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The Photoreduction and Photosensitized Reduction of Dyes Bound to a Surfactant Micellar Surface

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The photochemical reduction of thionine(Th) and Methylene Blue(MB) bound to anionic sodium dodecyl sulfate(SDS) micelles in an aqueous solution was inhibited at the lower concentration range of a reductant anion, EDTA, because of the electrostatic repulsion between the micelles and the reductant. The concentration dependence of EDTA on the quantum yield of photoreduction has shown to be, anomalously a sigmoidal type: this is explained by mechanistic interpretation based on the cooperative effects of the ionic strength and the essential concentration of EDTA. The enhancement effect for the quantum yield of the photoreduction of eosine bound to a cationic micelle by the EDTA anion was conversely observed, because of the electrostatic attraction. When 10-dodecyl) (Acridine Orange) was incorporated into SDS micelles in water containing EDTA and ascorbic acid, and the mixture was excited, the photosensitized reduction of MB bound to the micelles occurred. It was found that the quantum yield of the sensitized reduction depended on the concentration of MB and was larger than the yield on the direct excitation of MB.

Mechanistic investigations of photooxidation, photoreduction, and photosensitization in a heterogeneous system such as micelles, vesicles and emulsions, are important from the several points of view regarding photobiological phenomena (photoreception, photodynamic action, *etc.*) and solar-energy utilization, as modefied by the photosynthetic phenomenon. In recent years, an increasing number of such studies have focused on the photochemical and photophysical properties of molecular assembly systems. For example, some specific micellar effects on the properties of the excited state have been investigated and reported for cases of excimer and exciplex formation,[1–4] excitation-energy transfer,[3–6] and electron-transfer phenomena.[3,4,7–9] However, the mechanistic study of the photochemical reaction between the micellar surface and the bulky phase has been rather insufficient in contrast to the many studies at the interior site of a micelle.

Previously, we attempted to study the effect of an anionic reductant, EDTA, on the photoreduction of Methylene Blue bound to sodium dodecyl sulfate micelles, semiquantitatively.[10] The photoreduction was considerably inhibited because of the electrostatic repulsion between the anionic reductant and the micelles. Further, the concentration dependence of EDTA on the quantum yield was shown as a sigmoidal type——a so-called micellar effect. In the present work, we have performed a detailed mechanistic investigation of the micellar effect which was observed on the photoreduction and the photosensitized reduction of organic dyes bound on the surface of ionic surfactant micelles from the standpoint of reaction kinetics.

Experimental

Materials. The thionine ($C_{12}H_{10}ClN_3S$; Th), Methylene Blue ($C_{16}H_{18}ClN_3S$; MB), and Eosine Yellowish ($C_{20}H_6O_5Br_4Na_2$; E) were recrystallized twice from methanol, 1-butanol, and ethanol respectively. The 10-dodecyl (Acridine Orange) ($C_{29}H_{44}N_3Br$; DAO) was prepared as previously described and was purified by means of alumina-column chromatography and recrystallization from a 1 : 1 ether and ethanol mixed solution.[11] The sodium dodecyl sulfate (SDS) was recrystallized twice from methanol. The ethylenediaminetetraacetic acid disodium salt (EDTA) was used without further purification.

Apparatus and Procedure. A degassed sample in a 1 × 1 × 4 cm^3 cell was irradiated by means of a steady illumination apparatus with a 300W tungsten lamp at 25 °C. The experimental procedure used to determine the quantum yield of dye-photoreduction was similar to that described previously.[12] Flash-photolysis experiments were carried out by using a pulsed dye laser (Phase-R: 2100B, Dye: G4, FWHM of pulse: ≈500 ns) and a monitoring system composed of a monochromator, a transient recorder, and a spectral data-analyser (Union Giken, RA-415).

Results and Discussion

Preliminary investigations of the photoreduction rate of Methylene Blue bound to anionic SDS micelles (MB/S) by EDTA trianion (HY^{3-}) were carried out at pH=8.0. The photoreduction of MB/S by HY^{3-} at a higher concentration proceeded at a rate which was proportional to the light quantities absorbed by the dye with a stationary irradiation. Then, in a way similar to that used for the reaction in an aqueous homogeneous solution, the quantum yield (Φ_{MB}) was determined from the slope of the linear relationship between $\ln(e^A-1)$ and time (A is the absorbance of the dye).[10,13] The reaction was significantly inhibited in a lower concentration range of the reductant, and the concentration dependence of HY^{3-} on Φ_{MB} was shown as a sigmoidal curve (Fig. 1). This inhibition may be supposed to be due to the environmental effect on the micellar periphery, *i.e.*, the so-called micellar effect.[10] In order to check the phenomenon as the electrostatic effect between the ionic micelle and the reductant, a kinetical investigation of the anomalous concentration effect on the photoreduction must be considered in the cases of several combinations of dyes, surfactants, and reductants.

Effect of the HY^{3-} Concentration on the Quantum Yield of Dye Photoreduction. As is shown in Fig. 1, we have observed that the rate of Th by HY^{3-} under the lower concentration at pH=8.0 was considerably retarded by the addition of SDS; *i.e.*, the photoreduction of thionine

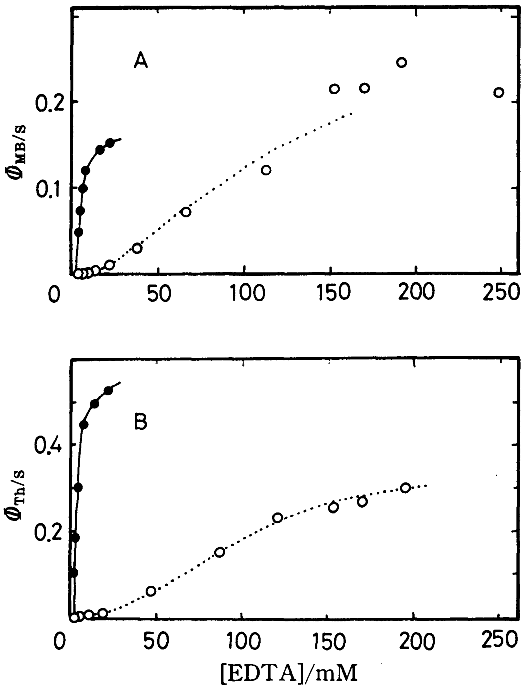


Fig. 1. Micellar charge effect on the photoreduction of Methylene Blue (A) and thionine (B).
(A) ○: In deaerated micellar solution, [MB] = 10 μM, [SDS] = 10 mM, pH = 7.0, ●: in deaerated aqueous solution. [MB] = 10 μM, pH = 6.7, $\Phi_{MB} = 3.6 \times 10^6 [\text{EDTA}]/(1.2 \times 10^4 + 2.5 \times 10^7[\text{EDTA}])$. (B) ○: In deaerated micellar solution, [Th] = 10 μM, [SDS] = 20 mM, pH = 8.0, ●: in deaerated aqueous solution, [Th] = 10 μM, pH = 8.0, $\Phi_{Th} = 1.3 \times 10^8[\text{EDTA}]/(8.0 \times 10^4 + 2.8 \times 10^8[\text{EDTA}])$. Dotted lines show EDTA concentration effect on $\Phi_{Th/S}$ ($\Phi_{MB/S}$) calculated from Eq. 9, where the copperative effect of the concentration and the ionic strength on the photoreduction is considered (see text and Table 1).

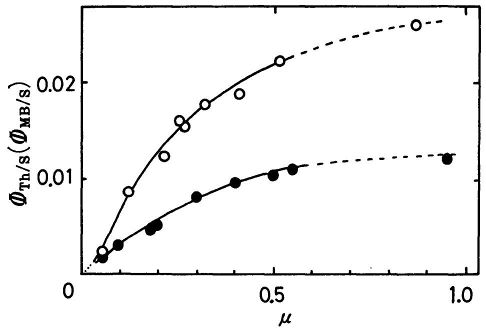


Fig. 2. Ionic strength effect on the photoreduction yields of Th/S and MB/S at a constant concentration of EDTA (5 mM).
●: [MB] = 10 μM, [SDS] = 10 mM, pH = 7.0, ○: [Th] = 10 μM, [SDS] = 20 mM, pH = 8.0. (Several inorganic neutral salt of NaCl, $NaNO_3$, and Na_2SO_4 were used for adjustment of μ.)

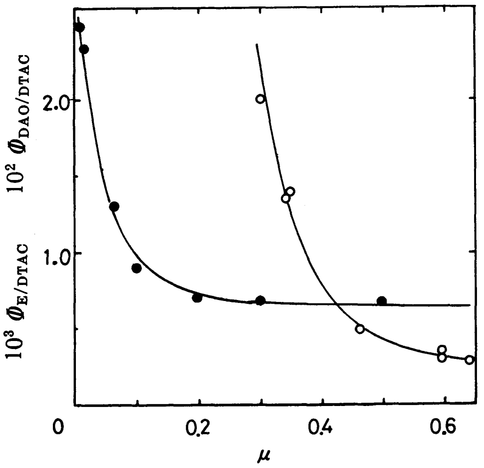


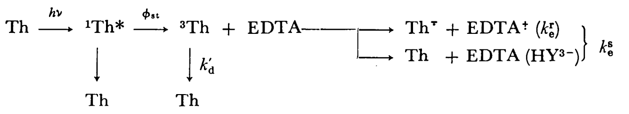
Fig. 3. Ionic strength effect on the photoreduction yield of E/DTAC and DAO/DTAC at a constant concentration of EDTA.
●: [E] = 10 μM, [DTAC] = 20 mM, $[HY^{3-}]$ = 10 mM, ○: [DAO] = 5 μM, [DTAC] = 25 mM, $[HY^{3-}]$ = 10 mM. (NaCl was used for adjustment of μ.)

bound to SDS micelles (Th/S + HY^{3-} system) is inhibited just as the case of the MB/S + HY^{3-} system.[10] On the contrary, the photoreduction of Eosine Y (E) by HY^{3-} was enhanced by binding to an oppositely charged cationic micelle of dodecyltrimethylammonium chloride (DTAC) at the lower concentration of HY^{3-} of 1.0×10^{-4} M (1 M = 1 mol dm^{-3}) : *i.e.*, the quantum yield for E/DTAC photoreduction was 5.5×10^{-3} at [DTAC] = 30 mM and pH = 8.0, and five times larger than the value without DTAC. Although the photoreduction occurs *via* electron transfer between a bound triplet dye and HY^{3-} because there is no fluorescence quenching of the bound MB/S by HY^{3-}, the observed decay constant (1.2×10^5 s^{-1}) of the triplet dye bound to the micelles of 2×10^{-4} M was scarcely affected by the addition of HY^{3-} in the lower-concentration range, thus exhibiting the inhibition of photoreduction shown in Fig. 1. The fluorescence of Methylene Blue and thionine bound to anionic SDS micelles is scarcely quenched by adding 0.36 M of $S_2O_3^{2-}$ or 0.1 M of SCN^- anion, which quench these dyes efficiently in an aqueous solution.[10] Judging from the above results, it seems that the reaction of triplet dyes with HY^{3-} was inhibited because of the electrostatic repulsion between the anionic SDS micelles and the reductant anion, HY^{3-}.

Effect of the Ionic Strength on the Photoreduction Yield. With the concentration of dye and HY^{3-} fixed at 10 μM and 5 mM respectively, the effect of the ionic strength (μ) on the quantum yield of the photoreduction of dye was investigated over the wide range of $0 \lesssim \mu \lesssim 1$. Figure 2 shows that $\Phi_{Th/S}$ or $\Phi_{MB/S}$ tends to the constant value of a maximum yield with μ : *i.e.*, there is a positive μ-effect. In order to confirm that a neutral salt effect for the electrostatic repulsion between HY^{3-} and triplet Methylene Blue or thionine bound on an anionic SDS micelle is responsible for the positive μ-effect, we tried to produce a μ-effect on the system of E/DTAC + HY^{3-}. Interference with the electrostatic attraction force between HY^{3-} and a cationic DTAC micelle fixing triplet eosine, *i.e.*, a negative μ-effect was observed during the reaction (Fig. 3). A comparison of the results shown in Figs. 2 and 3 shows that these remarkable opposite effects support the idea that the μ-effect on the electrostatic interaction between the micelle ion and the HY^{3-} anion is very sensitive to the yield of photoreduction.

$\Phi_{Th/S}$ value around $\mu=0.8$ at $[HY^{3-}]=5$ mM in Fig. 2 is smaller by a factor of ten than the yield of thionine reduction obtained in an aqueous homogeneous solution at $\mu=0.8$, and also smaller than the yield at the concentration of HY^{3-} of 0.16 M in a micellar solution where the calculated ionic strength relative to EDTA is 0.80. Thus, it may be supposed that both the HY^{3-} concentration and ionic strength of the reductant affect the yield of photoreduction in a Th/S+HY^{3-} or MB/S+HY^{3-} system. Also, the μ-effect on the photoreduction of 10-dodecyl (Acridine Orange) (DAO) dissolved in cationic DTAC micelles with HY^{3-} was performed where the DAO was anchored in the micelles. As is shown in Fig. 3, a μ-effect on the yield similar to that in the case of E/DTAC+HY^{3-} system was observed, but the effective values of μ were larger than the case of the photoreduction occurring on the micellar surface (the E/DTAC+HY^{3-} system).

Effect of the HY^{3-} Concentration on the $\Phi_{Th/S}$ under a Constant Ionic Strength. In a degassed aqueous solution of Th and HY^{3-}, the effect of the HY^{3-} concentration on the yield of the photoreduction was checked. The Φ_{Th} increased with the HY^{3-} concentration and tended to constant saturation value. A fairly linear relationship of $1/\Phi_{Th}$ against $1/[HY^{3-}]$ was obtained. Judging from the kinetical results and the results of an investigation previously reported,[10,13,14] the following scheme and equation of Φ_{Th} can be obtained:



$$\Phi_{Th} = \frac{\phi_{st}k_e^r\,[HY^{3-}]}{k_d' + k_e^s\,[HY^{3-}]} \qquad (1)$$

The k_e^r and k_e^s values were obtained from the plot of Φ_{Th}^{-1} *vs.* $[HY^{3-}]^{-1}$ to be 2.3×10^8 mol^{-1} dm^3 s^{-1} and 2.8×10^8 mol^{-1} dm^3 s^{-1} respectively, using ϕ_{st} (0.55) and k_d' (8.0×10^4 s^{-1}) values.[14,15]

In the case of the Th/S+HY^{3-} system, at a constant ionic strength of 0.1 or 0.8, the dependence of $\Phi_{Th/S}$ on the concentration of HY^{3-} shows not the sigmoidal curve, but the usual saturation-type one as was checked in an aqueous solution. The results are expressed as a linear relationship between $1/\Phi_{Th/S}$ and $1/[HY^{3-}]$ in Fig. 4. By analogy with the kinetical treatment for the data obtained in the MB/S+HY^{3-} system,[10] $\Phi_{Th/S}$ can be tentatively expressed at a constant μ as follows:

$$\Phi_{Th/S} = \frac{\phi_{st}k^r[HY^{3-}]_s}{k_d + k^s[HY^{3-}]_s} = \frac{\phi_{st}k^rA(\mu)[HY^{3-}]}{k_d + k^sA(\mu)[HY^{3-}]}, \qquad (2)$$

where the HY^{3-} concentration on the surface of a micelle, $[HY^{3-}]_S$, is assumed to be proportional to the concentration of HY^{3-} added, *i.e.*, $[HY^{3-}]_S = A(\mu)[HY^{3-}]$. $A(\mu)$ is a constant, depending on the ionic strength of the solution. The intersystem crossing probability, ϕ_{st}, of Th/S is assumed to be the same (0.55) as that in an aqueous solution referring in the case of MB/S photoreduction.[10] k_d is the decay constant of the bound triplet dye. k^r and k^s are the reaction and quenching-rate parameters respectively for the reaction of triplet dye with HY^{3-} on the surface of a micelle. From the values of an intercept of the line in Fig. 4 and the ϕ_{st} value of Th, the reactivity ratio, k^r/k^s for Th bound with HY^{3-} was obtained as 0.06 at a constant μ value of 0.1; this is smaller than the value (0.83) in an aqueous solution. At a constant μ value of 0.8, k^r/k^s equals 0.7—1.0, which is comparable to the value obtained in an aqueous solution. Judging from the finding that the value of the degree of the fluorescence depolarization, P (0.24) of thionine at $\mu=0.8$ was almost the same as the value at $\mu=0.1$, it was supposed that the molecular rotation of the dye was still restricted and that the dye was bound to the micelles even at such a high ionic strength as 0.80 ($P=0.095$ in an aqueous solution). Therefore, the micellar effect of the inhibition for the photoreduction might be responsible for the decrement in the k^r/k^s value as a parameter for the reactivity ratio of the bound dye. Incidentally, the concentration effect of HY^{3-} on $\Phi_{Th/S}$ did not obey any relationship such as Eq. 2 at a given concentration of electrolytes.

Kinetic Analysis for $\Phi_{Th/S}$ Values from the Ionic-strength Effect. As for the kinetic treatment of the intramicellar photochemical processes, several theoretical considerations have been given.[9,16–21] Mostly, these studies have dealt with the reaction between molecules

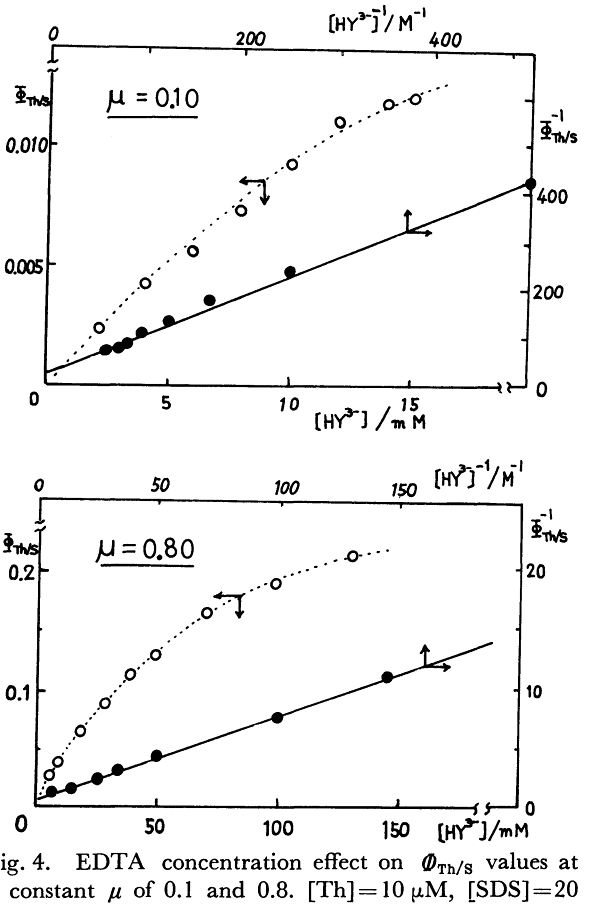


Fig. 4. EDTA concentration effect on $\Phi_{Th/S}$ values at constant μ of 0.1 and 0.8. [Th]=10 μM, [SDS]=20 mM, pH=8.0.

or ions which are located on a micellar surface or at the micellar interior. In our systems, the treatment for the positional situation should be considered as that of the reaction of excited dye bound on the Stern layer or the outer layer (Gouy-Chapman layer) of an ionic micelle with HY^{3-} located in the aqueous bulk phase. Further, from the standpoint of the quantitative explanation of the anomalous effects on the photoreduction yield, it can not yet be decided how much these theoretical models suggested for the reactions on the micelle are applicable to the present situation of the systems.

Thus, for the reaction molecules far from a micellar surface, we attempted to use the well-known model of the electrostatic interaction introduced by Debye and Hückel. Since a spherical micelle is held at $\mu \lesssim 0.4$ at the dilute solution of SDS ($\approx$10 mM. CMC is 8.1 mM), let us assume approximately that such a deformation of the micelle occuring at $\mu > 0.4$ does not affect on the following kinetic treatment.[22] Then, the distribution of HY^{3-} at a distance, r, apart from a center of the charged micelle under a given ionic strength, μ, is denoted as $n_Y(r,\mu)$, which means the number of molecules per cm^3, and it is expressed by the Boltzmann equation, using the Debye-Hückel's theory. At an infinite ionic strength, $n_Y(r,\mu)$ is denoted as $n_Y(r,\infty)$, in which the value of the number on HY^{3-} ions in the bulk phase, n_{Yb}, can be taken as approximately equal, because the electrostatic repulsion is negligible at an infinite ionic strength when a large amount of electrolytes is added, *i.e.*, this is the neutral salt effect. This means that $n_Y(r,\mu)$ converges to n_{Yb} according to the following Boltzmann equation upon an increase in r or μ to infinity:

$$n_Y(r,\mu) = n_{Yb}\exp(-eZ\Psi/kT), \tag{3}$$

where Z indicates the charge number and where the following potential, Ψ, obeys the well-known Poisson-Boltzmann equation:

$$\Psi = \frac{Ze}{4\pi\varepsilon r}\exp(-\sqrt{\beta}\,r) \tag{4}$$

$$\beta = 2 \times 10^3 N_A e^2 \mu/\varepsilon kT.$$

[Abbreviations: Ze-central charge, ε-dielectric constant, N_A-Avogadro number, k-Boltzmann constant, T-absolute temperature] Denoting the HY^{3-} concentration at the distance (r_{Th}) of the Th binding site on the surrounding micelle as $[HY^{3-}]_{Th}$, the relation of $[HY^{3-}]_{Th}$ with $A(\mu)$ in Eq. 2 can be written as:

$$[HY^{3-}]_{Th} = \left(\frac{n_Y(r_{Th},\mu)}{n_{Yb}}\right)[HY^{3-}] \equiv A(\mu)[HY^{3-}]. \tag{5}$$

Using Eq. 5, $\Phi_{Th/S}$ can be expressed approximately as Eq. 6 at a lower concentration of HY^{3-} from Eq. 2;

$$\Phi_{Th/S} \approx \frac{\phi_{st}k^r}{k_d}[HY^{3-}]_{Th} = \frac{\phi_{st}k^r A(\mu)}{k_d}[HY^{3-}]. \tag{6}$$

When the electrostatic potential, Ψ, on the surrounding micelles becomes small at a long distance of r, the treatment by the Debye-Hückel theory can be performed for the following evaluation.[23,24] When $eZ\Psi < kT$, the Ψ of Eq. 3 satisfies the Poisson-Boltzmann equation; a similar treatment is also possible for the cases on an ionic sphere of macromolecules. Using Ψ in the $n_Y(r,\mu)$-Boltzmann equation, the correlation of $n_Y(r,\mu)$ with μ is given as follows:

$$n_Y(r,\mu) = n_{Yb}\exp(-Ae^{-\alpha\sqrt{\mu}}), \tag{7}$$

where $A = Ze^2/4\pi\varepsilon rkT$ and $\alpha = r\sqrt{2\times 10^3 N_A e^2/\varepsilon kT}$.

The charge number of micelles was estimated from the product of the aggregation number of SDS (62) and the fraction of charge (0.17).[25] Putting the charge numbers of HY^{3-} and micelles as $-3e$ and $-10e$ respectively, the numerical values of A and α are $210r^{-1}$ and $0.325r$ at a given parameter of the distance, r. $A(\mu)$ defined in Eq. 5 can be calculated as the function of μ from the $n_Y(r,\mu)/n_{Yb}$ ratio in Eq. 7. Further, for the observed ionic strength effect on $\Phi_{Th/S}$, the dependence of $\Phi_{Th/S}$ on μ can be compared with that of $A(\mu)$ on μ, normalizing the $A(\mu)$ value to $\Phi_{Th/S}$ at a given parameter, r, because $\Phi_{Th/S}$ is proportional to $A(\mu)$, as is shown in Eq. 6. The correlation of the μ-effects on both $A(\mu)$ and $\Phi_{Th/S}$ is investigated in the region of r=10—30 Å; the degree of coincidence is shown in Fig. 5. The figure shows that the correlation is fairly good around r=18—20 Å, about three times of the micellar radius;[25] *i.e.*, it is shown to be the thionine binding position where the bound triplet dye will react with HY^{3-}. For the case of MB/S+HY^{3-}, the similar results are obtained, as is shown in Fig. 5.

In the plots of $\Phi_{Th/S}$ against μ in Fig. 5, $\Phi_{Th/S}$ is taken as a function of μ at a given concentration of HY^{3-}, *i.e.*, $\Phi_{Th/S}(\mu)$. Putting the ratio of $\Phi_{Th/S}(\mu)$ to the normalized quantum yield, $\Phi_{Th/S}(\mu)_N$, as $\gamma(\mu)$, *i.e.*, $\gamma(\mu)=\Phi_{Th/S}(\mu)/\Phi_{Th/S}(\mu)_N=A(\mu)/A(\mu)_N$, the relation of $[HY^{3-}]_S=A(\mu)[HY^{3-}]=\gamma(\mu)A(\mu)_N[HY^{3-}]$ can be obtained. Thus, the quantum yield given in Eq. 2 can be written as:

$$\Phi(\mu) = \frac{\phi_{st}k^r\gamma(\mu)[HY^{3-}]}{(k_d/A(\mu))+k^s\gamma(\mu)[HY^{3-}]}. \tag{8}$$

The $\gamma(\mu)$ factor indicates a correction for the ionic strength by the HY^{3-} anion itself. Now, estimating the $\gamma(\mu)$ value from Fig. 2 at the ionic strength corresponding

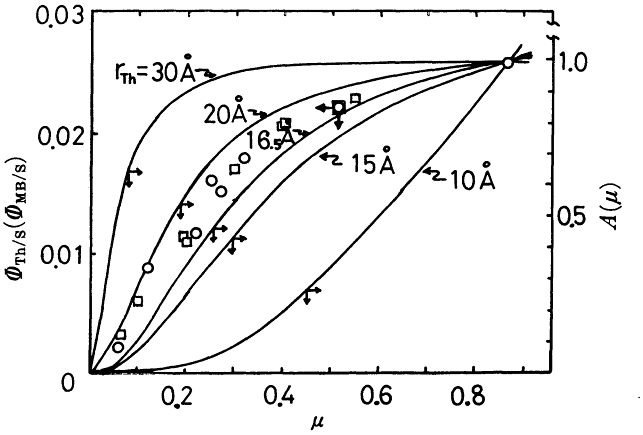


Fig. 5. Comparison of the effects of $\Phi_{Th/S}$ on μ and of $A(\mu)$ on μ.
○: [Th]=10 μM, [SDS]=20 mM, $[HY^{3-}]$=5 mM, pH=8.0. □: [MB]=10 μM, [SDS]=10 mM, $[HY^{3-}]$=5 mM, pH=7.0. (The curves of $A(\mu)$ *vs.* μ are drawn with a parameter of r_{Th} or r_{MB} normalizing at μ=0.88.)

Table 1. COMPARISON OF OBSERVED QUANTUM YIELDS WITH THAT CORRECTED FOR THE μ-EFFECT OF THE HY^{3-} ION

$[HY^{3-}]/M^{a)}$	$\gamma(\mu)[HY^{3-}]/M^{b)}$	$\Phi_{Th/S}$ Obsd$^{c)}$	$\Phi_{Th/S}$ Calcd$^{d)}$
0.19	0.19	0.257	0.271
0.17	0.167	0.256	0.253
0.15	0.143	0.241	0.232
0.13	0.124	0.213	0.213
0.085	0.0635	0.141	0.142
0.045	0.0261	0.0583	0.0641
0.018	0.00575	0.0213	0.0155
0.0094	0.00158	0.0048	0.0044
0.0050	0.00034	0.0026	(0.001)

a) Concentrations of HY^{3-} examined in Fig. 1. b) $\gamma(\mu)$ was estimated from the μ-effect in Fig. 2 at the μ-values corresponding to the HY^{3-} concentrations in column a). c) Quantum yields observed in Fig. 1 at the concentration in column a). d) Calculated quatum yields from Eq. 9 (see text).

to the HY^{3-} concentration which were examined in the experiment on the HY^{3-}-concentration effect on $\Phi_{Th/S}$, and calculating the vaue of $\gamma(\mu)[HY^{3-}]$, we can plot $1/\Phi(\mu)$ against the $1/\gamma(\mu)[HY^{3-}]$ values. Since the linear relationship was observed for the double reciprocal plots, the following numerical equation can be written by using the values of the slope and intercept:

$$\Phi(\mu) = \frac{\gamma(\mu)[HY^{3-}]}{0.36+1.8\gamma(\mu)[HY^{3-}]}. \qquad (9)$$

On the other hand, by multiplying the correction factor $\gamma(\mu)$ by the values of $[HY^{3-}]$, which are examined in Fig. 1, we can compare the values of the quantum yield with that observed for the HY^{3-} concentration effect, as is shown in Table 1, where a fair coincidence of both the numerical equation 9 and the observed yield is obtained. Thus, since the quantum yields were quantitatively evaluated by the correction of the ionic strength upon the concentration effect of HY^{3-}, the relationship between the calculated $\Phi_{Th/S}$ values in Table 1 and the concentration of HY^{3-} can be shown as the sigmoidal curve in Fig. 1 (dotted line), and the cooperative effect of the HY^{3-} concentration and the ionic strength on the photoreduction for the micellar system can be considered to hold, judging from the agreement between the calculated curve and the observed values shown in Fig. 1.

Photoreduction of 10-Dodecyl (Acridine Orange), DAO in Micelles by HY^{3-}. DAO is a little soluble in water and is likely to be incorporated into SDS micelles. From an eye to comparing a micellar effect on the photoreduction with the different binding situation of dyes, the effects of HY^{3-} concentration and ionic strength were investigated in the cases of the DAO/S or DAO/DTAC+HY^{3-} systems.

The photoreduction of DAO/S by HY^{3-} was not observed either at a high ionic strength (0.6) or at a high concentration of the reductant (200 mM). For the DAO/DTAC+HY^{3-} system, the photoreduction yield (Φ_{DAO}) in the micellar solution was found to be about 5 times larger than that in a mixture of 30% ethanol and water ($[HY^{3-}]=10$ mM). Such an enhancement was also observed to a considerable extent in the case of the E/DTAC+HY^{3-} system because the electrostatic attraction between the cationic micelles and the HY^{3-} anion was more effective on the surface. Since the DAO/DTAC fluorescence quenching by added bromide ions increased about thirty times over that for the mixture of 30% methanol and water, the Acridine Orange chromophore must be located near the surface in a micellar particle. It was considered that the efficient quenching was due to the electrostatic attraction between the micelle and the bromide ion.

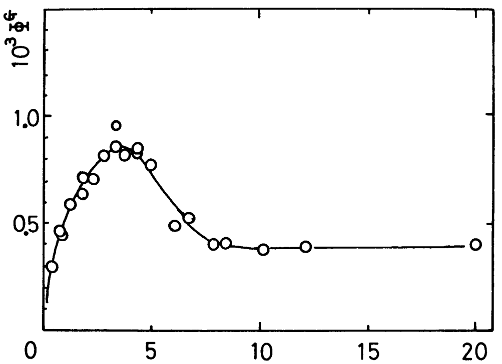


Fig. 6. Concentration effect of Methylene Blue on 10-dodecyl (Acridine Orange)-sensitized reduction yield Φ^G. $[DAO]=8$ μM, $[SDS]=8$ mM, $[HY^{3-}]=10$ mM.

When the ionic strength effect on Φ_{DAO} was compared to that in the case of the E/DTAC+HY^{3-} system, as is shown in Fig. 3, a decreasing effect on Φ_{DAO} by μ was observed in the higher region of 0.3—0.5, where the effect reached saturation in the case of the E/DTAC+HY^{3-} system. This result might be caused by the different position of the binding site of these dyes. At a constant μ, the effect of the HY^{3-} concentration on Φ_{DAO} was analysed by holding the linear relationship between $1/\Phi_{DAO}$ and $1/[HY^{3-}]$. Thus, it was confirmed that the results could also be explained by Eq. 8 in the case of the DAO/DTAC+HY^{3-} system.

Photosensitized Reduction of Methylene Blue by 10-Dodecyl (Acridine Orange) in SDS Micellar Solution. When DAO was incorporated into MB/S micelles (DAO/S/MB) and was excited, the photosensitized reduction of the MB bound at the surface by HY^{3-} occurred. The quantum yield of the sensitized reaction, Φ^G, depends on the MB concentration and is larger than that of the direct excitation of MB, Φ_R at the optimal concentration region, as is shown in Fig. 6. At the higher concentrations of MB over 10 μM, the quenching of DAO fluorescence by MB becomes considerable, involving the phenomenon of the DAO-sensitized fluorescence of MB *via* the dipole-dipole interaction (Förster mechanism), as has been reported previously.[5] If triplet MB can be formed from the singlet-excited state of MB produced by the singlet energy transfer on the micelles, the quantum yield of the photoreduction, Φ^G, must be smaller that that by the direct excitation of MB as a part of the efficiency of the energy transfer. When the decrement at a higher concentration of MB in Fig. 6 is due to the contribution of the singlet energy transfer, the sensitized reaction mechanism can be discussed from the stand-points of both singlet and triplet energy transfer between DAO and MB on the micelles. The DAO-sensitized reduction of MB by ascorbic acid as a reductant also occurred in a homogeneous solution and more efficiently in a DAO/S/MB micellar solution ($\Phi^{G}_{max} \simeq 0.1$, pH=3.0). Similarly, the quantum yield of the sensitized reduction of DAO/S/MB depended on the concentration of MB and was larger than that of the direct excitation of MB bound in micelles. By laser-flash photolysis it was found that triplet DAO was rapidly quenched by the MB on the micelles. The observed decay constant of triplet DAO in micelles is $9.5 \times 10^{2}\ s^{-1}$ without MB and $1.4 \times 10^{4}\ s^{-1}$ with MB (5 μM), at pH=6.2. This may suggest that the increase in the yield Φ^{G} in the lower-concentration region of MB is responsible for the triplet energy transfer from DAO to MB. Further mechanistic investigations are required to elucide the reason why the value of Φ^{G} is larger than that of Φ^{R} in the micellar system.

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