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Effect of Micellar Environment on the Photoreduction of Azo Dyes Sensitized by Tetraphenyl Porphyrin Derivatives

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Photoelectron transfer from tris(hydroxymethyl)aminomethane (Tris) to methyl orange (MO) or methyl yellow (MY) as an electron acceptor was studied with $\alpha,\beta,\gamma,\delta$-tetraphenyl porphyrin (TPP) and $\alpha,\beta,\gamma,\delta$-tetraphenyl porphyrin trisulfonic acid (TPPS) as sensitizers. The reaction efficiency was reduced when the sensitizer was solubilized in heptaethyleneglycol dodecyl ether (HED) micelles. The partitioning of the sensitizers (TPP, TPPS) and the electron acceptors (MO, MY) was estimated by means of absorption spectral measurements in the micellar solution. At HED concentrations above 0.5 mM in aqueous solution, the sensitizers (TPP, TPPS) were completely solubilized in the micellar phase and thus the reaction environment was transferred from the aqueous phase to the micellar phase. The decrease of the reaction rate in the micellar environment can be explained in terms of the lower polarity in the micellar phase which inhibits charge separation in the sensitizer-acceptor excited complex (exciplex). The reaction rate of the TPPS–MO system was the highest and that of the TPP–MY system was the lowest in the micellar phase, because the former system was accommodated in a rather polar micellar environment, while the latter system was located in a less polar micellar environment. It was also observed that an increase in micellar concentration resulted in a decrease of the reaction rate. This was found to be caused by the decreases in the local concentrations of sensitizer and acceptor, not by a change of the reaction environment.

Keywords——photoreduction; sensitizer; tetraphenyl porphyrin; azo dye; heptaethyleneglycol dodecyl ether; charge separation; micellar solution; micellar environment

Surfactant micelles have been widely investigated in connection with the solubilization, stabilization and absorption of various drugs.[1-3] The catalytic and retarding effects of micelles on the degradation of drugs are considered to be related to the micelle–drug interactions.[3] To clarify the micellar effect on the reaction, the effective polarity and the mutual orientation and accessibility of reactants at micellar surfaces have been taken into consideration.[1,2,4,5]

For photoreactions in micellar solution the following factors are considered to play important roles; (1) the distribution of reagents between micelles and aqueous bulk phase, and the local concentrations in the micellar phase, (2) the stability of photoexcited states of the sensitizer in micellar solution, (3) the mutual orientation and accessibility of electron donor and acceptor in the micellar phase, and (4) the effect of micellar polarity on charge separation

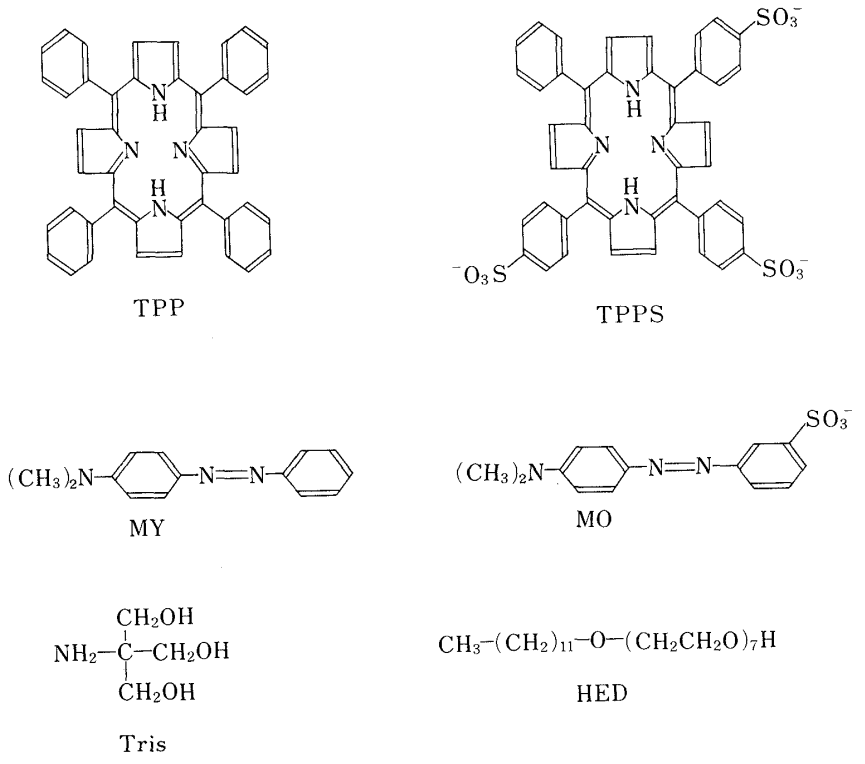

Fig. 1. Structures of Sensitizers (TPP, TPPS), Electron Acceptors (MO, MY), Electron Donor (Tris) and Surfactant (HED)

of the excited complex.[1,2,5-7)]

In our previous work, dioctadecyl and diethyl thiacarbocyanines were employed to sensitize the photo-induced electron transfer from ethylenediamine tetraacetic acid (EDTA) to methyl viologen in the micellar or liposome phase.[5a)] The high viscosity and the low polarity in micellar and liposome phases as compared with the aqueous bulk phase gave rise to remarkable stabilization of the excited states of the sensitizer (factor 2). Further, the accessibility of the sensitizer and the electron acceptor at the micellar surface, determined by means of fluorescence quenching studies (factor 3), was found to be important in the reaction. In previous work, we investigated the photoreduction of methyl orange (MO) sensitized by $\alpha,\beta,\gamma,\delta$-tetraphenyl porphyrin in anionic, cationic and zwitterionic surfactant micelles. The efficiency of charge separation was significantly dependent on the kind of surface charge of the micelles.[5b)]

In this study, we measured the photo-induced electron transfer from tris(hydroxymethyl)aminomethane (Tris) to MO or methyl yellow (MY) sensitized by $\alpha,\beta,\gamma,\delta$-tetraphenyl porphyrin (TPP) and $\alpha,\beta,\gamma,\delta$-tetraphenyl porphyrin trisulfonic acid (TPPS) incorporated in nonionic micelles of heptaethyleneglycol dodecyl ether (HED) in aqueous solution. The electron acceptors, MO and MY, have the same chromophore with and without a sulfonate group, and the sensitizers, TPP and TPPS, also have the same chromophore with and without three sulfonate groups (see Fig. 1). The addition of sulfonate groups in the reagent molecules will result in a change in location of the reagent in the micellar phase and will affect the charge separation in the exciplexes. The anomalous effect of micellar concentration on the reaction rate was interpreted in terms of the micellar local concentration of the reagents.

Experimental

Materials——MO and MY were obtained from Wako Pure Chemical Industries, Ltd. TPP and TPPS were

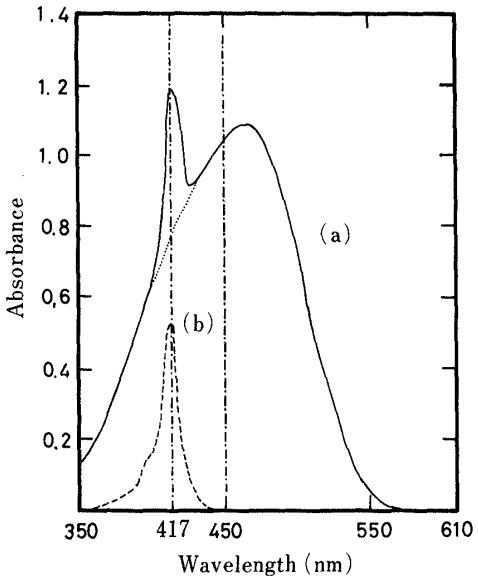

Fig. 2. Absorption Spectra of MO and TPPS
(a) (------) MO; 5×10^{-5} M. (b) (– – – –) TPPS; 1×10^{-6} M. The medium contained 1 mM Tris-HCl at pH 7.3, 20 °C.

purchased from Dojindo Laboratories. Nonionic surfactant, HED, was obtained from Nikko Chemicals Co., Ltd. The surface tension and concentration curve for aqueous HED solution gave no minimum around the critical micelle concentration, and the value of the latter (8×10^{-5} M) agreed well with the reported value.[8] Tris(hydroxymethyl)-aminomethane of analytical grade was obtained from Nakarai Chemicals Co., Ltd. All solvents were distilled before use.

Measurements——Aliquots of TPP or MY were removed from the stock solution in benzene; the solvent was evaporated off and the residue was dried under a vacuum. These reagents were solubilized by HED in 1 mM Tris-HCl buffer solution. The water-soluble TPPS and MO were directly diluted from their stock solutions with the HED micellar solution or the buffer solution. The pH of the aqueous solution was maintained at 7.3. The concentrations of sensitizer (TPP or TPPS), acceptor (MO or MY) and electron donor (Tris) used in this work were 1×10^{-6}, 5×10^{-5} and 1×10^{-3} M, respectively.

The irradiation source used was a 1 kW tungsten lamp for a slide projector. The well-stirred sample solution was contained in a quartz jacket and kept at 20 °C by circulation of thermostated water. The decrease of absorbance of azo dyes was monitored with a Hitachi model 100-10 spectrophotometer at 450 nm. These procedures gave excellent reproducibility in the photoreduction of azo dyes. The absorbance spectra of TPP, TPPS, MO and MY in aqueous or micellar solutions were measured with a Shimadzu UV-180 spectrophotometer at 20 °C. The sensitizing dyes, TPP and TPPS, have sharp Soret bands around 417 nm. The electron acceptors, MO and MY, have rather broad absorption bands around 450 and 410 nm respectively. When a sensitizer was absent, no decrease of the electron acceptors by irradiation was observed. The acceptor absorption bands have appreciable intensities at the sensitizer Soret bands and therefore, correction of the irradiation intensity for the effect of the sensitizer is necessary to estimate the exact photoelectron transfer rate (see Fig. 2).

The fluorescence spectra of TPP and TPPS in the HED micellar solution were measured with a Jasco model FP-550 spectrofluorometer (Jasco, Tokyo, Japan). The relative fluorescence yields were evaluated as the integrated fluorescence intensities and divided by the absorbance at the exciting wavelength (415 nm).

Results

Photoreduction of MO and MY

Photoreduction rates of the azo dyes, MO and MY, in the HED micellar solution and in the aqueous buffer solution were measured with TPP or TPPS as a sensitizer. The electron donor used here was tris(hydroxymethyl)aminomethane (Tris). The structures of TPP, TPPS, MO, MY and Tris are presented in Fig. 1.

The electron transfer mechanism can be represented briefly as

$$S \xrightarrow{h\nu} {}^1S^* \quad (1)$$

$${}^1S^* \longrightarrow {}^3S^* \quad (2)$$

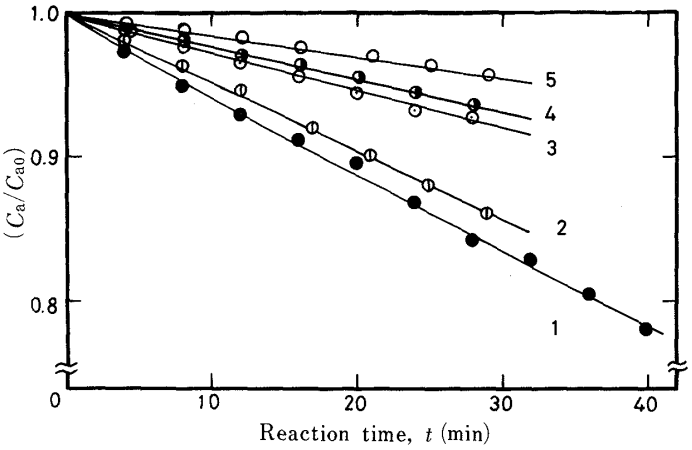

Fig. 3. Decreases of MO Concentration by Photoreduction

(C_a/C_{a0}) is the ratio of MO concentration to the initial value, obtained from absorbance measurements at 450 nm. The medium contained 5×10^{-5}, 1×10^{-6}, 1×10^{-3} M MO, TPP and Tris-HCl respectively. pH = 7.3. 20 °C. HED concentration (mM): (1) 0.8; (2) 2; (3) 5; (4) 8; (5) 15.

$$^3S^* + A \longrightarrow (S-A)^* \quad (3)$$

$$(S-A)^* \longrightarrow S^+ + A^- \quad (4)$$

$$S^+ + D \longrightarrow S + D^+ \quad (5)$$

Here, S, $^1S^*$ and $^3S^*$ represent the sensitizers in the ground state, in the singlet excited state, and in the triplet excited state, respectively. A and D indicate the electron acceptor and the donor. $(S-A)^*$ is the exciplex (excited complex) of sensitizer and acceptor. S^+ and A^- represent the cation radical of sensitizer and the anion radical of acceptor.

In Fig. 3, the decreases of MO concentration as the ratio to the initial value, C_a/C_{a0}, caused by the photoreduction are plotted as a function of reaction time for various HED micellar concentrations. The value of C_a/C_{a0} was determined by measuring the absorbance of MO at 450 nm, where the absorbance of the sensitizer was small enough to be neglected. The sensitizer used was TPP. The reduction rate of MO was found to be higher at lower HED concentrations. A 50-fold change in Tris concentration did not affect the reduction rate of MO.

As described in the experimental section, the absorption bands (the Soret bands) of TPP and TPPS have considerable overlaps with the absorption of the acceptor (MO, MY) and therefore, the effective irradiation intensity for the sensitizer (TPP, TPPS) increases with the progress of photoreduction of MO or MY (see Fig. 2).

The effective light intensity at a distance x from the cell front, I, is related to the absorbances of the sensitizer, A_s, and the acceptor, A_a, as follows:

$$dI = -I[(A_s + A_a)\ln 10]\,dx \quad (6)$$

The light absorbed by the sensitizer in a cell of 1 cm length, Q, is given by Eq. 7 as

$$Q = \int_0^1 A_s(\ln 10) I dx \quad (7)$$

and

$$Q = \frac{A_s}{A_s + A_a}\left\{1 - \exp[-(A_s + A_a)\ln 10]\right\} I_o \quad (8)$$

Because a change in the concentration of Tris had no effect on the reaction rate, the photoreduction is considered to be a first-order reaction with respect to the acceptor concentration, *i.e.*,

$$\frac{dC_a}{dt} = (k/I_o) Q C_a \quad (9)$$

Here, k is the apparent reaction rate constant, which includes the effect arising from the light intensity at the cell front ($x=0$), I_0. Equation 8 can be substituted into Eq. 9 to give the following equation:

$$-\mathrm{d}\ln C_a = k\left(\frac{A_s}{A_s+A_a}\right)\left\{1-\exp\left[-(A_s+A_a)\ln 10\right]\right\}\mathrm{d}t \qquad (9')$$

Integration of Eq. 9′ with the use of the relation, $-\mathrm{d}\ln C_a = -\mathrm{d}\ln A_a$, leads to Eq. 10.

$$kA_s t = -\int \frac{A_s+A_a}{1-\exp\left[-(A_s+A_a)\ln 10\right]}\mathrm{d}\ln A_a \qquad (10)$$
$$\equiv -\alpha$$

The values of α can be obtained by graphical integration at 417 nm. In Fig. 4, the values of $-\alpha$ thus obtained are shown as a function of the reaction time, t, for various concentrations of HED. The slopes of the linear relations obtained here give the values of kA_s. Since A_s is constant and can be obtained by absorption measurement, we can obtain the values of k. The values were estimated for TPP–MO, TPPS–MO, TPP–MY and TPPS–MY systems in the

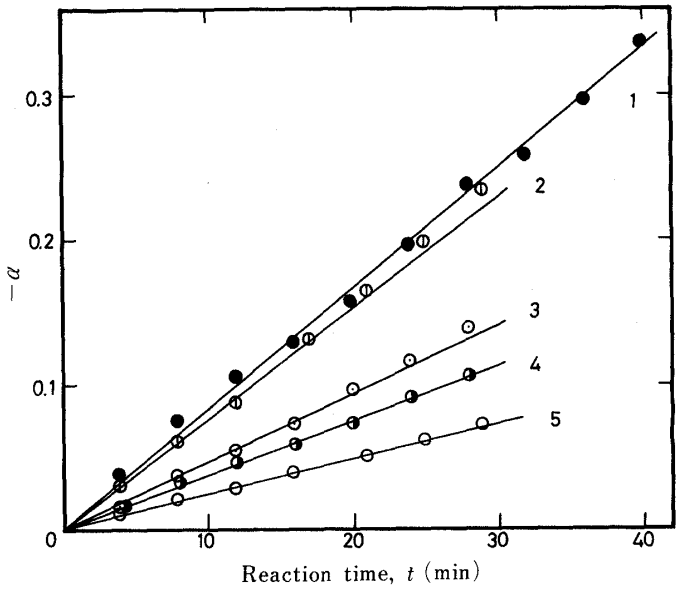

Fig. 4. Variation of the $-\alpha$ Value as a Function of Reaction Time t

The medium was the same as in Fig. 2. HED concentration (mM): (1) 0.8; (2) 2; (3) 5; (4) 8; (5) 15.

TABLE I. Rate Constant of Photoreduction

Acceptor[a]	Sensitizer[b]	Medium HED concentration (mM)	Apparent rate constant k (s^{-1})	Rate constant in micellar phase k_m (s^{-1})
MO	TPP	0.8	3.84×10^{-4}	
MO	TPP	2	2.01×10^{-4}	
MO	TPP	5	1.33×10^{-4}	4.88×10^{-7}
MO	TPP	8	1.11×10^{-4}	
MO	TPP	15	0.73×10^{-4}	
MO	TPPS	0	5.55×10^{-4}	—
MO	TPPS	4	4.54×10^{-4}	
MO	TPPS	8	2.65×10^{-4}	1.21×10^{-6}
MO	TPPS	16	1.36×10^{-4}	
MY	TPP	4	0.58×10^{-4}	1.15×10^{-7}
MY	TPPS	4	1.08×10^{-4}	2.13×10^{-7}

a) 5×10^{-5} M. b) 1×10^{-6} M, donor 1×10^{-3} M Tris-HCl (pH = 7.3).

HED micellar solutions.

In Table I, the k values obtained are shown; it was found that they decrease remarkably with increase of the surfactant concentration, and at a given HED concentration they are larger when TPPS is used as sensitizer than when TPP is employed. It was also found that MY is less reactive than MO, although these two dyes have the same chromophore.

The photoreduction of MO with TPPS was also examined in mixtures of water and dioxane. It is clear that the k value decreases as the dioxane content increases and the dielectric constant of the mixture of water and dioxane decreases (see Table II).

Distribution of Reagents between Micelles and Aqueous Bulk Phase

For a reaction in a heterogeneous system such as a micellar solution, the determination of the distributions of reagents participating in the reaction is essential. As shown in Fig. 5, MO exhibits a large shift of the absorption maximum upon addition of HED to the aqueous phase. The absorption maxima in the aqueous solution and 10 mM HED micellar solution are 463 and 426 nm, respectively. Further addition of HED to the solution did not give rise to an appreciable change in the absorption spectra. The absorbances of MO at 410, and 470 nm in HED micellar solutions, A_1 and A_2, respectively, are therefore,

$$A_1=(\varepsilon_1^b n_b+\varepsilon_1^m n_m)/V \tag{11}$$

$$A_2=(\varepsilon_2^b n_b+\varepsilon_2^m n_m)/V \tag{12}$$

Here, n_b and n_m are the amounts (mol) of MO in the bulk and the micellar phases. ε_1^b and ε_2^b are the molar extinction coefficients in the aqueous phase at 410 and 470 nm, respectively, and ε_1^m and ε_2^m are those in the micellar phase. V is the volume of the solution containing the micelles, and the volume of the micellar phase, v, is negligibly small as $v \ll V$. The total amount (mol) of MO in the solution, $n_t=n_b+n_m$. The partition coefficient, P, for the

TABLE II. Rate Constant of Photoreduction

Acceptor[a]	Sensitizer[b]	Medium Dioxane volume fraction	Dielectric constant	Apparent rate constant k (s^{-1})
MO	TPPS	0	78.6	5.55×10^{-4}
MO	TPPS	0.2	60.5	2.10×10^{-4}
MO	TPPS	0.5	33.0	1.05×10^{-4}
MO	TPPS	0.8	10.5	0.33×10^{-4}

a) 5×10^{-5} M. *b*) 1×10^{-6} M, donor 1×10^{-3} M Tris-HCl (pH = 7.3).

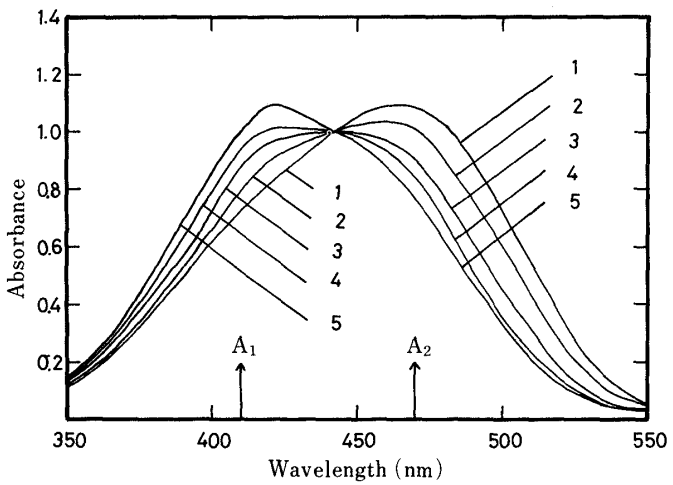

Fig. 5. Absorption Spectra of MO

MO; 5×10^{-5}, Tris-HCl 1×10^{-3} M (pH = 7.3). HED concentration (mM): (1) 0; (2) 0.52; (3) 1.2; (4) 2; (5) 8. See Eqs. 11—14.

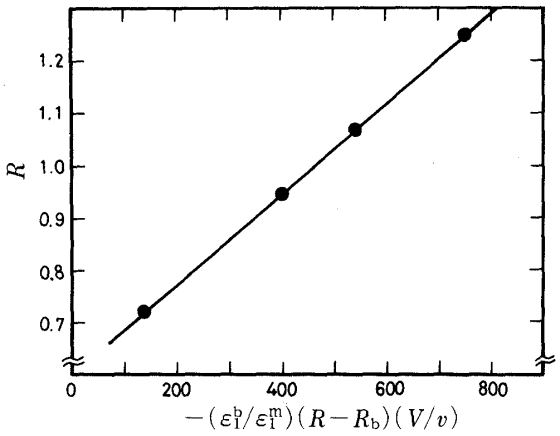

Fig. 6. Variation of R Value for MO as a Function of $-(\varepsilon_1^b/\varepsilon_1^m)(R-R_b)(V/v)$

$(\varepsilon_1^b/\varepsilon_1^m)=0.727$, $R_b=1.473$. The v values were estimated as $v=M_{HED}(c-cmc)\rho$, $M_{HED}=494$, cmc$=8\times10^{-5}$ M, $\rho=1\,cm^3/g$. See Eqs. 11—14.

partition equilibrium of MO between the bulk and the micellar phase is given as

$$P=(n_m/v)/(n_b/V) \tag{13}$$

From Eqs. 11, 12 and 13, the ratio of absorbances, $R=(A_2/A_1)$, can be represented as follows:[5)]

$$R=R_m-(1/P)(\varepsilon_1^b/\varepsilon_1^m)(R-R_b)(V/v) \tag{14}$$

Here, $R_m=\varepsilon_2^m/\varepsilon_1^m$ and $R_b=\varepsilon_2^b/\varepsilon_1^b$. In Fig. 6, the experimental values of R for various amounts of HED in MO solutions are plotted against the values of $-(\varepsilon_1^b/\varepsilon_1^m)(R-R_b)(V/v)$, where the volume of micellar phase, v, is evaluated by the use of the value of $1.0\,g/cm^3$, which is the density of the micellar phase in aqueous solution.[9)] The linear relation obtained in this figure gives a value of P of 1.2×10^3. The mol fraction of MO in the micellar phase (n_m/n_t) can be calculated by the use of Eq. 15:

$$n_m/n_t=\frac{P(v/V)}{1+P(v/V)} \tag{15}$$

On the other hand, the acceptor, MY, and the sensitizer, TPP, are solubilized in aqueous solution only with the help of the surfactant, and therefore, they are incorporated exclusively in the micellar phase. On the basis of the absorption spectral measurements, TPPS, which is soluble in water, is completely transferred from the bulk aqueous phase to the micellar phase with a very small amount (less than 0.5 mM HED) of the surfactant. Consequently, in the micellar solution, almost all TPPS exists in the micellar phase over the HED concentration range studied here.

Thus, in the micellar solution, both sensitizers exist only in the micellar phase. Since the formation of an exciplex between the sensitizer and the electron acceptor is essential for the reaction, the reaction is considered to occur in the micellar phase, irrespective of the distribution of acceptor between the micellar and the bulk phases.

Discussion

Local Concentration of Reagents in Micellar Phase

Since the sensitizers TPP and TPPS are completely solubilized in the micellar phase, the photoreduction of MO or MY takes place only in the micellar phase. The following factors must be considered in connection with the reaction in the micellar phase; (1) the reaction occurs only in the small volume fraction of micellar solution, v/V, (2) the real concentration of sensitizer and acceptor in the micellar phase is not (n_t/V) but (n_m/v).

Taking the above factors into account, Eq. 9 can now be reexamined. Because $C_a=$

(n_t/V), the following equation can be written:

$$-\mathrm{d}(n_t/V)/\mathrm{d}t=(k/I_o)Q(n_t/V) \tag{16}$$

If, however, k_m is defined as the reaction rate constant in the micellar phase, the following equation (analogous to Eq. 16) may be written by replacing (n_t/V) with (n_m/v) and also by replacing Q with $Q(V/v)$:

$$-\mathrm{d}(n_m/v)/\mathrm{d}t=(k_m/I_o)(QV/v)(n_m/v) \tag{16a}$$

Since the reaction takes place exclusively in the micellar phase, the decrease of total amount of MO accompanying the photoreduction is equal to that in the micellar phase, that is, $\mathrm{d}n_m=\mathrm{d}n_t$. Further, v and V are independent of t, so the following equation is derived:

$$-\mathrm{d}(n_t/V)/\mathrm{d}t=(k_m/I_o)Q(n_m/v) \tag{16b}$$

When MO, which is distributed between the micelle and aqueous phases, is employed as an acceptor, n_m is related with n_t by Eq. 15, and Eq. 16b is obtained

$$-\mathrm{d}(n_t/V)/\mathrm{d}t=(k_m/I_o)Q\frac{P}{1+P(v/V)}(n_t/V) \tag{17}$$

because,

$$(n_m/v)=\frac{P}{1+P(v/V)}(n_t/V) \tag{18}$$

and therefore,

$$k=k_m\frac{P}{1+P(v/V)} \tag{19}$$

On the other hand, when MY, which is insoluble in the aqueous bulk phase, is used as acceptor, we have

$$(n_m/v)=(n_t/v)=(V/v)(n_t/V) \tag{20}$$

and Eq. 16 is reduced to

$$\begin{aligned}-\mathrm{d}(n_t/V)/\mathrm{d}t&=(k/I_o)Q(n_t/V)\\&=(k_m/I_o)Q(V/v)(n_t/V)\end{aligned} \tag{21}$$

and thus

$$k=k_m\frac{V}{v} \tag{22}$$

Equations 19 and 22 indicate that the apparent rate constant k is dependent on the volume fraction of micellar phase in solution, $(v/V)[\fallingdotseq v/(V+v)]$. When the v/V value increases, the apparent rate constant k decreases.

In Fig. 7, the variations of k in the photoreduction of MO with surfactant concentration are shown for TPP and TPPS as sensitizers. The theoretical value of k is calculated by the use of Eq. 19 based on k_m obtained from the slope and the intercept of the line in Fig. 8. The theoretical curves are in good agreement with the experimental data. The k_m values thus obtained are shown in Table I. For the reaction with MY as an acceptor, Eq. 22 is used to evaluate the k_m values. The variation of k with (v/V) can be understood in terms of the local concentration of the acceptor in the micellar phase, (n_m/v), obtained from Eq. 18 for MO, and from Eq. 20 for MY. In both cases, the ratio of the local concentration in the micellar phase to

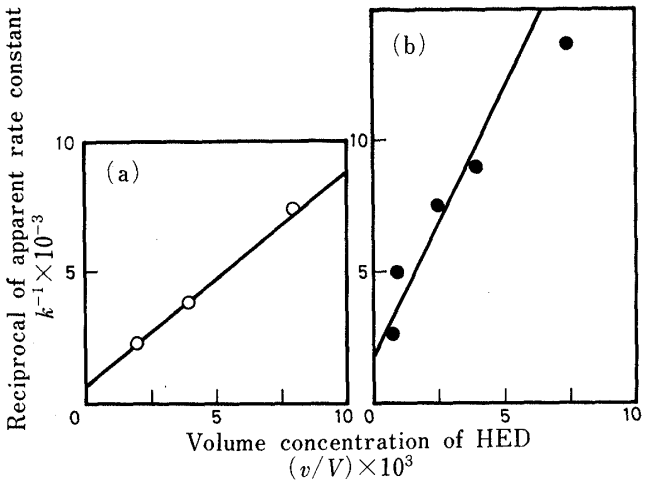

Fig. 7. Apparent MO Photoreduction Constant k as a Function of Volume Concentration of HED, (v/V)

(a) Sensitizer TPPS. (b) Sensitizer TPP. The solid line represents the theoretical result with k_m=(a) $1.21\times10^{-6}\,s^{-1}$, (b) $4.88\times10^{-7}\,s^{-1}$ and $P=1.2\times10^3$. See Eq. 19.

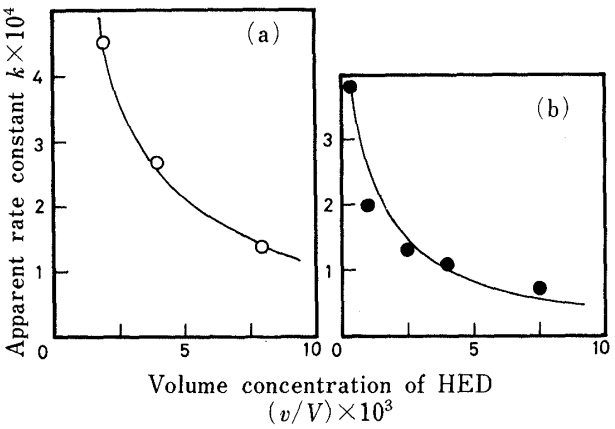

Fig. 8. Reciprocal of Apparent MO Photoreduction Constant k as a Function of Volume Concentration of HED, (v/V)

(a) Sensitizer TPPS. (b) Sensitizer TPP. The slope of the line gives $1/k_m$ and the intercept $1/k_mP$. See Eq. 19.

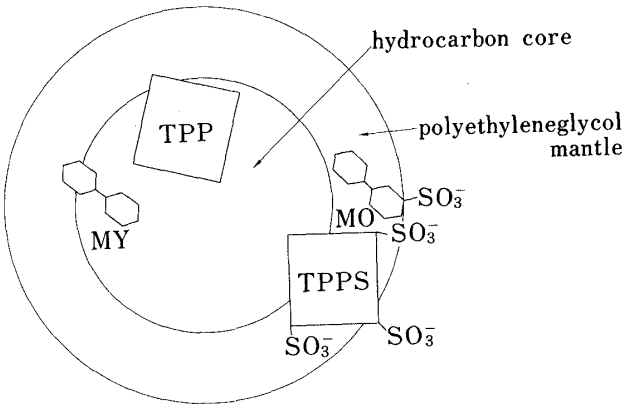

Fig. 9. Schematic Representation of the Locations of Acceptors (MO, MY) and Sensitizers (TPP, TPPS) in HED Micelles

the overall concentration, $(n_m/v)/(n_t/V)$, decreases with increasing micellar volume, v.

In the MO–TPPS system, both reagents are soluble in water and k is largest in the absence of HED. Therefore, it may seem that the apparent rate constant should be reduced because the concentrations of both reactants in the aqueous bulk phase decrease with increasing amount of the surfactant. However, the experimental data agreed well with the theoretical curve which is based on the assumption that the reaction occurs only in the micellar phase, thus providing confirmation of the validity of this assumption even in the MO–TPPS system.

Effect of Location of Sensitizer and Acceptor

It is particularly noteworthy that k_m is highest when both sensitizer and acceptor have sulfonate groups, (MO–TPPS), while k_m is the lowest if neither sensitizer nor acceptor has the hydrophilic sulfonate group (TPP–MY). In these photoreductions, the process shown in Eq. 2, is mainly controlled by the stability of the excited state, $^1S^*$. The stability of the $^1S^*$ state is closely related to the (relative) fluorescence yield. The measured relative fluorescence yields of TPP and TPPS were almost the same and therefore, the process presented by Eq. 2 has little effect on the difference of the reaction rate constants, k_m, of TPP and TPPS. The process shown by Eq. 3 is controlled by the local concentration of acceptor and sensitizer and was

dealt with in the preceding section. The efficiencies of fluorescence quenching of TPP and TPPS by MO in the micellar solution were measured and found to be similar to each other. These results suggest that the accessibilities of MO to TPP and TPPS are comparable. The process shown by Eq. 4 is the charge separation of the exciplex of sensitizer and acceptor, and plays an important role in the photoreaction.[10,11] When the medium surrounding the exciplex is polar, the cation and the anion radicals generated from the exciplex are stabilized by solvation by the polar solvent molecules. On the other hand, when the environment of the exciplex is nonpolar, the cation and the anion radicals are not stabilized by solvation and the recombination of the radicals is enhanced.

To investigate the effect of the medium on the photoreduction, mixtures of water and dioxane with various compositions were examined as reaction media. The results obtained are shown in Table II, and indicate that the larger the water content is, the higher the reaction rate is. A large water content in the mixture provides a polar environment for the exciplex and enhances the charge separation.

A micelle is considered to be a combination of a nonpolar hydrocarbon core and a rather polar surface layer,[12] and therefore, a micelle supplies environments of various polarities. TPPS and MO have strong hydrophilic sulfonate groups and are located in the outer surface layer of micelles, while TPP and MY are solubilized in the rather nonpolar environment. The charge separation of the exciplex formed between TPPS and MO occurs at the polar surface layer in the micelles and the cation and the anion radicals separated from the exciplex are stabilized by interaction with the environment, whereas the exciplex composed of TPP and MY is accommodated in the rather nonpolar environment and the recombination of the radicals generated from the exciplex takes place quite easily. These processes are shown schematically in Fig. 9.

It is known that even aromatic hydrocarbons such as benzene, naphthalene and pyrene are incorporated not in the central hydrocarbon core but in the region near the surface of micelles.[1,13,14] It is likely that the rather large molecules of TPP and MY are embedded over the core and the polyethyleneglycol mantle, while TPPS and MO are located at the mantle and expose their sulfonate groups to the aqueous phase. The ion radicals generated from the exciplex composed of TPPS and MO are thus stabilized in the rather polar micellar environment, and the stabilization leads to the highest reaction efficiency of the TPPS–MO system in the micellar phase. On the other hand the TPP and MY molecules are located in the nonpolar environment and have the lowest reaction efficiency. The k_m values for the TPP–MO and TPPS–MY systems shown in Table I are intermediate between those of the TPPS–MO and TPP–MY systems, and these systems are considered to be located in environments with intermediate polarity.

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