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Effects of Alkyl Chains of Thiacarbocyanine as the Sensitizer for the Photoreduction of Methylviologen in Micellar Phase

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Photoinduced reduction of methylviologen (MV^{2+}) by ethylenediaminetetraacetate was investigated with 3,3′-dialkylthiacarbocyanines as a sensitizer in the micellar solution of a nonionic surfactant, heptaethylene glycol monododecyl ether. The alkyl chains of the dyes were found to have considerable effects on the reaction rate. The fluorescence yield of a dye having two long alkyl chains, 3,3′-dioctadecylthiacarbocyanine (C_{18-18}) in the micellar phase was larger than that of the dye having only one long alkyl chain, 3-methyl-3′-octadecylthiacarbocyanine (C_{1-18}). This result was discussed in terms of the large effective volume associated with the intramolecular twisting motion in the excited state of C_{18-18}. Also, from the fluorescence quenching experiments, it was found that MV^{2+} was of easier access to C_{18-18} than C_{1-18} in the micellar phase. Thus, the relatively higher stability of the excited state of C_{18-18} and the easier access of MV^{2+} to C_{18-18} were considered to be responsible for the faster reaction rate achieved by C_{18-18} than by C_{1-18} in the micellar solution.

Molecular organization plays important roles in complex biochemical processes. Components of metabolic pathways are compartmentalized in membranes which provide suitable microenvironments and which control the flow of reactants, transients and products. Micelles, monolayers and vesicles (liposomes) have been exploited as membrane mimetic agents.[1-6] Micelles have been extensively used to mimic membrane mediated processes in relatively simple systems.[6-8] To explain the enhancement of enzyme reactions in micelles, the involvements of hydrophobic interaction of the enzyme with the micelles, steric effects of the micelles and specific physical states of the substrates in the micelles have been suggested.[9-11]

For photoinduced reactions, micellar effects on the charge separation in exciplexes and on the prevention of the recombination of the photoproducts have been demonstrated.[12-14] On the other hand, the stability of the excited states of sensitizers and also the accessibility of substances to the sensitizers could be important factors in determining the efficiency of photoinduced reaction. The former would be closely correlated with the microenvironment around the sensitizer, that is, with the local effective polarity and viscosity in the vicinity of the sensitizers.[15] If an amphiphatic dye molecule having distinct hydrophobic and hydrophilic portions is used as a sensitizer, it can be expected that the sensitizer is provided with a different microenvironment in the micelle by changing the hydrophobic-hydrophilic balance, that is, by changing the numbers and/or length of the alkyl chains of the sensitizer. In this study, we investigate the photoinduced reduction of methylviologen by ethylenediaminetetraacetate, sensitized in aqueous solution by 3,3′-dialkylthiacarbocyanine incorporated in the nonionic micelle, heptaethylene glycol monododecyl ether. The effects of the alkyl chains of the sensitizers on the reaction are examined. The results obtained are discussed in relation to the stabilization of the excited state of the sensitizers in the micellar microenvironment and the accessibility of substrates from the aqueous phase to sensitizers in the micellar phase.

Experimental

3-Methyl-3′-octadecyl-2,2′-thiacarbocyanine (C_{1-18}) and 3,3′-dioctadecyl-2,2′-thiacarbocyanine (C_{18-18})(their structures are shown in Fig. 1) were purchased from the Japan Research Institute for Photosensitizing Dye Co., Ltd and used without further purification. Methylviologen (1,1′-dimethyl-4,4′-bipyridinium, MV^{2+}) dichloride (Sigma) and disodium ethylenediaminetetraacetate (EDTA) (Dojindo Laboratories) were used as received. The nonionic surfactant, heptaethylene glycol monododecyl ether (HED) was obtained from Nikko Chemicals Co., Ltd. The surface tension *versus* concentration curve for the aqueous HED solution gave no minimum around the critical micelle concentration (cmc), and the value of cmc agreed with the reported value,[16] 8×10^{-5} M.†† Sodium dodecyl sulfate (SDS) supplied from Nakarai Chemicals Co., Ltd was recrystallized twice from ethanol. Tris(hydroxymethyl)-aminomethane (Tris) of analytical grade was used as recieved. Water was doubly distilled from a quartz still and other solvents were distilled once.

For sample preparations, chloroform solutions of the cyanine dyes and HED were mixed and the solvent evaporated. The residue was dried overnight in a vacuum desiccator and then solubilized with 2×10^{-3} M MV^{2+} solution which was buffered with 2×10^{-3} M Tris and 2×10^{-3} M $EDTA^{3-}$ at pH 7.0, where EDTA (pK_a=2.0, 2.8, 6.1, 10.2)[17] is present as the trivalent anion. C_{1-18} and C_{18-18} are insoluble in water, and therefore, all of the dye is incorporated in the micellar phase. The sample solution was placed in a quartz cell (1×1×4 cm) fitted with a stopcock and was freed of oxygen by bubbling nitrogen gas and then degassed by aspiration at 2700 Pa (20 mmHg) prior to irradiation. The cell was immersed in a water bath (25.0 °C) with a quartz window.

Irradiations were carried out using a Kondo Sylvania

†† 1 M=1 mol dm^{-3}.

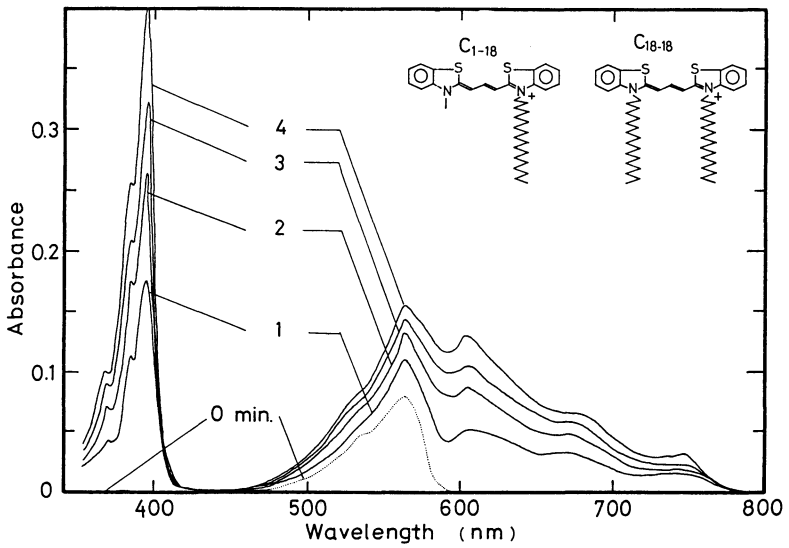

Fig. 1. Structures of sensitizers (C_{1-18} and C_{18-18}) and spectral changes of the solution due to the photoreduction of MV^{2+} using C_{18-18} as a sensitizer at 25.0 °C. 5×10^{-7} M of C_{18-18} is solubilized in 2×10^{-2} M HED micellar solution (2×10^{-3} M $EDTA^{3-}$, 2×10^{-3} M MV^{2+}, and 2×10^{-3} M Tris at pH 7.0). The solution is irradiated by a visible light ($\lambda>460$ nm) for 0, 1, 2, 3, and 4 min. The absorption band at 395 and 603 nm are contributed from MV^{+} formed by the reaction, and the band at 563 nm is attributed to C_{18-18} in the HED micellar phase.

1 kW tungsten halogen lamp. A Toshiba Y-46 cut-off filter was used to eliminate light of $\lambda<460$ nm. The distance from the irradiation source to the center of the cell containing sample solution was 10 cm. The sensitizer dyes had an absorption band around 560 nm in the micellar solution. On the other hand, reduced methylviologen (MV^{+}) formed by irradiation had an absorption maximum at about 603 nm. The latter band, however, resulted in faint reduction of the irradiation intensity (in this study, the reduction after 30 min's irradiation was at most 8% of the initial intensity).

The production of MV^{+} after intervals of irradiation was monitored by the absorption spectra on Shimadzu UV-180 spectrophotometer. The concentration of MV^{+} was calculated from the absorbance of the solution at 395 nm by taking $\varepsilon_{395nm}=3.8\times10^{4}$ M^{-1} cm.[18]

The measurement of the fluorescence yield was carried out for the dyes solubilized by HED in the buffer solution (2×10^{-3} M $EDTA^{3-}$ and 2×10^{-3} M Tris at pH 7.0) without MV^{2+}. The fluorescence spectra (excited at 530 nm) were observed with a Jasco FB-550 spectrofluorometer. The temperature was regulated at 25.0 °C by circulating water through the cuvette holders.

In order to determine the wavelength of the absorption maxima of the dyes in various solvents and micellar solutions, the first derivative absorption spectra were measured with a Hitachi-220 spectrophotometer.

The measurement of the viscosity of the various solvents has been described elsewhere.[19]

Results

Photoreduction of MV^{2+}. The deoxygenated solution containing a sensitizer dye in HED micellar phase and MV^{2+} in aqueous phase was irradiated with visible light. As a result, a blue color was developed in the presence of $EDTA^{3-}$. In Fig. 1, the changes of the absorption spectra are shown at varying irradiation times using C_{18-18} as a sensitizer. The development of absorption maxima at about 395 and 603 nm is charactaristic of the formation of MV^{+}.[20] Then, introduction of air into the cuvette resulted in the prompt reoxidation of MV^{+} to MV^{2+}

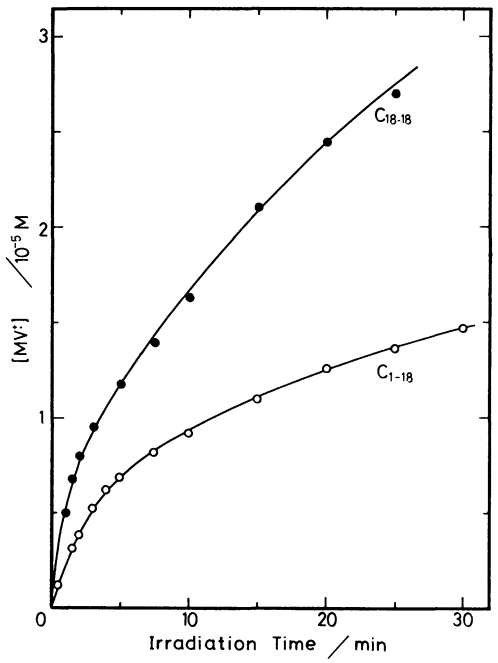

Fig. 2. Built-up of MV^{+} as a function of irradiation time.

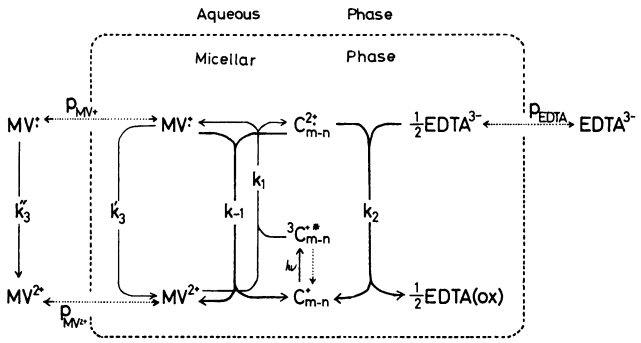

Fig. 3. The proposed mechanism of the photoreduction of MV^{2+} by $EDTA^{3-}$. C^{+}_{m-n} and $^3C^{+*}_{m+n}$ ($m=1$ or 18, $n=18$): sensitizer in the ground and the triplet exited state in the micellar phase, $C^{2+\cdot}_{m-n}$: sensitizer cation radical, EDTA(ox): the oxidized form of $EDTA^{3-}$, P_{MV2+}, P_{MV+}, and P_{EDTA}: the partition coefficient of MV^{2+}, MV^{+}, and $EDTA^{3-}$ from the aqueous to the micellar phase, and k_1, k_{-1}, k_2, and k_3: the rate constant of each reaction, respectively.

as manifested by decolorization.[20] The reduction of the concentration of the sensitizer dye after 30 min's irradiation was less than 5% of that before irradiation. Therefore, the contribution of the decrease of sensitizer to the formation rate of MV^{+} was not taken into account. In the dark or in the absence of $EDTA^{3-}$, no MV^{+} was produced.

In Fig. 2, the concentrations of MV^{+} formed are plotted against the irradiation time. The sensitizer dye having two long alkyl chains, C_{18-18}, exhibited faster formation of MV^{+} than C_{1-18} having only one long alkyl chain. In both cases, the formation rate of MV^{+} decreased with increase of the irradiation time. After removal of the light, the concentration of MV^{+} gradually decreased with increasing time owing to the reoxidation of MV^{+} to MV^{2+} by the small amount of dissolved oxygen in the solution. This reoxidation in the dark followed pseudo first-order kinetics, and the rate constant, k_3, had the same value in both sensitizers, being $5.4\times10^{-5}\ s^{-1}$. Such a reoxidation of MV^{+} to MV^{2+} may be considered to proceed not only after removal of the light but also during irradiation with light.

The proposed mechanism of the reaction is depicted in Fig. 3. Assuming that the concentration of the sensitizer cation radical ($C^{2+\cdot}_{m-n}$, $m=1$ or 18, $n=18$) is in the stationary state, and that mole of MV^{2+}, MV^{+}, and $EDTA^{3-}$ in the micellar phase is much smaller than the total mole in the micellar solution, the observed formation rate of MV^{+} can be written as

$$\frac{d[MV^{+}]_t}{dt} = \frac{k_1k_2[^3C^{+*}_{m-n}]_m[MV^{2+}]_m[EDTA^{3-}]^{1/2}_m}{k_{-1}(P_{MV+}[MV^{+}]_t)+k_2[EDTA^{3-}]^{1/2}_m} - k_3[MV^{+}]_t, \quad (1)$$

where $k_3=k'_3P_{MV+}+k''_3$. Here, $^3C^{+*}_{m-n}$ represents the sensitizer in the triplet excited state and P_{MV+} stands for the partition coefficient of MV^{+} from the aqueous to the micellar phases, $P_{MV+}=[MV^{+}]_m/[MV^{+}]_a$. The subscripts a, m, and t denote the concentration at the aqueous and the micellar phases and the total concentration in the micellar solution, respectively. For the case that $[MV^{+}]_t$ is small and $[MV^{2+}]_m$ is nearly equal to its initial value, $[MV^{2+}]^0_m$, and that $k_{-1}(P_{MV+}[MV^{+}]_t) \ll k_2[EDTA^{3-}]^{1/2}_m$, Eq. 1 reduces to

$$\frac{d[MV^{+}]_t}{dt} = k_1[^3C^{+*}_{m-n}]_m[MV^{2+}]^0_m, \quad (2)$$

which is the initial rate of formation of MV^{+} (V_{init}),

$$V_{init} = k_1[^3C^{+*}_{m-n}]_m[MV^{2+}]^0_m. \quad (3)$$

Since $[MV^{2+}]_t \gg [MV^{+}]_t$ and $[MV^{2+}]_m$ in Eq. 1 is, in this experiment, nearly equal to $[MV^{2+}]^0_m$ which is constant, Eq. 1 becomes

$$\frac{d[MV^{+}]_t}{dt} = \frac{V_{init}k_2[EDTA^{3-}]^{1/2}_m}{k_{-1}(P_{MV+}[MV^{+}]_t)+k_2[EDTA^{3-}]^{1/2}_m} - k_3[MV^{+}]_t, \quad (4)$$

which may be written as

$$\frac{1}{\frac{d[MV^{+}]_t}{dt}+k_3[MV^{+}]_t} = \frac{k_{-1}P_{MV+}}{V_{init}k_2[EDTA^{3-}]^{1/2}_m}[MV^{+}]_t + \frac{1}{V_{init}}. \quad (5)$$

Plots of $1/(d[MV^{+}]_t/dt+k_3[MV^{+}]_t)$ *versus* $[MV^{+}]_t$ according to Eq. 5 are shown in Fig. 4. Here, the observed values evaluated from Eqs. 6 and 7 were substituted for the values of $d[MV^{+}]_t/dt$ and $[MV^{+}]_t$, respectively.

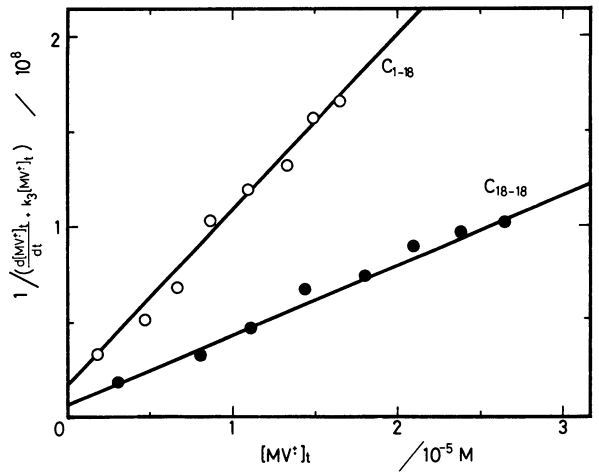

Fig. 4. Variation of $1/(d[MV^{+}]_t/dt+k_3[MV^{+}]_t)$ as a function of $[MV^{+}]_t$ according to Eq. 5.

$$\frac{d[MV^{+}]_t}{dt} = \frac{[MV^{+}]_{t(n+1)}-[MV^{+}]_{t(n)}}{t(n+1)-t(n)} \quad (6)$$

and

$$[MV^+]_t = \frac{[MV^+]_{t(n)} + [MV^+]_{t(n+1)}}{2} \quad (7)$$

where $[MV^+]_{t(n)}$ and $[MV^+]_{t(n+1)}$ are $[MV^+]_t$ at measuring time t=t(n) and $t(n+1)$, respectively. These plots give straight lines and its intercept leads to values for V_{init} of 6.1×10^{-8} and 1.3×10^{-7} M·s^{-1} and $k_{-1}P_{MV+}/k_2[EDTA^{3-}]_m^{1/2}$ of 5.2×10^5 and 5.3×10^5 M^{-1} for C_{1-18} and C_{18-18}, respectively.

Absorption Maxima of Sensitizer Dyes in Various Solvents. In our previous studies,[19] it was found that C_{18-18} showed a marked dependence of its absorption maximum on the solvent polarity (solvatchroism). The solvatchroism for C_{1-18} was measured. C_{1-18} also showed considerably large shifts in its absorption maximum in various aliphatic alcohols as solvents. Figure 5 shows the relationship between the wave number at the absorption maximum ($\tilde{\nu}_{max}$) and the dielectric constant (D) of alcohols. In both dyes, the values of $\tilde{\nu}_{max}$ of sensitizer dyes increased linearly with increasing of D. The values of $\tilde{\nu}_{max}$ of sensitizer dyes in the HED micellar phase are shown by the arrows in Fig. 5. The D in the vicinity of dye molecules in the miceller phase, which is defined as the effective dielectric constant (D_{eff}) in this study, was estimated using the values of $\tilde{\nu}_{max}$ and D for alcohols. These procedures lead to values for D_{eff} of 18.5 and 20.0 for C_{1-18} and C_{18-18}, respectively. These results indicate that effective micropolarity in the vicinity of the chromophore of the dye in the micellar phase corresponds to that of 1-propanol or 1-butanol.

Fluorescence Quantum Yield of the Sensitizer Dyes. The fluorescence yields of the sensitizer dyes in the micellar phases and aliphatic alcohols were evaluated as the fluorescence intensities integrated over the spectra and divided by the absorbance at the excited wavelength (530 nm). Their results are presented in Fig. 6 as the value (ϕ_f^R) relative to that of 3,3′-diethyl-2,2′-thiacarbocyanine (C_{2-2}) in the aqueous phase (2×10^{-3} M EDTA-Tris buffered solution, pH 7.0) at 25.0 °C. Both C_{1-18} and C_{18-18} showed larger yields in the solvent of lower polarity, *e.g.* C_{1-18} had the yield of about 2.5 times larger in 1-octanol than in methanol. Furthermore, C_{18-18}, which has two long alkyl chains, has greater fluorescence yields than C_{1-18} in all solvents studied here. The fluorescence yields in the micellar phases are larger than that in the solvents where dyes are provided with the same dielectric constant in the micellar phases.

Fluorescence Quenching of Sensitizer Dyes in Micellar Phase by MV^{2+} in Aqueous Phase. Fluorescence quenchings of sensitizers solubilized in HED and HED–SDS mixed micellar phases by MV^{2+} as a quencher were measured. In the HED micellar solution, the quenching was slight, while in the mixed micellar solution, intense quenching was observed. If the Langmuir adsorption isotherm is applied to adsorption on the micellar surface of the quencher, MV^{2+}, the Stern-Volmer equation[21] can be written as

$$\frac{\phi_f^R}{\phi_f^{R(MV)}} = k_q\tau\frac{[MV^{2+}]_\infty P[MV^{2+}]}{1+P[MV^{2+}]}. \quad (8)$$

Here, $\phi_f^R/\phi_f^{R(MV)}$ is the ratio of relative fluorescence quantum yields with and without the quencher, k_q is the rate constant of quenching, τ is the lifetime of the excited state of the sensitizer, $[MV^{2+}]_\infty$ is the concentration of saturated adsorption of MV^{2+} on the micellar surface, and P is a constant giving the strength of adsorption of MV^{2+}. Equation 8 is rewritten as

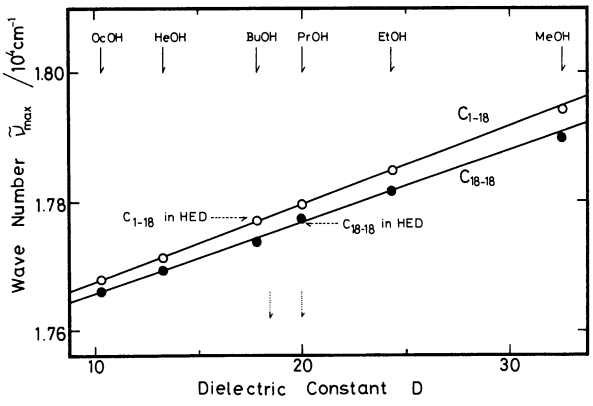

Fig. 5. Relationship of the wave number of absorption maxima ($\tilde{\nu}_{max}$) for C_{1-18} and C_{18-18} with dielectric constant D of solvent. MeOH: methanol, EtOH: ethanol, PrOH: 1-propanol, BuOH: 1-butanol, HeOH: 1-hexanol and OcOH: 1-octanol.

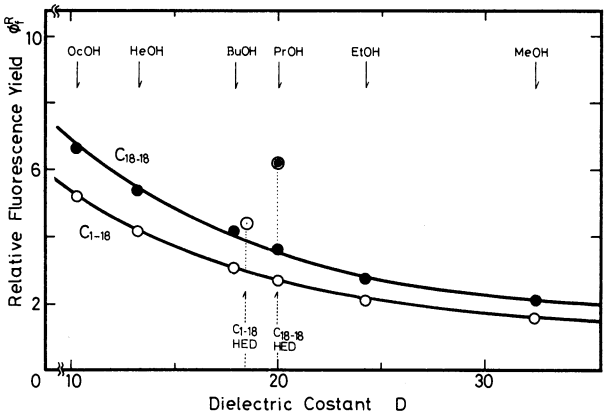

Fig. 6. Relationship of the relative fluorescence yield (ϕ_f^R) for C_{1-18} and C_{18-18} with dielectric constant D of solvent. ϕ_f^R is relative to the value for 3,3′-diethyl-2,2′-thiacarbocyanine (C_{2-2}) in the aqueous phase at 25.0 °C. (○) and (●): C_{1-18} and C_{18-18} in solvents, (⊙) and (◉): C_{1-18} and C_{18-18} in HED micellar phase.

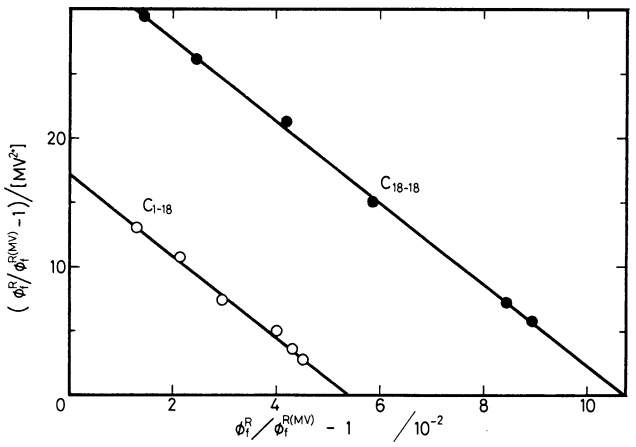

Fig. 7. Plots for fluorescence quenching of C_{1-18} and C_{18-18} in HED-SDS mixed micellar phase by MV^{2+} as a quencher, according to Eq. 9. The mole fraction of SDS in the mixed micelle is 0.1 (the total concentration of surfactants is 2×10^{-2} M). $\phi_f^R/\phi_f^{R(MV)}$ is the ratio of relative fluorescence yields without and with MV^{2+}.

$$\left(\frac{\phi_f^R}{\phi_f^{R(MV)}}-1\right)\frac{1}{[MV^{2+}]} = P\left\{k_q\tau[MV^{2+}]_\infty-\left(\frac{\phi_f^R}{\phi_f^{R(MV)}}-1\right)\right\}. \quad (9)$$

In Fig. 7, the experimental values of $(\phi_f^R/\phi_f^{R(MV)}-1)/[MV^{2+}]$ for various amounts of MV^{2+} are plotted against the values of $(\phi_f^R/\phi_f^{R(MV)}-1)$ for the mole fraction of SDS in the mixed micelle of 0.1 (the total concentration of surfactants is 2×10^{-2} M). These plots yield straight lines, giving the same slope, P, in both dyes, with a value of P of 3.2×10^2. The intercept on the $(\phi_f^R/\phi_f^{R(MV)}-1)$ axis gives values for $k_q\tau[MV^{2+}]_\infty$ of 5.4×10^{-2} and 1.1×10^{-1} for C_{1-18} and C_{18-18}, respectively. These results indicate that C_{18-18} is more easily quenched by MV^{2+} than C_{1-18} in the micellar solution.

Discussion

Photoinduced reduction of MV^{2+} by EDTA was first observed with tris-(2,2′-bipyridine)ruthenium as a sensitizer by M. Calvin *et al.*[22] In our study, 3,3′-dialkylthiacarbocyanines in a nonionic micelle were adopted as a sensitizer. With increase of irradiation time, the concentration of MV^+ increased but the formation rate of MV^+ decreased. Equation 1, which represents the formation rate of MV^+, indicates that the decrease in the rate with irradiation time arises from the increase of $[MV^+]_t$. After removal of the light, the rate of disappearance of MV^+ due to reoxidation to MV^{2+} is equal to the second term, $k_3[MV^+]_t$, on the right-hand side of Eq. 1.

The initial rate of formation of MV^+, V_{init}, presented by Eq. 3 is proportional to the product of k_1 and $[^3C^{+*}_{m-n}]_m$, because $[MV^{2+}]_m$ is constant independent of a sensitizer. Therefore, the difference in V_{init} is estimated from the differences in k_1 and $[^3C^{+*}_{m-n}]_m$ for C_{1-18} and C_{18-18}.

Effects of Microenvironment on Fluorescence Yield. According to the proposed mechanism shown in Fig. 3, it is clear that the concentration of the sensitizer in the triplet excited state ($^3C^{+*}_{m-n}$) generated from the sensitizer in the singlet excited state ($^1C^{+*}_{m-n}$) plays an important role in the reaction. The relative yield of the intersystem crossing from the singlet excited state (ϕ^R_{isc}) is given by

$$\phi^R_{isc} = \alpha\frac{k_{isc}}{k_{rl}+k_f+k_{isc}}. \quad (10)$$

On the other hand, the relative fluorescence yield of the sensitizer (ϕ_f^R) is

$$\phi_f^R = \alpha'\frac{k_f}{k_{rl}+k_f+k_{isc}}, \quad (11)$$

and therefore, their ratio is

$$\frac{\phi^R_{isc}}{\phi_f^R} = \alpha''\frac{k_{isc}}{k_f}. \quad (12)$$

Here, k_{rl}, k_f, and k_{isc} are the rate constants for radiationless relaxation, radiative (fluorescence) relaxation and intersystem crossing of the excited state, $^1C^{+*}_{m-n}$, and α, α', and α'' are proportionality constants. Since k_f and k_{isc} are considered to be less dependent on the environmental properties,[23-25] the increase in ϕ_f^R is accompanied by the increase in ϕ^R_{isc} as shown in Eq. 12. Since $[^3C^{+*}_{m-n}]_m$ is proportional to ϕ^R_{isc}, $[^3C^{+*}_{m-n}]_m$ can be estimated using ϕ_f^R.

The increase in ϕ_f^R would result from the decrease of the rate constant of radiationless process, k_{rl}. It has been suggested that k_{rl} largely depends on the interaction of the excited dye molecule and the environment around it,[23] that is, the microenvironment in the vicinity of the dye molecule. The microenvironment would actually mean the local effective micropolarity and microviscosity around the dye molecule.

In order to evaluate the micropolarity, the wave number at the absorption maxima of dyes solubilized in the micellar phases were compared with their dependencies on solvent polarity. The reason for employing aliphatic alcohols to calibrate the micropolarity in the micellar phase have already been discussed in detail.[26-28] As seen from Fig. 5, the chromophores of C_{1-18} and C_{18-18} accommodated in the micellar phases are provided with a remarkably less polar environment in comparison with that in the aqueous phase, but they seem to be in a more polar environment than in a liquid hydrocarbon. These results indicate that the chromophores are

located in the surface region of the micelle. The chromophore having two long alkyl chains, C_{18-18}, seems to be located in a somewhat more polar environment than C_{1-18}.

As shown in Fig. 6, the fluorescence yields of both dyes are larger in the micellar phases than in the solvents where dyes are provided with the same dielectric constant in the micellar phases. The microenvironmental effects on the fluorescence yield of dyes would contain polarity and also viscosity factors. These are usually associated with each other in a complex way and can not be investigated separately.

Carbocyanine dyes have been known to exhibit intense twisting modes along the polymethine chain in the electronically excited state.[29-31] This is because in the excited state, the conjugated π electronic structure is broken; this allows twisting modes of the substituents at each end and a destruction of the initial planar structure. The ability of such an intramolecular twisting, which may be strongly affected from the viscosity in the vicinity of the dye molecule, is associated with the internal conversion process of the singlet excited state to the ground state and therefore, with the fluorescence yield.

The radiationless relaxation process of the excited state is divided as

$$k_{rl} = k_a + k_b. \tag{13}$$

Here, k_a is the rate constant of the usual internal conversion which is independent of the viscosity in the vicinity of the dye molecule but dependent on the polarity around the dye molecule. The quantity k_b is the rate constant for relaxation *via* a twisting mode which is influenced by the microscopic viscosity around the dye molecule. Using the Stokes equation, k_b is given as[32,33]

$$k_b = \beta\left(\frac{T}{\eta}\right). \tag{14}$$

Here, β is a function of the effective volume associated with the intramolecular twisting, η is the viscosity of the medium and T is absolute temperature. From Eqs. 11, 13, and 14, the following equation is derived[33]

$$\frac{1}{\phi_f^R} = \frac{1}{\phi_f^{0R}} + \left(\frac{A}{k_f}\right)\left(\frac{T}{\eta}\right). \tag{15}$$

Here, $A=\beta/\alpha'$ and ϕ_f^{0R} is the relative fluorescence yield when the relaxation via twisting mode is absent as $\phi_f^{0R}=\alpha' k_f/(k_a+k_{isc}+k_f)$. It is already known that the relation between the fluorescence yield of Auramine O and the viscosity of the mixed solvent is well described by Eq. 15.[32,38] Equation 15 was examined for C_{1-18} and C_{18-18} in aliphatic alcohols at 25 °C. In these cases, however, no simple correlation, as expected from Eq. 15, was obtained and this is explained by the effective polarity in these solvents. Eq. 15 was, therefore, examined for the viscosity change of a single solvent with change of temperature. Plots of the reciplocal of ϕ_f^R for C_{1-18} and C_{18-18} in ethanol, 1-propanol and 1-butanol *versus* T/η gave straight lines as expected from Eq. 15 (its figure[19] is not shown). The slope and the intercept of the lines allow k_f/A and ϕ_f^{0R} to be evaluated. Figure 8 shows plots of k_f/A and ϕ_f^{0R} as functions of D for C_{1-18} and C_{18-18}. It is seen from Fig. 8 that the greater the polarity of the solvent, the smaller is ϕ_f^{0R} and the larger is k_f/A. The k_f/A is the value which increases with increase of the effective volume associated with the twisting, because $A=\beta/\alpha'$. The larger value of k_f/A in a polar solvent is ascribed to the solvation of the dye molecule. In the same solvent, the value of k_f/A for C_{18-18} is about twice as large as that for C_{1-18}. This indicates that the twisting of the dye molecule affects the radiationless relaxation process of the electronic excited state remarkably and that long alkyl chains such as octadecyl groups have an important effect upon the twisting of the dye molecules and make a great contribution to the effective volume associated with

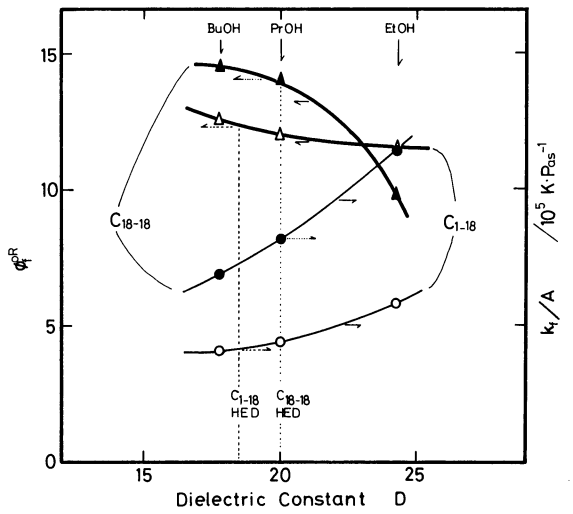

Fig. 8. ϕ_f^{0R} and k_f/A shown as functions of dielectric constant (D). ϕ_f^{0R}: the relative fluorescence yield when the relaxation via intrarotational mode is absent, k_f/A: the value increasing with increase of the effective volume associated with the twisting.

Table 1. Experimental results of C_{1-18} and C_{18-18} in micellar phase

Sensitizer Dye	ϕ_f^R	ϕ_f^{0R}	k_f/A / 10^5 K·Pa·s^{-1}	η_{eff} / 10^{-3} Pa·s
C_{1-18}	4.1	12.3	4.2	4.4
C_{18-18}	6.2	14.0	7.4	4.5

ϕ_f^R: Relative fluorescence yield, η_{eff}: effective microviscosity, ϕ_f^{0R} and k_f/A: see Eq. 15.

Table 2. Experimental values of C_{1-18} and C_{18-18} in micellar solution

Sensitizer dye	$\frac{V_{init}}{M \cdot s^{-1}}$	$\frac{\left(\frac{k_{-1}P_{MV+}}{k_2[EDTA^{3-}]_m^{1/2}}\right)}{M^{-1}}$	$k_q \cdot \tau \cdot [MV^{2+}]_\infty$	k_q^R
C_{1-18}	6.1×10^{-8} (1)	5.2×10^{5}	5.4×10^{-2} (1)	1
C_{18-18}	1.3×10^{-7} (2.1)	5.3×10^{5}	1.1×10^{-1} (2.0)	1.3

V_{init}: The initial rate of formation of MV^+, τ: the life time of the excited state of sensitizer dye, k_q^R: the relative value of the rate constant of quenching.

the twisting.

If the polarity of the solvent is constant, Eq. 1 gives a straight line as mentioned before. Rearrangement of Eq. 15 leads to

$$\eta = \frac{T\phi_f^{0R}\phi_f^R}{(\phi_f^{0R}-\phi_f^R)\frac{k_f}{A}}. \quad (16)$$

When Eq. 16 is applied to micellar systems, the values in the solvent where dyes are provided with the same effective polarity in the micellar phase should be used. Therefore, the values of ϕ_f^{0R} and k_f/A of dye in alcohols of D, 18.5 for C_{1-18} and 20.0 for C_{18-18}, are assigned to those in the micellar phase (See Fig. 8). Substituting the value of ϕ_f^R in the micellar phase for ϕ_f^R in Eq. 16 yields values for the effective microviscosity in the micellar phase (η_{eff}). Table 1 shows the values of η_{eff} together with ϕ_f^R and k_f/A in the micellar phase. The η_{eff} has about the same value in both dyes, being 4.5×10^{-3}—4.6×10^{-3} Pas (4.5—4.6 cP).

As seen from Table 1, the difference in the values of ϕ_f^{0R} between both dyes is slight. Therefore, the large ϕ_f^R of C_{18-18} in the micellar phase compared with C_{1-18} can be ascribed to the relatively large effective volume ($1/A$) associated with the twisting. This indicates that the two long alkyl chains of C_{18-18} play an important role in the enhancement of the fluorescence yields. On the basis of an estimation of the fluorescence yield, it is suggested that the concentration of the sensitizer dye in the triplet excited state for C_{18-18} having two long alkyl chains is larger than that for C_{1-18} having only one long alkyl chain.

Access of MV^{2+} to Sensitizer Dye in Micellar Phase. As shown in Eq. 3, the initial rate of photoinduced reduction studied here is subject to the reaction between the sensitizer dye in the triplet state and MV^{2+} approching from aqueous to micellar phases. The D of dyes in the micelle indicated that the chromophore of C_{18-18} is located nearer to the micellar surface than that of C_{1-18}, and that C_{18-18} is more easily attacked by MV^{2+} at the miceller surface than C_{1-18}.

In order to obtain additional information about the accesibility of MV^{2+} to the excited sensitizer dye in the micellar phase, measurements of the quenching efficiency of fluorescence of the dye by MV^{2+} were carried out. From the experimental results, it was found that the value of P in Eq. 8 was the same for both dyes, indicating that the adsorption on the micellar surface of the quencher is not influenced by dyes in the micellar phase, and that the value of $k_q\tau[MV^{2+}]_\infty$ evaluated from experimental results was about 2.0 times larger for C_{18-18} than C_{1-18}. On the assumption that $(\tau)_{C(18-18)}/(\tau)_{C(1-18)} \approx (\phi_f^R)_{C(18-18)}/(\phi_f^R)_{C(1-18)}$, the following relation is obtained,

$$\frac{(k_q\tau[MV^{2+}]_\infty)_{C(18-18)}}{(k_q\tau[MV^{2+}]_\infty)_{C(1-18)}} = \frac{(k_q\tau)_{C(18-18)}}{(k_q\tau)_{C(1-18)}} \approx \frac{(k_q\phi_f^R)_{C(18-18)}}{(k_q\phi_f^R)_{C(1-18)}}, \quad (17)$$

because $[MV^{2+}]_\infty$ has the same value for both sensitizer dyes. Here, the parentheses show the terms for C_{1-18} and C_{18-18}, respectively. By using Eq. 17 and the values of ϕ_f^R and $k_q\tau[MV^{2+}]_\infty$ for C_{1-18} and C_{18-18}, the values of $(k_q)_{C(18-18)}/(k_q)_{C(1-18)}$ were evaluated. The results are presented in Table 2 as the value (k_q^R) relative to that of C_{1-18}. The value of k_q^R for C_{18-18} is 1.3 times larger than C_{1-18}. This difference in k_q^R may probably be ascribed to the difference in the location of the chromophores of these dyes in the micellar surface. Thus, it is also indicated from the data for the fluorescence quenching that C_{18-18} is more easily attacked by MV^{2+} than C_{1-18} at the micellar surface.

As shown in Table 2, the product of ϕ_f^R in the micellar phase and k_q^R, that is, $k_q\tau[MV^{2+}]_\infty$ is 2.0 times larger for C_{18-18} and agrees with the ratio of V_{init}, being 2.1. This indicates that the difference in V_{init} of C_{1-18} and C_{18-18} may be explained in terms of the difference in the fluorescence yield of the sensitizer dye in the micellar phase and in the accessibility of MV^{2+} to excited sensitizer dyes in the micellar phase.

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