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Kinetic Studies of Photosensitized Oxygenation by Singlet Oxygen in Aqueous Micellar Solutions

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Singlet oxygen produced by the dye-sensitized reaction in an aqueous solution penetrates into the interior of the surfactant micelles of sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium chloride (DTAC), reacting with the solubilized acceptors such as 9,10-dimethylanthracene, 2,5-diphenyloxazole, and 1,3-diphenylisobenzofuran. From the acceptor concentration effect on the photooxygenation quantum yield, the reactivity index (β), the ratio of the rate constant of the spontaneous decay of singlet oxygen to that of the reaction with an acceptor, is obtained in the aqueous micellar solution. It has been shown that the lifetime of singlet oxygen is mainly dependent on the solvent composition in the bulk phase from the kinetic analysis of the mixed solvent effect on the quantum yield in SDS and DTAC micellear solutions and that in a homogeneous solution.

Singlet oxygen is one of the active species for the oxidative process in a biological system as well as supperoxide ion, hydroxyl radical, hydrogen peroxide, ozone, *etc.* Investigation of the dye-sensitized photooxidation by singlet oxygen in a solution in which an acceptor is dissolved in the surfactant micelles affords significant information on their use in the study of photodynamic inactivation of enzyme and cells.[1–5] Since a surfactant micelle serves as both structural and functional models for complex bioaggregates of proteins or biomembrances, kinetic investigations are required to determine the mechanism of the micelles with singlet oxygen produced by the energy transfer from the dye bound on micelles or dissolved in a liquid phase.

Studies on the fluorescence quenching of aromatic compounds within some surfactant micelles by oxygen dissolved in an aqueous solution suggest that an oxygen molecule can undergo unrestricted diffusion into the micelles.[6,7] In the case of singlet oxygen, although such diffusion into the micelles is also expected, its lifetime in the liquid phase which is highly dependent on the type of solvent can be responsible for the reaction efficiency for the micellar system. In order to explain the solvent effect on the lifetime of singlet oxygen an electronic-to-vibrational energy transfer theory (*i.e.*, to the C–H or O–H streching vibrational mode of solvent) was introduced.[8] It seems that singlet oxygen is subjected to deactivation by water and surfactant micelles. However, despite the fact that the lifetime in aqueous solution (2 μs) is the shortest among those observed in a number of solvents, it is of interest that singlet oxygen is scarcely quenched by micelles itself and reacts with the acceptor dissolved in micelles efficiently.[9,10]

In this paper, the reaction mechanism in some micellar systems has been discussed from the concentration effect of singlet oxygen acceptor and the mixed solvent effect upon the quantum yield of the disappearance of the acceptor in micelles as compared with the effects in the homogeneous solutions.

Experimental

Materials. Sodium dodecyl sulfate and dodecyltrimethylammonium chloride (Tokyo Kasei, G. R.) were recrystallized from methanol. 9,10-Dimethylanthracene, 2,5-diphenyloxazole, 2,5-dimethylfuran, tryptophan, histidine (Tokyo Kasei, G. R.), and 1,3-diphenylisobenzofuran (Aldrich Co.) were used without further purification. Methylene blue (MB) and eosine (EOS) were recrystallized twice from 1-butanol and ethanol, respectively. Singlet oxygen acceptors were solubilized in each surfactant (0.1 M) by gentle stirring of the mixture at 50—70 °C in the dark.

Procedures. A fresh sample in a 1×1×4 cm³ or 0.3×1×4 cm³ cell was irradiated by a cross-illumination apparatus with a steady light at 25.0 °C. The experimental procedure to determine the quantum yield was similar to that described previously.[11] Flash photolysis experiments were carried out by using a Q-switched ruby laser (NEC, SLG-2007). A suitable cut-off filter and an interferance filter (λ=410 nm) were placed in the analyzing beam from a tungsten lamp in order to avoid the photolysis of singlet oxygen acceptor. The fluorescence spectra were measured with a Shimadzu RF-500 fluorimeter.

Results and Discussion

Acceptor Concentration Dependence on the Quantum Yield in a Homogeneous Solution. The essential reaction scheme and the disappearance quantum yield $\Phi_{-\mathrm{A}}$ of a singlet oxygen acceptor (A) in solution are expressed as follows:[11–13]

$$ {}^1\mathrm{Sens} \xrightarrow{h\nu} \longrightarrow {}^3\mathrm{Sens}^* \qquad \phi_{\mathrm{st}} \tag{1} $$

$$ {}^3\mathrm{Sens}^* \longrightarrow {}^1\mathrm{Sens} \qquad k_{\mathrm{d}} \tag{2} $$

$$ {}^3\mathrm{Sens}^* + {}^1\mathrm{Sens} \longrightarrow \mathrm{Sens}^+ \cdots \mathrm{Sens}^-,\ {}^1\mathrm{Sens} + {}^1\mathrm{Sens} \qquad k_{\mathrm{D}} \tag{2'} $$

$$ \left.\begin{array}{l} {}^3\mathrm{Sens}^* + {}^3\mathrm{O}_2 \longrightarrow {}^1\mathrm{Sens} + {}^1\mathrm{O}_2 \quad (k^{\mathrm{r}}_{\mathrm{O}_2}) \quad (3) \\ \qquad\qquad\quad \searrow {}^1\mathrm{Sens} + {}^3\mathrm{O}_2,\ \mathrm{Sens}^+ \cdots \mathrm{O}_2{}^- \quad (4) \end{array}\right\} k^{\mathrm{s}}_{\mathrm{O}_2} $$

$$ {}^3\mathrm{Sens}^* + \mathrm{A} \longrightarrow {}^1\mathrm{Sens} + \mathrm{A} \qquad k^{\mathrm{s}}_{\mathrm{TA}} \tag{5} $$

$$ {}^1\mathrm{O}_2 \longrightarrow {}^3\mathrm{O}_2 \qquad k'_d \tag{6} $$

$$ \left.\begin{array}{l} {}^1\mathrm{O}_2 + \mathrm{A} \longrightarrow \mathrm{AO}_2 \quad (k'^{r}_{\mathrm{A}}) \quad (7) \\ \qquad\qquad \searrow \mathrm{A} + {}^3\mathrm{O}_2 \quad (8) \end{array}\right\} k'^{\mathrm{s}}_{\mathrm{A}} $$

$$ \Phi_{-\mathrm{A}} = \Phi_{\mathrm{so}}\alpha r\frac{[\mathrm{A}]}{\beta+[\mathrm{A}]} \tag{9} $$

where $\Phi_{\mathrm{so}}=\phi_{\mathrm{st}}\gamma_{\mathrm{so}}$ (yield of singlet oxygen formation), $r=k'^{\mathrm{r}}_{\mathrm{A}}/k'^{\mathrm{s}}_{\mathrm{A}}$ (reaction probability of A with singlet oxygen), $\beta=k'_{\mathrm{d}}/k'^{\mathrm{s}}_{\mathrm{A}}$ (reactivity index of A with singlet oxygen), γ_{so} stands for the singlet oxygen formation probability ($=k^{\mathrm{r}}_{\mathrm{O}_2}/k^{\mathrm{s}}_{\mathrm{O}_2}$) from triplet sensitizer (^{3}Sens) *via* process 3, and α is the reaction probability of AO_2 to its successive processes. If these is no successive reaction following AO_2, the relation of the double reciprocal plot of $\Phi_{-A}{}^{-1}$ *vs.* $[A]^{-1}$ on Eq. 9 would be linear. From the slope and intercept the value of β can be obtained and the k'^{s}_{A} value is estimated by substituting the value of k'_d in the solvent.

The values of k'_d and k'^{s}_{A} are independently determined by means of the laser flash photolysis utilizing the kinetic analysis proposed by Kearns *et al.*,[8] Adams and Wilkinson,[14] and Young *et al.*[15] The reaction parameters obtained by these methods are given in Table 1 including some of the reference data.

TABLE 1. RATE CONSTANTS OF DECAY AND REACTIONS OF SINGLET OXYGEN IN VARIOUS SOLUTION

Acceptor	Solvent	Sens	k'_d 10^{-3} (s^{-1})	k'^{S}_{A} 10^{-8} (M^{-1} s^{-1})	β (M)
HIS	H_2O	MB	500[a)]	54.3	9.2×10^{-5}
HISA	H_2O	MB	500[a)]	2.0	2.5×10^{-3}
DMF	H_2O	MB	500[a)]	15.6	3.2×10^{-4}
	MeOH	MB	110	3.9	2.8×10^{-4}
	MeOH[13)]	MB	—	—	2.8×10^{-4}
	EtOH	MB	83[a)]	3.8	2.2×10^{-4}
DMA	EtOH	MB	83[a)]	0.39	2.1×10^{-3}
	EtOH	EOS	83[a)]	0.44	1.9×10^{-3}
DPO	H_2O/ D_2O[b)]	MB	258[a)]	1.6	1.6×10^{-3}
DPBF	MeOH	MB	110	16.2	6.8×10^{-5}
	MeOH	MB	110	16.4	6.7×10^{-5} (L)
	MeOH[15)]	MB	88	13.0	6.7×10^{-5} (L)
	MeOH	ERY	110	15.5	7.1×10^{-5}
	EtOH	EOS	83[a)]	12.8	6.5×10^{-5}
	TeCE	MB	8.3	4.4	1.9×10^{-5} (L)
	TeCE	MB	8.3	5.9	1.4×10^{-5}
	DeCE	MB	15	6.0	2.5×10^{-5} (L)
	DeCE	MB	15	10	1.5×10^{-5}
	CH_2Cl_2	MB	16	10.8	1.5×10^{-5} (L)
	CH_2Cl_2	MB	16	16	1.0×10^{-5}
	$CHCl_3$[19)]	MB	16.7	6.0	2.8×10^{-5}
	$CHCl_3$	MB	9.0	7.0	1.3×10^{-5} (L)
	$CHCl_3$	MB	9.0	9.0	1.0×10^{-5}
	CCl_4	MB	1.4[a)]	1.1	1.2×10^{-5}
	n-BuOH[15)]	MB	52	8.0	6.5×10^{-5} (L)
	Dioxane[15)]	MB	29	12.1	2.4×10^{-5} (L)
	Pyridine[15)]	MB	31	21	1.5×10^{-5} (L)
	Glycol[15)]	MB	51	15	3.1×10^{-5} (L)
DMA/ DTAC	H_2O	MB	500[a)]	7.5	6.6×10^{-4}
	D_2O	MB	50[a)]	7.4	6.8×10^{-5}
	H_2O	EOS/ DTAC	500[a)]	9.1	5.5×10^{-4}
DPO/ DTAC	H_2O/ D_2O[c)]	MB	275[a)]	1.6	2.2×10^{-3}
DPBF/ SDS	H_2O	MB/ SDS	500[a)]	47.1	1.1×10^{-4}
	H_2O	EOS	500[a)]	42.4	1.2×10^{-4}

a) Data of Kearns *et al.* for k'_d are used in the calculation of k'^{S}_{A} values.[8] b) $\chi_{MeOH}=0.3$, $\chi_{D_2O}=0.5$. c) $\chi_{D_2O}=0.5$. Abbreviations: Histidine (HIS), histamine (HISA), methanol (MeOH), ethanol (EtOH), 1-butanol (*n*-BuOH), 1,1,2,2-tetrachloroethane (TeCE), 1,1-dichloroethane (DeCE), and erythrosine (ERY). L denotes the value obtained by laser flash experiment.

In air-saturated aqueous or ethanol solution, the triplet state of methylene blue reacts predominantly with dissolved oxygen; $k^s_{O_2}$ $[O_2] \gg k_d + k_D[MB] + k^s_{TA}$ [A]. Thus, the value of Φ_{so} would be that of ϕ_{st} (=0.52) since γ_{so} is approximately equal to unity.[8] For efficient acceptors such as 9,10-dimethylanthracene (DMA), 1,3-diphenylisobenzofuran (DPBF), and 2,5-dimethylfuran (DMF) which can react without the deactivation reaction of singlet oxygen (Eq. 8, $r \simeq 1$), the maxmum value for the reaction quantum yield Φ^{max}_{-A} should be close to ≈ 0.52 (ϕ_{st} value). However, the observed value of Φ^{max}_{-A} is about twice of ϕ_{st} (≈ 1.2) as shown in Fig. 1. Although it can be expected that a complex chain reaction is involved to consume a couple of these acceptor molecules, the following results seems to deny the existence of the chain reaction in the case of the photooxygenation of DMF in an aqueous solution.

1) The UV-absorption spectrum of the $MB-O_2-$DMF system changes with an isobestic point at 233 nm during the course of irradiation.

2) *cis*-3-Hexene-2,5-dione is a main oxidation product from DMF, the concentration of the peroxide produced being smaller than 20% of the initial concentration of DMF at $\approx 10^{-4}$ M. From the results it can be proposed that the following successive reaction of A with AO_2 occurs efficiently at higher concentrations of acceptors:[11,16]

$$AO_2 + A \longrightarrow 2AO. \tag{10}$$

If we assume that AO_2 is a certain intermediate such as the collisional adduct or the charge transfer complex between A and $^1O_2$, the quantum yield of Φ_{-A} including the competitive unimolecular decay of AO_2 (rate constant ratio; γ) *via* process 10 is given by

$$\Phi_{-A} = \Phi_{so}\frac{[A]}{\beta+[A]}\left(1+\frac{[A]}{\gamma+[A]}\right), \tag{11}$$

where $1+([A]/(\gamma+[A]))$ corresponds to α in Eq. 9. When Reaction 10 is predominant in the decay of AO_2 ($\gamma \ll [A]$), Eq. 11 approximately becomes

$$\Phi_{-A} = 2\Phi_{so}\frac{[A]}{\beta+[A]}. \tag{12}$$

In the case that AO_2 is an *endo*-peroxide and Reaction 10 is involved, Eq. 12 can similarly be applied. Thus, the maximum value of Φ_{-A} at higher concentrations of A ($\gamma \ll \beta \ll [A]$) tends to be $2\Phi_{so}$ which approaches the value of ≈ 1.2 as shown in Fig. 1.

By addition of the acceptor in high concentration, Process 5 can compete with Process 3 for the singlet oxygen formation. When the acceptor on a triplet sensitizer causes mostly its deactivation and the decomposition of A is negligible in Process 5, the quantum yield of disappearance of A is given by

$$\Phi_{-A} = \phi_{st}\alpha\frac{k^s_{O_2}[O_2]}{k_d+k^s_{TA}[A]+k^s_{O_2}[O_2]}\,\frac{r[A]}{\beta+[A]}. \tag{13}$$

Thus, the concentration effect of A on Φ_{-A} has a maximum where the concentration of A is given by $\sqrt{(k_d+k^s_{O_2}[O_2])/k^s_{TA}}$. In the system of $MB-O_2-$DPBF for example, Φ_{-DPBF} decreases at higher concentration

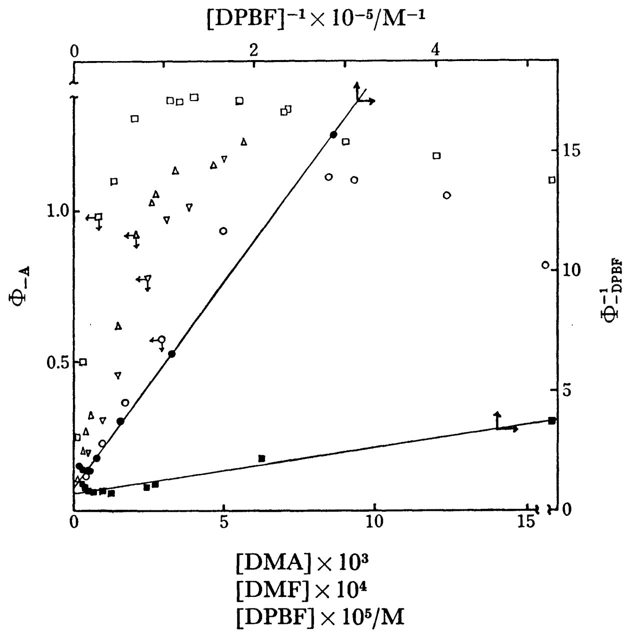

Fig. 1. Effect of [A] on Φ_{-A} and the double reciprocal plots. A: DMF in H_2O (▽), DMA in EtOH (△), DPBF in TeCE (□ and ■), and MeOH (○ and ●). [MB]: 10 μM.

of DPBF as shown in Fig. 1. The rate constant k^s_{TA} for MB and DPBF was estimated to be 2.7×10^9 M^{-1} s^{-1} (in 1,1,2,2-tetrachloroethane, TeCE) and 5.8×10^9 M^{-1} s^{-1} (in methanol, MeOH) by means of the laser flash apparatus. If we use the values of β in Table 1 and those of $(k_d+k^s_{O_2}[O_2])$, 1.5×10^6 s^{-1} in TeCE and 4.0×10^6 s^{-1} in MeOH, the calculated concentrations of DPBF give the maximum quantum yield at 9.7×10^{-5} M and 2.1×10^{-4} M for the respective solvents. The coincidence of these values with the results in Fig. 1 shows that Process 5 is appreciable to the concentration of DPBF above $\approx1\times10^{-4}$ M. Thus, when a reactive acceptor is added with a sensitizer it should be noted that the reaction scheme switches from the singlet oxygen reaction (Type II mechanism) to the direct reaction of A with the triplet sensitizer (D–R or D–O mechanism[17]) depending on the concentration of A.

Solvent Effect of the Quantum Yield in a Homogeneous Solution. The lifetime of singlet oxygen ($^1\Delta_g$) depends highly on the type of solvent. Kearns *et al.* ortedrep that the lifetime is related to the optical densities (O.D.) of the solvents at the waven umbers of 7880 and 6280 cm^{-1} corresponding 0-0 and 0-1 components of the $^1O_2(^1\Delta)-{}^3O_2(^3\Sigma)$ transition as follows:[8]

$$k_d'\times10^{-6} \simeq 0.5(\mathrm{O.D.})_{7880} + 0.05(\mathrm{O.D.})_{6280} \equiv D. \quad (14)$$

Under the conditions $\beta\gg$[A] in Eq. 9, the solvent effect on the value of Φ_{-A} should explicitly reflect the solvent sensitivity of k_d', $k_A'^s$, Φ_{so}, and αr. If the maximum quantum yields Φ^{max}_{-A} ($=\Phi_{so}$ αr) in two kinds of solvents are equal to each other, the possibility that Φ_{so} and αr afford the large solvent effect on Φ_{-A} can be neglected. Further, since the rate constant k'^s_{-DPBF} does not seem to be so sensitive to solvents as compared with the solvent sensitivity of $k_d'^T$ (Table 1), the large solvent effect on Φ_{-DPBF} could reflect the solvent sensitivity of the lifetime of singlet oxygen to the photooxygenation of DPBF.

In the mixture of solvent 1 and 2 at the mole fractions of χ_1 and χ_2, it can be assumed that Kearns'-type equation for the solvent quenching to singlet oxygen is expressed as

$$k_d'\times10^{-6} \simeq D_{mix} = \chi_1 D_1 + \chi_2 D_2, \quad (15)$$

where D_1 and D_2 stand for the sum of Eq. 14 to solvents 1 and 2, respectively. When the condition $\beta\gg$ [DPBF] holds for the mixed solvent, Φ_{-DPBF} in the mixture would be given by

$$\Phi_{-DPBF} = \Phi_{so}\alpha r(k_d'/k_A'^s)^{-1}[\mathrm{DPBF}]. \quad (16)$$

Substituting Eq. 15 into Eq. 16 and neglecting the solvent effects on the values of Φ_{so}, αr, and $k_A'^s$, we obtain the ratio of $\Phi^{(2)}_{-DPBF}$ in the pure solvent 2 against Φ_{-DPBF} in the mixture in a linear form with respect to χ_1 as follows.

$$\Phi^{(2)}_{-DPBF}/\Phi_{-DPBF} = 1 - \left(1-\frac{D_1}{D_2}\right)\chi_1. \quad (17)$$

In several mixtures (Fig. 2) where the relation $D_{mix}=\chi_1D_1+\chi_2D_2$ holds, the experimental points of $\Phi^{(2)}_{-DPBF}/\Phi_{-DPBF}$ coincide with the predicted lines from Eq. 17. The relation can be applied to the mixture of water and deuterium oxide too.

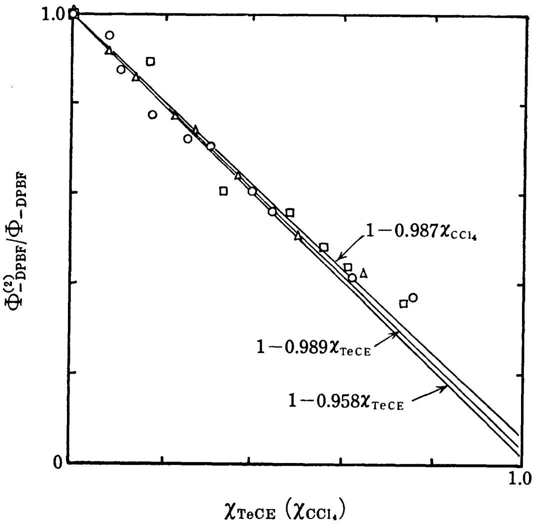

Fig. 2, Effect of mixed solvent on Φ_{-DPBF}. [MB]: 4 μM. [DPBF]: 35 μM. MeOH (solv. 2)–TeCE (solv. 1) (△), Hexane (solv. 2)–TeCE (solv. 1) (○), and Hexane (solv. 2)–CCl_4 (solv. 1) (□).

The relation $D_{mix}=\chi_1D_1+\chi_2D_2$ does not hold for the mixture of water and ethanol. In such case, the k_d' value has to be estimated directly by measuring the values of D_{mix} over each ratio of the mixture. If the value of $k_A'^s$ does not depend on the mole fraction of alcohol, the following equation can be derived in the range $\beta\gg$[A] since Φ^{max}_{-A} equals to Φ_{so} αr.

$$\frac{\Phi^{(1)}_{-A}}{\Phi^{max(1)}_{-A}} \Big/ \frac{\Phi_{-A}}{\Phi^{max}_{-A}} = \frac{D_{mix}}{D_1} = k_d'/k_d'^{(1)} \quad (18)$$

However, for the systems of MB–O_2–DMF and MB–O_2–DPBF in the water–ethanol or water–methanol mixture, the quantum yields differ a great deal from what is expected in Eq. 18. The solvent effect on $\Phi_{\text{-A}}$ shows a maximum around $\chi_{\text{ethanol}} \simeq 0.3$, decreasing gradually in the region of χ_{ethanol} over 0.3. Since Young *et al.* reported the values of k'^s_{DPBF} as 1.2—1.3×10^9 M^{-1} s^{-1} in methanol and 5.1×10^9 M^{-1} s^{-1} in 1 : 1 methanol–water mixture, the k'^s_{DPBF} value depends on the mole fraction of methanol.[15] Using these values of k'^s_{DPBF}, the ratio of the quantum yield (2.3) in the 1 : 1 mixture of methanol and water to that in methanol is explained by the corrections ($\approx$2.9) for both k'_d and k'^s_{DPBF} values.

Sensitized Photooxygenation in Micelles. Acceptor Concentration Dependence on the Quantum Yield: Recently it was reported that DPBF and 2,5-diphenylfuran solubidized in sodium dodecyl sulfate (SDS) micelles can be oxidized by the photosensitized reaction.[9,10] In order to determine the reaction mechanism in other micellar systems for several combinations of the sensitizing dyes, the acceptor and the micelles, kinetic investigations were carried out on the effects of the acceptor concentration, solvent composition, and the surfactant concentration upon the quantum yield.

In the region of 1st CMC of dodecyltrimethylammonium chloride (DTAC) micelles, most of MB does not bind to the micelle but exists in a bulk phase because of an electrostatic repulsion between the cationic DTAC micelle and dye. Thus, DMA or 2,5-diphenyloxazole (DPO) which is dissolved into Hartley's cubic micelles of DTAC, reacts with singlet oxygen produced by energy transfer from dye in the bulk phase.

The concentration effect of DMA/DTAC on $\Phi_{\text{-DMA/DTAC}}$ is shown in Fig. 3 and the reciprocal plot of $1/\Phi_{\text{-DMA/DTAC}}$ against 1/[DMA/DTAC] exhibits a linear relationship similar to that in a homogeneous solution. The β value obtained from Eq. 19 in a water–micellar solution is about ten times greater than that in a deuterium oxide–micellar solution (Table 1). Since the same value of $\Phi^{\max}_{\text{-DMA/DTAC}}$ is obtained both in water– and deuterium oxide–micellar solutions it is resposible for the result that the k'_d value in water is just ten times greater than that in deuterium oxide as shown by Kearns *et al.*[8] The $\Phi^{\max}_{\text{-DMA/DTAC}}$ value $\approx$0.5, which is about a half of that obtained from the concentration effect in ethanol, may be explained as reasonable since photooxygenated DMA in the micelles is hard to react with another DMA molecule, indicating that process 10 is not involved in this system. The deuterium oxide effect on β and $\Phi^{\max}_{\text{-DPO/DTAC}}$ value was also observed in the case of DPO/DTAC-oxygenation sensitized by MB in the bulk phase. The results suggest that the α value in Eq. 9 is close to unity. The following equation can be written for an aqueous micellar solution.

$$\Phi_{\text{-DMA/DTAC}} = \Phi_{\text{so}} \frac{k'^r_A[\text{DMA/DTAC}]}{k'_d + k'^s_A[\text{DMA/DTAC}]}. \qquad (19)$$

The DMA/DTAC concentration dependence on $\Phi_{\text{-DMA/DTAC}}$ was investigated in the photooxygenation sensitized by an anionic dye of eosine (EOS) adsorbed on the micelles. The result also gives a linear relationship between $1/\Phi_{\text{-DMA/DTAC}}$ and 1/[DMA/DTAC] ([EOS/DTAC]: 10 μM, [DTAC]: 50 mM, and [DMA/DTAC]: 0.6—18.5×10^{-5} M). Referring to the case sensitized by MB, a similar β value 5.5×10^{-4} M is obtained in the water–micellar solution. If we substitute the k'_d value obtained in an aqueous solution for the micellar systems into Eq. 19, the estimated rate constant $k'^s_{\text{DMA/DTAC}}$ becomes greater than that for DMA in ethanol. Thus, it is confirmed that singlet oxygen readily penetrate into the micellar phase, reacting with DMA efficiency in spite of whether dye is electrostatically bound on the ionic surfactant micelles or not. From the results putting A/micelle instead of A, the schemes (1)—(8) might be accepted.

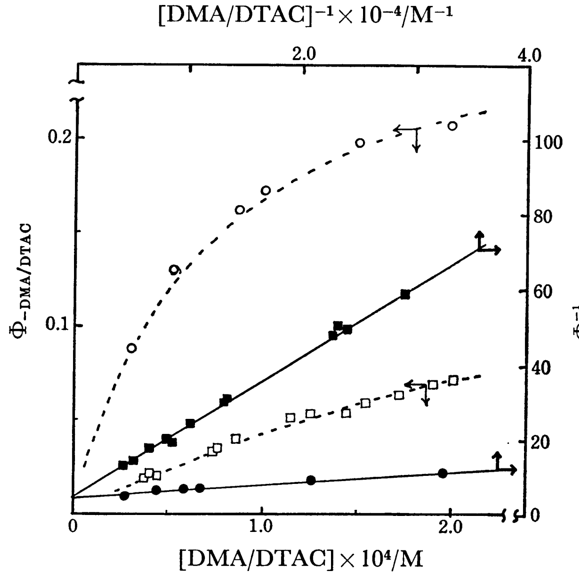

Fig. 3. Effect of [DMA/DTAC] on $\Phi_{\text{-DMA/DTAC}}$ in H_2O and in D_2O. [MB]; 10 μM. [DTAC]: 50 mM.

Solvent Effect on the Quantum Yield in Micellar Solution. From the results mentioned above, the mixed solvent effect on the quantum yield for a micellar system can be

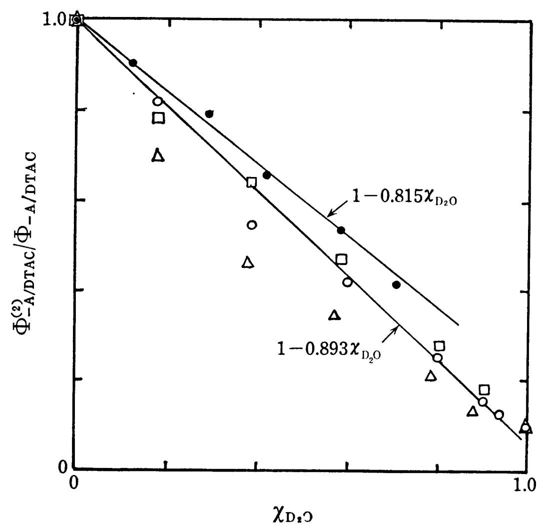

Fig. 4. Effect of mixed solvent of H_2O–D_2O on $\Phi_{\text{-DMA}}$ in water and $\Phi_{\text{-A/DTAC}}$ in DTAC micellar solution (50 mM). ●; [MB]: 10 μM, [DMA]: 1.0×10^{-4} M, [DTAC]: 0 M, $\chi_{\text{EtOH}}=0.3$. △; [MB]: 10 μM, [DMA/DTAC]: 100 μM. ○; [MB]: 5 μM, [DPO/DTAC]: 25 μM. □; [EOS/DTAC]: 10 μM, [DMA/DTAC]: 37 μM.

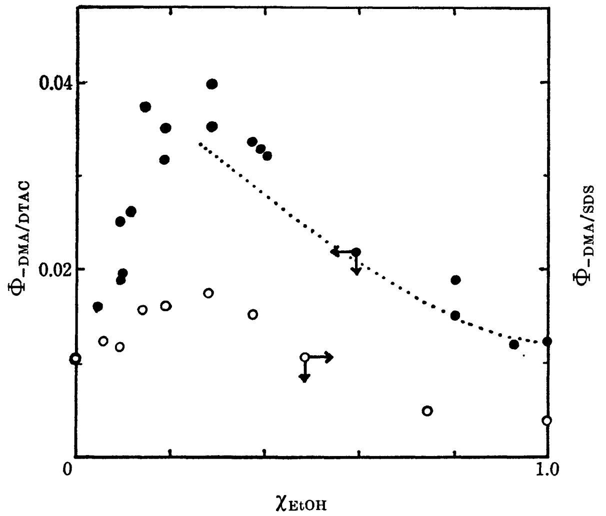

Fig. 5. Effect of mixed solvent of H_2O–EtOH on $\Phi_{\text{-DMA/DTAC}}$ and $\Phi_{\text{-DMA/SDS}}$. [MB]: 5 μM, [DMA/DTAC]: 26 μM, [DTAC]: 50 mM (●) and [EOS]: 20 μM, [DMA/SDS]: 14 μM, [SDS]: 20 mM (○). Data on the mixture without DTAC (dotted line) are normalized at $\chi_{\text{EtOH}}=1$.

treated by means of Eq. 17, and specified by the lifetime of singlet oxygen in bulk phase as well as in a homogeneous solution. The effect of deuterium oxide on the $\Phi_{\text{-DMA/DTAC}}$ (or $\Phi_{\text{-DPO/DTAC}}$) value sensitized by MB or EOS/DTAC can be explained by Eq. 17 as shown in Fig. 4.

In the case of water and ethanol mixture, the results for MB–O_2–DMA/DTAC and EOS–O_2–DMA/SDS systems are anomalous. At the mole fraction of ethanol $\chi_{\text{EtOH}}\approx 0.2$, $\Phi_{\text{-DMA/DTAC}}$ has a maximum (≈ 0.04 for the system of MB–O_2–DMA/DTAC), decreasing in the χ_{EtOH} region over 0.3 where the degree of decrement coincides with the dotted line in Fig. 5. This seems to be due to the decomposition of DTAC micelles in the region $\chi_{\text{EtOH}}>0.3$. On the other hand, the Φ_{SO} value could not be affected by the addition of ethanol in the region $\chi_{\text{EtOH}}\lesssim 0.3$. The β values at $\chi_{\text{EtOH}}=0$ and 0.2, were about 6.6×10^{-4} and 5.2×10^{-4} M, respectively. If DMA/DTAC micelles start to decompose into the homogeneous solution even in the region $\chi_{\text{EtOH}}<0.3$, the quantum yield of DMA disappearance would decrease with increasing χ_{EtOH} beyond 0.3, since the β values at $\chi_{\text{EtOH}}>0.3$ are greater than that at $\chi_{\text{EtOH}}=0$. However as shown in Fig. 5, the effect of ethanol on $\Phi_{\text{-DMA/DTAC}}$ shows a reverse tendency. The increment in $\Phi_{\text{-DMA/DTAC}}$ may be due to the DMA liberation from the micelles by the swelling effect of ethanol because the existence of free DMA molecules contributes to the disappearance of DMA in the region $\chi_{\text{EtOH}}<0.3$ (Eq. 9).

Micelle Concentration Effect on the Quantum Yield. In order to check the deactivation of the excited states of sensitizer and singlet oxygen by micelles, the micelle concentration effect on the quantum yield was tested. As shown in Fig. 6, in the region between 1st and 2nd CMC the quantum yield does not depend on the micelle concentration, the effect being negligible for the systems of MB–O_2–DMA/DTAC, MB–O_2–DPO/DTAC, MB/SDS–O_2–DPBF/SDS, and EOS–O_2–DPBF/SDS. In contrast, under 1st CMC the complex features are shown for each case.

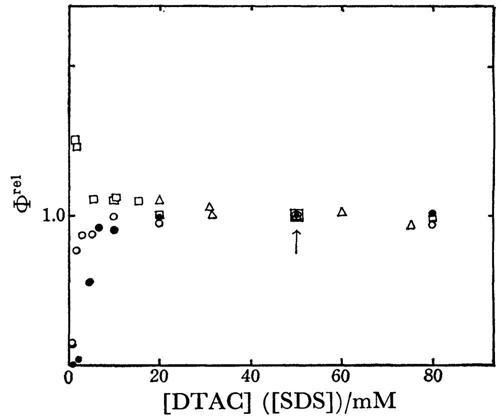

Fig. 6. Surfactant concentration effect on the relative quantum yields normalized at 50 mM. MB–O_2–DMA/DTAC (△), MB–O_2–DPO/DTAC (□), MB/SDS–O_2–DPBF/SDS (●) and EOS–O_2–DPBF/SDS (○).

Effect of N_3^- Addition on DPO Fluorescence and the Quantum Yield. Fluorescence quenching of some substances in the micelles by an ionic quencher deviates from the Stern-Volmer plot because of the electrostatic interaction on the Stern layer of charged micelle.[18] In the case of the quenching of DPO in DTAC micelles by azide ion N_3^-, the Stern-Volmer plot deviates from the concentration of N_3^- ion over 80 mM, becoming saturated around 300 mM as shown in Fig. 7. The quenching of DPO fluorescence in the micelles by N_3^- is about ten times greater than that in a 10% EtOH–H_2O solution. Since the Stern-Volmer plot in the solution does not deviate at the concentration of N_3^- around $\approx 10^{-1}$ M, the quenching of DPO in DTAC micelles can occur by N_3^- adsorbed electrostatically on

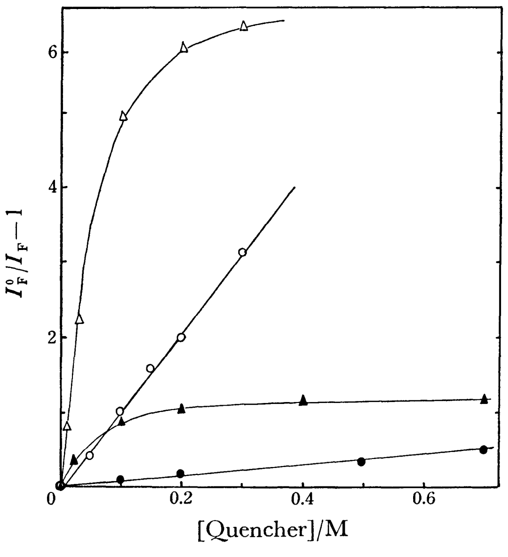

Fig. 7. Stern-Volmer plots for the fluorescence quenching of DPO/DTAC. Quencher; NaN_3 (△; in 50 mM DTAC and ○; in 10% EtOH–H_2O) and NaBr (▲; in 50 mM DTAC and ●; in 10% EtOH–H_2O).

the micelles, simultaneously. A similar feature was observed on NaBr quenching (Fig. 7).

It is well-known that the N_3^- ion is an efficient quencher to singlet oxygen. In the case of photooxygenation of DPO/DTAC the quantum yield $\Phi_{-\mathrm{DPO/DTAC}}$ becomes small by the addition of NaN_3 of 50 mM (3.1×10^{-4}, [DPO/DTAC]: 14.4 μM), no deuterium oxide effect being observed on the $\Phi_{-\mathrm{DPO/DTAC}}$ value. Singlet oxygen would be predominantly deactivated by N_3^- bound to the micelles and in solution, where DPO/DTAC is protected from the attack by singlet oxygen. Although the effect of N_3^- bound to the DPO/DTAC micelles on the DPO fluorescence seems to be significant at the order of 10^{-1} M (Fig. 7), the degree of N_3^- bound on the micellar periphery is too small to affect the quantum yield in the concentration lower than 1 mM. The binding effect on the singlet oxygen reaction was checked by measurements of $\Phi_{-\mathrm{DMA/DTAC}}$ values in the presence of another anion (1 mM NaCl) or the high micelle concentration ([DTAC micelle]: 0.936 mM). Since both effects of the NaCl addition and the micelle concentration are scarcely observed, the contribution of bound N_3^- ion is negligible for the singlet oxygen reaction in such lower concentration of N_3^-.

Table 2. Rate constants of N_3^- ion with singlet oxygen in aqueous and micellar solutions

System (solv. pH)	k_N ($M^{-1}\ s^{-1}$)
$MB-O_2$-Tryptophan (H_2O, 8.37)	$1.7\pm0.2\times10^9$
$MB-O_2$-DPO/DTAC (H_2O, 7.0)	$2.2\pm0.3\times10^9$
$MB-O_2$-DMA/DTAC (H_2O, 7.0)	$2.3\pm0.3\times10^9$

In order to confirm the results of solvent effect on the quantum yield in a micellar solution which shows that the lifetime of singlet oxygen is restricted by the property or the composition of a solvent mixture in the bulk phase, we studied the effect of N_3^- on $\Phi_{-\mathrm{DPO/DTAC}}$ in the range $[N_3^-] < 1$ mM, where the reaction of N_3^- with the excited state of sensitizer is negligible.[20] The quenching rate constant of singlet oxygen by N_3^- (k_N) can be estimated from the slope and intercept in the following equation:

$$1/\Phi_{-\mathrm{DPO/DTAC}} = \frac{k'_d + k'^{s}_{A}[\mathrm{DPO/DTAC}] + k_N[N_3^-]}{\phi_{st}k'^{r}_{A}[\mathrm{DPO/DTAC}]}. \qquad (20)$$

The value of k_N obtained are given in Table 2. The coincidence of k_N values both in micellar solutions and in an aqueous solution within experimental error shows that singlet oxygen is quenched in the bulk phase as in the aqueous solution. There is no specific effect on the surface in the dilute concentration of N_3^-. Therefore, this supports the view that the lifetime and behaviour of singlet oxygen are mainly affected by the condition or the solvent composition in the bulk phase.

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