the fluorescence band and the absorbance at the exciting wavelength (520 nm), as a funciton of [SLS]. It gives a rough measure of fluorescence quantum yield. The intensity

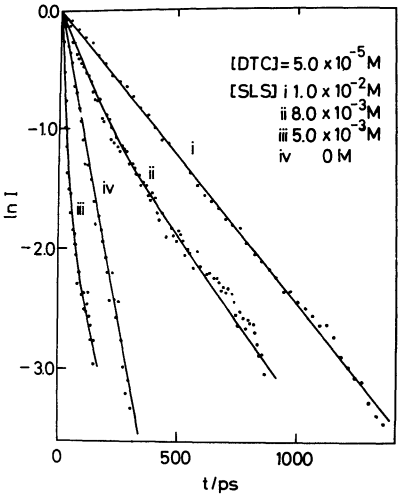

Fig. 1. Fluorescence decay curves.

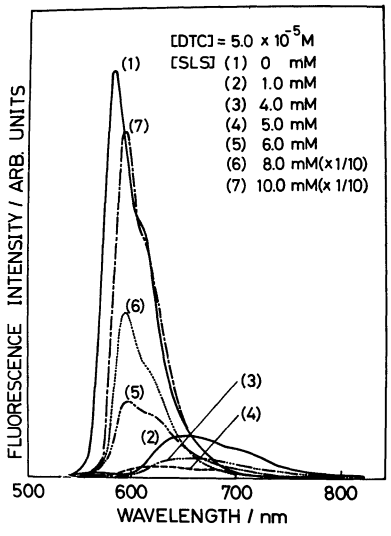

Fig. 2. Fluorescence Spectra.

of 594 nm fluorescence decreased with decreasing [SLS]. It was very weak at [SLS] = 5.0×10^{-3} M and hardly observable for 5.0×10^{-4} M $\lesssim$ [SLS] $\lesssim 4.0 \times 10^{-3}$ M.

The absorption spectra are shown in Fig. 4. For [SLS] > 8.0×10^{-3} M, i.e., above cmc, the 510 nm band decreased in intensity in comparison with the 560 nm band. The former band is related to the dimer band in aqueous solution, and the latter to the monomer band. For [SLS] < 8.0×10^{-3} M, the 510 nm band/560 nm band absorbance ratio increased with decreasing [SLS]. Broad absorption bands appeared on the shorter and longer wavelength side of these two bands for 5.0×10^{-4} M $\lesssim$ [SLS] $\lesssim 4.0 \times 10^{-3}$ M.

For [SLS] $\gtrsim 8.0 \times 10^{-3}$ M, the absorption spectra, together with the increased fluorescence intensity, indicate the deaggregation of dye molecules. Several authors[7,8] reported the deaggregation effect of Triton X-100, a nonionic detergent, on dyes above cmc. The fluorescence decay for [SLS] = 1.0×10^{-2} M was exponential. Its lifetime, 410 ps, was much longer than that of the monomer in aqueous solution mentioned above. This difference will be due to the environmental change (the hydrophobic environment) and/or to some immobilization of the dye molecules in the micellar media. The immobilization effect of dye molecules when they are incorporated in micelles has been shown by Lessing and Jena[9] by the change in rotational diffusion. Deaggregation effect plus such a factor cause a large increase in the fluorescence lifetime and quantum yield. The role of detergents when they are used to improve the dye laser action will be based on such an effect.

Mataga and Koizumi[3] observed the change in absorption spectra and fluorescence quenching for the Rh-6G-SLS system. They attributed the effect to the aggregation of dye ions and an orderly array of electrolyte (detergent) ions interacting together. Mukerjee and Mysels[1] studied the pinacyanol-SLS system by absorption spectra and by conductivity. This system is noted for the color change, i.e., the change in absorption spectra by the variation of [SLS]. The solution is red for [SLS] $\lesssim 4 - 5 \times 10^{-3}$ M, while it is blue above cmc. The transition region is found between them. They concluded the presence of two

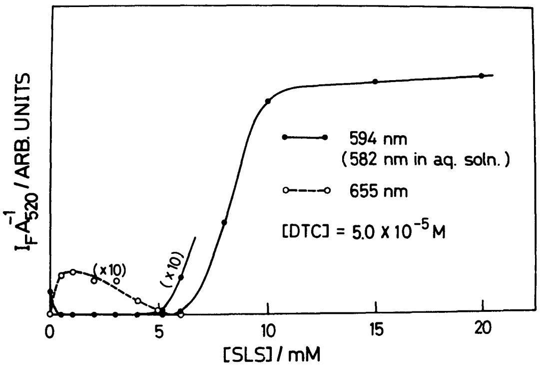

Fig. 3. Fluorescence intensity *vs.* [SLS].

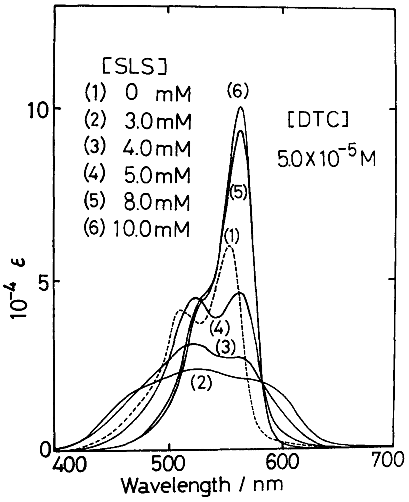

Fig. 4. Absorption spectra.

types of dye-detergent aggregate below cmc: (1) "dye-detergent salt which forms a stable suspension in the presence of somewhat more than stoichiometric amounts of detergent", and (2) "dye-rich induced micelles which solubilize the water-insoluble dye-detergent salt", in the red and transient region, respectively. DTC, being also a cationic dye, will form such an aggregate with SLS below and around cmc. Our recent studies[10,11] revealed the presence of dye-rich induced micelles below and around cmc on the basis of the enhanced energy transfer observed in the mixed dye system Rh-6G-DTC-SLS.

The significant change in absorption and fluorescence spectra indicate different types of DTC-SLS interaction for 5.0×10^{-4} M $\lesssim$ [SLS] $\lesssim$ 4.0×10^{-3} M and 5.0×10^{-3} M $\leq$ [SLS] $\leq$ cmc. The presence of dye-detergent aggregate of type (1) is plausible in the former region.[12] For [SLS] = 5.0×10^{-3} M, however, the aggregate of type (2), i.e., dye-rich induced micelles, overwhelms that of type (1), since the absorption spectrum shows only a little contribution of the broad bands. The fluorescence spectrum is a superposition of 594 nm fluorescence and 655 nm fluorescence, where the latter seems to be enhanced by the energy-transfer from the former. The decay for [SLS] = 5.0×10^{-3} M is that of the 594 nm fluorescence in dye-rich induced micelles (affected by the energy transfer mentioned above) plus that of the 655 nm fluorescence.

For [SLS] = 8.0×10^{-3} M, the curveture in the decay indicates that sizable number of dye molecules are in the dye-rich environment. This is reasonable, since a considerable number of micelles will incorporate several dye molecules from [micelle] = ([SLS] - cmc)/62 M = $(8.0 \times 10^{-3} - 7.5 \times 10^{-3})/62$ M = 8.1×10^{-6} M, where the number 62 is the aggregation number.[5]

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6) This is not from an irreversible reaction product, since an increase in [SLS] (> 5.0×10^{-3} M) recovered the 594 nm fluorescence intensity.
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12) Our recent study on pinacyanol-SLS system revealed the presence of a long-wavelength fluorescence band in the red solution. Its intensity change with [SLS] was quite similar to that of 655 nm fluorescence presently studied.

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