THE PRIMARY PROCESSES OF THE PHOTOSENSITIZED REDUCTION OF METHYLENE BLUE IN AN AQUEOUS SODIUM DODECYLSULPHATE MICELLAR SOLUTION

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Summary

In the presence of an anionic reductant the photosensitized reduction of methylene blue (MB^+) with 10-dodecyl(acridine orange) (DAO^+) as a sensitizer occurred in a 30vol.%alcohol–water mixture and in sodium dodecylsulphate aqueous micellar solution where DAO^+ is incorporated into the micelles. The quantum yield Φ^S for the photosensitized reduction is smaller than the quantum yield Φ for direct photoreduction in the homogeneous solution and is larger than Φ in the heterogeneous solution. These results were attributed to the difference between the primary processes of the photosensitized reduction in these solutions. In the homogeneous solution photosensitized reduction occurs through triplet–triplet (T–T) energy transfer from DAO^+ to MB^+ followed by the reaction of triplet MB^+ with the reductant, whereas in the heterogeneous solution it occurs through three kinds of primary processes: (i) singlet–singlet energy transfer from DAO^+ to MB^+ followed by the intersystem crossing of excited singlet MB^+, (ii) T–T energy transfer from DAO^+ to MB^+ and (iii) electron transfer from triplet DAO^+ to MB^+.

1. Introduction

Mechanistic investigations for photosensitized reactions in heterogeneous systems such as micelles, vesicles and emulsions are important in relation to photobiological phenomena and the photochemical utilization of solar energy [1 - 3]. The photosensitized reaction in a micellar system is influenced by the compartment effect, the electrostatic effect, restrictions on the orientation of the molecules and other factors [4, 5].

In a previous work on the photoreduction of dyes bound to a surfactant micellar surface [6] it was found that the electrostatic interaction between

ionic micelles and reductant ions strongly affects the rate of photoreduction of the dyes. The photoreduction of methylene blue (MB^+) bound to sodium dodecylsulphate (SDS) micelles in an aqueous solution was inhibited in the low range of the ethylenediaminetetraacetic acid (edta) concentration (below 10 mM) because of the electrostatic repulsion between the anionic micelle and the reductant anion. In contrast, when 10-dodecyl(acridine orange) (DAO^+) was incorporated into the micelles as a sensitizer (*i.e.* in the DAO^+–SDS–MB^+ micellar system), the photosensitized reduction of MB^+ occurred even at the low concentration of edta. It was also found that the Φ^S value depends on the MB^+ concentration and the ionic strength [6].

In the present work we studied the detailed reaction mechanism for the photosensitized reduction of MB^+ on SDS micelles using DAO^+ as a photosensitizer. Important primary processes were found to be singlet–singlet (S–S) and triplet–triplet (T–T) energy transfer from DAO^+ to MB^+ and electron transfer from triplet DAO^+ to MB^+.

2. Experimental details

Methylene blue (MB^+Cl^-) (Merck) was recrystallized twice from 1-butanol. 10-Dodecyl(acridine orange) bromide (DAO^+Br^-) was synthesized and purified as described previously [6]. SDS (Tokyo Kasei Special Use grade) was recrystallized twice from methanol. The disodium salt of edta (Nakarai Guaranteed Reagent grade) and ascorbic acid (AA) (Tokyo Kasei Guaranteed Reagent grade) were used as received.

The degassed sample solution was exposed to continuous irradiation in a 1 cm × 1 cm × 4 cm cell. The light source was a 300 W tungsten lamp with a Kenko R-64 cut-off filter and a G-530 bandpass filter for direct and sensitized photoreduction respectively. The quantum yield of the photoreduction was determined as reported previously [7]. The fluorescence spectra were recorded using a Hitachi MPF-2 fluorescence spectrophotometer. A conventional flash (200 J; full width at half-maximum (FWHM), 15 μs) together with a Toshiba V-051 cut-off filter or a Toshiba V-B46 bandpass filter combined with a green plastic plate was used for excitation. The method of measuring transient absorption and time-integrated fluorescence intensity during a flash has been reported elsewhere [8]. A pulsed dye laser (Phase-R 2100B with dye G4; 3 J; FWHM, 0.5 μs) was used for the laser experiments. The fluorescence lifetime was measured using a phase fluorometer modulated at 10.7 MHz.

The 30vol.%ethanol–water mixture was buffered at pH 9.0 by the addition of 1 mM Na_2HPO_4 and 10 mM Na_2SO_4.

The aqueous SDS micellar solutions used to obtain the results reported in Section 3.2.1 were buffered by adding 1 mM CH_3COOH–CH_3COONa solution or 1 mM KH_2PO_4–Na_2HPO_4 solution. The aqueous SDS micellar solutions used to obtain the results reported in Sections 3.2.2 - 3.2.4 were buffered at pH 9.3 by adding 5 mM Na_2HPO_4. All the micellar solutions

contained 10 mM SDS unless otherwise noted. The sample solutions were degassed by means of freeze–pump–thaw cycles. All measurements were made at 23 °C.

3. Results and discussion

3.1. Photosensitized reduction of methylene blue in the 30vol.%ethanol–water mixture at pH 9.0

3.1.1. Steady light photolysis

Neither direct nor sensitized photoreduction of MB^+ occurs in the absence of a reductant such as edta or AA but both take place in its presence. The quantum yield Φ of the direct photoreduction for the disappearance of MB^+ was determined to be 0.65 for the solution containing 10 μM MB^+ and 10 mM edta. The quantum yield Φ^S of the photosensitized reduction for the disappearance of MB^+ was determined to be 0.09 for the solution containing 8 μM DAO^+, 10 μM MB^+ and 10 mM edta. The ratio Φ^S/Φ is 0.14. When the photoreduction of MB^+ occurs only through the reaction between triplet methylene blue ($^3MB^+$) and a reductant, Φ and Φ^S can be expressed as follows:

$$\Phi = \Phi_{isc}\beta \tag{1}$$

$$\Phi^S = \Phi_{isc}{}^S\alpha\beta \tag{2}$$
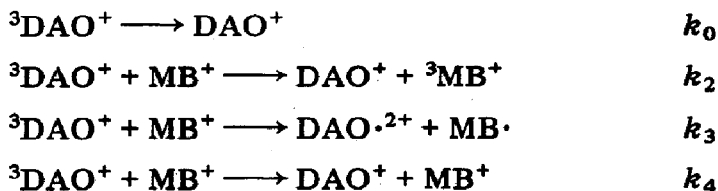
where Φ_{isc} and $\Phi_{isc}{}^S$ are the triplet yields of MB^+ and DAO^+ respectively, β is the reaction efficiency of $^3MB^+$ with the reductant and α is the efficiency of the triplet energy transfer from DAO^+ to MB^+. It is noted that (i) the β value depends on the reductant concentration, (ii) eqn. (1) is valid when the excited singlet state $^1MB^{+*}$ of MB^+ is not quenched by the reductant and (iii) eqn. (2) is valid when the excited singlet state $^1DAO^{+*}$ and triplet state $^3DAO^+$ of DAO^+ are not quenched by the reductant. Since the Φ_{isc} value has been reported to be 0.52 in both water and ethanol [9, 10], the value in the 30vol.%ethanol–water mixture is considered to be the same. The $\Phi_{isc}{}^S$ value was determined to be 0.13 by an emission–absorption flash technique using proflavine (triplet yield, 0.40 in ethanol [11]) as a standard. The fluorescence of DAO^+ and MB^+ was not quenched by edta at a concentration of 10 mM. As described in Section 3.1.2 the quenching of $^3DAO^+$ with edta is neglected for the solution containing 10 μM MB^+ and 10 mM edta. Therefore the value of α is calculated to be 0.56.

3.1.2. Flash photolysis

Flashing of a dilute solution of DAO^+ (less than about 10 μM) gives only the T–T absorption spectrum. The triplet decay is first order with a rate constant k_0 of 6×10^2 s^{-1}. The triplet is quenched by edta with a bimolecular rate constant k_1 of 3×10^5 M^{-1} s^{-1}.

Flashing of DAO^+ in the solution containing 10 μM DAO^+ and 10 μM MB^+ gives the T–T absorption spectrum of MB^+ instead of that of DAO^+,

indicating the occurrence of a triplet energy transfer from DAO^+ to MB^+. After the disappearance of the T–T absorption of MB^+ the spectrum of protonated semimethylene blue $MBH \cdot^+$ was observed. Since (i) the fluorescence of DAO^+ was not quenched by MB^+, (ii) the selective excitation of MB^+ did not yield $MBH \cdot^+$ and (iii) the pK_a value for $MBH \cdot^+$ was reported to be 9.0 [12], it was concluded that electron transfer from $^3DAO^+$ to MB^+ followed by proton transfer occurred in competition with the triplet energy transfer. Therefore the decay of $^3DAO^+$ in the solution containing DAO^+ and MB^+ can be described by the following scheme:

$$^3DAO^+ \longrightarrow DAO^+ \qquad\qquad k_0$$

$$^3DAO^+ + MB^+ \longrightarrow DAO^+ + {}^3MB^+ \qquad\qquad k_2$$

$$^3DAO^+ + MB^+ \longrightarrow DAO \cdot^{2+} + MB \cdot \qquad\qquad k_3$$

$$^3DAO^+ + MB^+ \longrightarrow DAO^+ + MB^+ \qquad\qquad k_4$$

where MB· stands for semimethylene blue. From the slope of the plot for the observed first-order decay constant *versus* the concentration of MB^+ we obtained $k_2 + k_3 + k_4 = 1.7 \times 10^9$ M^{-1} s^{-1}. The efficiency $k_2/(k_2 + k_3 + k_4)$ of the triplet energy transfer was determined to be 0.60 by simulating the decay curve of $^3DAO^+$ and the rise curve of $^3MB^+$ using the following molar extinction coefficients for T–T absorption: 7.2×10^3 M^{-1} cm^{-1} at 620 nm for $^3DAO^+$ and 2.1×10^4 M^{-1} cm^{-1} at 825 nm for $^3MB^+$. The value for k_2 is calculated to be 1.0×10^9 M^{-1} s^{-1}. Since α is defined by

$$\alpha = \frac{k_2[MB^+]}{k_0 + k_1[edta] + (k_2 + k_3 + k_4)[MB^+]}$$

the α value for the solution containing 10 μM MB^+ and 10 mM edta is calculated to be 0.4_9, which agrees with that obtained in Section 3.1.1. The agreement between the steady state and flash photolysis values of α implies that the assumption used in the derivation of eqn. (2) is valid: electron transfer from $^3DAO^+$ to MB^+ is negligible in the 30vol.%ethanol–water mixture.

Similar results were obtained when AA was used as the reductant.

3.2. Photosensitized reduction of methylene blue in the aqueous sodium dodecylsulphate micellar solution

3.2.1. Steady light photolysis

AA was used as the reductant in the investigation of the effects of electrostatic repulsion on photoreduction because it exists as a neutral molecule at low pHs (the pK_a value for AA is 4.1 [13]).

Figure 1 shows the effects of pH on Φ and Φ^S. Both Φ and Φ^S decrease with increasing pH in the neighbourhood of the pK_a value for AA. It is obvious that the dissociation of the AA molecule to the ascorbate ion retards the photoreduction. The pK_a value for $^3MB^+$ has been reported to be 7.2 - 7.5 [14, 15]. Nevertheless Φ does not change when the pH is reduced
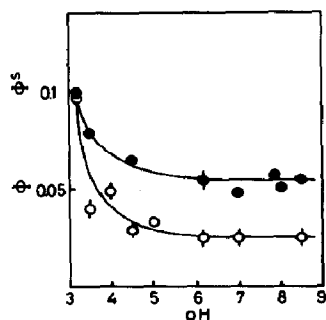
Fig. 1. pH effects on Φ (O) and Φ^S (●) (MB$^+$ concentration, 9 μM; SDS concentration, 10 mM; AA concentration, 0.2 mM; DAO$^+$ concentration, 0 M (O) and 10 μM (●)).
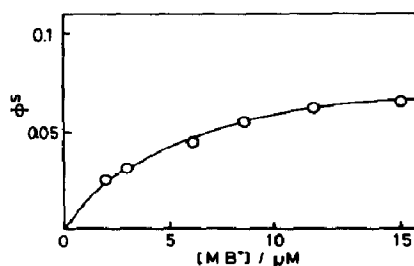
Fig. 2. The effect of the MB$^+$ concentration on Φ^S at pH 6.2 (DAO$^+$ concentration, 10 μM; SDS concentration, 10 mM; AA concentration, 0.2 mM).

from 8.5 to 5. This result means either that the yield of the reaction of triplet methylene blue with AA is the same for the basic triplet ^{3}MB$^+$ and the acid triplet ^{3}MBH^{2+} or that ^{3}MB$^+$ reacts with AA before ^{3}MB$^+$ is protonated.

Figure 2 shows the effect of the MB$^+$ concentration on Φ^S at pH 6.2. The Φ^S value increases with increasing MB$^+$ concentration up to 15 μM.

3.2.2. The quenching of 10-dodecyl(acridine orange) fluorescence by methylene blue

DAO$^+$ dissolves in SDS micelles but is insoluble in water, whereas MB$^+$ can move between the aqueous and micellar phases. The fluorescence lifetime τ_0 of DAO$^+$ in the micellar solution was determined to be 2.1 ns in the absence of MB$^+$. On the time scale of τ_0 and for a low concentration of MB$^+$, no MB$^+$ molecules leave or enter a micelle. Tachiya's equation [16 - 18] then reduces to [19]

$$\frac{I}{I_0} = \exp(-\langle q \rangle) \sum_{n=0}^{\infty} \frac{\langle q \rangle^n}{\{1 + n(k_q \tau_0)\}n} \tag{3}$$

where I and I_0 are the fluorescence intensities of DAO$^+$ in the presence and the absence respectively of MB$^+$, n is the number of MB$^+$ molecules contained in a micelle, k_q is the rate constant of fluorescence quenching in a micelle containing only one MB$^+$ molecule and $\langle q \rangle$ is the mean number of MB$^+$ molecules contained in a micelle. $\langle q \rangle$ is related to the total concentration [MB$^+$] of MB$^+$ in the micellar solution:

$$\langle q \rangle = \frac{K[\text{MB}^+]}{1 + K[\text{M}]} \tag{4}$$

where [M] is the concentration of SDS micelles and $K = k_+/k_-$ is the ratio of the rate constant k_+ for the entry of an MB$^+$ molecule into a micelle to the rate constant k_- for the exit of an MB$^+$ molecule from a micelle contain-

ing one MB^+ molecule. When $k_q\tau_0$ is much larger than unity, eqn. (3) is further reduced to

$$\ln\left(\frac{I_0}{I}\right) = \langle q \rangle = \frac{K[MB^+]}{1 + K[M]} \qquad (5)$$

According to the Förster mechanism for fluorescence quenching, k_q is expressed as $\tau_0^{-1}(R_0/r)^6$. The critical distance R_0 for the Förster-type energy transfer was estimated to be 140 Å from the absorption spectrum of MB^+ and the fluorescence spectrum of DAO^+. The maximum distance r between DAO^+ and MB^+ in the micelle is equal to the sum of the micellar radius and the thickness of the Stern layer and is about 30 Å. Hence the value for $k_q\tau_0$ is calculated to be larger than 10^4. It is concluded that $^1DAO^{+*}$ decays completely through the S–S energy transfer to MB^+ when DAO^+ and MB^+ are present in the same micelle. Figure 3 shows plots of $\ln(I_0/I)$ *versus* $[MB^+]$. The linearity of the plots indicates the validity of eqn. (5) and the above conclusion.

The S–S energy transfer can be confirmed by the observation of the sensitized fluorescence of MB^+. The sensitized fluorescence intensity I' of MB^+ should be proportional to the concentration of $^1MB^{+*}$ produced through the S–S energy transfer, which is proportional to $I_0 - I$. Therefore we obtain

$$\frac{I'}{I_0} = \frac{\gamma(I_0 - I)}{I_0} \qquad (6)$$

where γ is a constant which depends on the experimental conditions. Figure 4 shows the plot of I'/I_0 *versus* $(I_0 - I)/I_0$. The linearity of the plot confirms the fluorescence quenching of DAO^+ by MB^+ via S–S energy transfer.
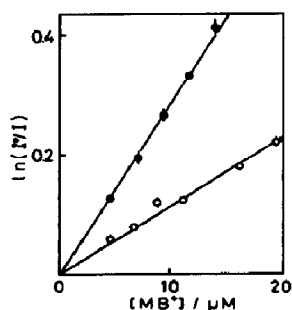

Fig. 3. Plots of $\ln(I_0/I)$ *vs.* $[MB^+]$: ●, 5 mM SDS and 4 μM DAO^+; ○, 10 mM SDS and 9 μM DAO^+.
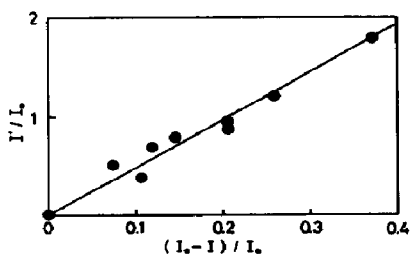
Fig. 4. Plot of I'/I_0 *vs.* $(I_0 - I)/I_0$.

3.2.3. The quenching of the triplet state of 10-dodecyl(acridine orange) by methylene blue

The decay of $^3DAO^+$ is first order in both the presence and absence of MB^+ and the observed decay constant k_{obs} is linear with respect to the MB^+

concentration as shown in Fig. 5. These results can be explained by a modi-
fied form of Tachiya's equation which is applicable to prolonged times after
flashing:

$$k_{obs} = k_{dt} + \frac{k_+ + k_e K[M]}{1 + K[M]} \frac{k_{qt}}{k_{qt} + k_- + k_e[M]} [MB^+] \qquad (7)$$

where k_{dt} is the rate constant for the deactivation of $^3DAO^+$ in the absence
of MB^+, k_{qt} is the first-order rate constant for the deactivation of $^3DAO^+$ by
MB^+ in the micelle and k_e is the rate constant for the MB^+ transfer from
micelle to micelle. When $k_{qt} + k_- \gg k_e[M]$ and $k_+ \gg k_e K[M]$, eqn. (7) is the
same as the equation derived by Pileni and Grätzel [20]. From the intercept
and the slope of the plot we obtained $k_{dt} = 4 \times 10$ s^{-1} and

$$\frac{k_{qt}(k_+ + k_e K[M])}{(1 + K[M])(k_{qt} + k_- + k_e[M])} \equiv k_{qt}' = 3.1 \times 10^6 \, M^{-1} \, s^{-1}$$

The formation of $^3MB^+$ through the T–T energy transfer from $^3DAO^+$ to
MB^+ was not detected, although it was observed in the 30vol.%ethanol–
water mixture. This can be attributed to the small population of $^3MB^+$
because of the slow decay of $^3DAO^+$ and the rapid decay of $^3MB^+$.

3.2.4. Formation of protonated semimethylene blue through the reaction of the triplet state of 10-dodecyl(acridine orange) with methylene blue

When DAO^+ was selectively flashed in the micellar solution containing
DAO^+ and MB^+, it was found that the decay of $^3DAO^+$ was accompanied by
the formation of $MBH^{.+}$ as shown in Fig. 6. In contrast, the selective excita-
tion of MB^+ did not yield $MBH^{.+}$. The rate constants for $^3DAO^+$ decay and
$MBH^{.+}$ formation are very similar. These results show that $MBH^{.+}$ is formed
through the reaction of $^3DAO^+$ with MB^+ in the micelle. The reaction can
be considered as an electron transfer from $^3DAO^+$ to MB^+ followed by the
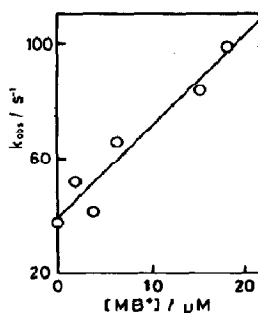protonation of $MB^.$. The efficiency of $MBH^{.+}$ formation was determined to

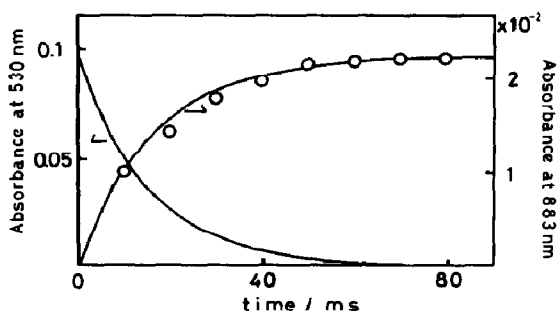Fig. 5. The dependence of the observed triplet decay constant for DAO^+ on the MB^+ concentration.

Fig. 6. The decay of $^3DAO^+$ observed at 530 nm and the formation of $MBH^{.+}$ observed at 883 nm.

be 0.08 ± 0.02 using the following molar extinction coefficients: 4.4×10^3 M^{-1} cm^{-1} at 530 nm for $^3DAO^+$ and 3.5×10^4 M^{-1} cm^{-1} at 883 nm for $MBH\cdot^+$.

3.3. The reaction mechanism for the photosensitized reduction of methylene blue in the aqueous sodium dodecylsulphate micellar solution at pH 6.2

The results described in Section 3.2 suggest that the photosensitized reduction of MB^+ by AA in the micellar solution occurs via the following three reaction pathways: (i) S–S energy transfer followed by intersystem crossing of $^1MB^{+*}$ and the reaction of $^3MB^+$ with AA; (ii) intersystem crossing of $^1DAO^{+*}$ followed by T–T energy transfer and the reaction of $^3MB^+$ with AA; (iii) intersystem crossing of $^1DAO^{+*}$ followed by the electron transfer reaction of $^3DAO^+$ with MB^+. The reaction scheme is summarized in Fig. 7.

The quantum yields Φ_1, Φ_2 and Φ_3 for photosensitized reactions via the reaction pathways (i), (ii) and (iii) are given by

$$\Phi_1 = \{1 - \exp(-\langle q \rangle)\}\Phi_{isc} \frac{\delta k_r[AA]}{k_t + k_r[AA]} \theta \tag{8}$$

$$\Phi_2 = \exp(-\langle q \rangle)\Phi_{isc}^S \frac{\zeta k_{qt}'[MB^+]}{k_{dt} + k_{qt}'[MB^+]} \frac{\delta k_r[AA]}{k_t + k_r[AA]} \theta \tag{9}$$

$$\Phi_3 = \exp(-\langle q \rangle)\Phi_{isc}^S \frac{\eta k_{qt}'[MB^+]}{k_{dt} + k_{qt}'[MB^+]} \theta \tag{10}$$

where δ, ζ, η and θ are the efficiencies of the corresponding reactions. Φ is given by

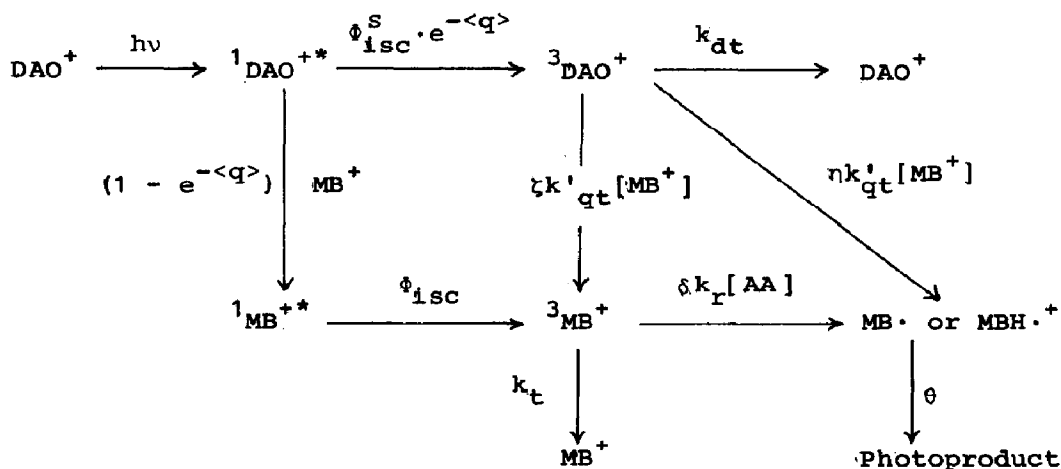$$\Phi = \Phi_{isc} \frac{\delta k_r[AA]}{k_t + k_r[AA]} \theta \tag{11}$$

Fig. 7. Reaction scheme.

TABLE 1

The values of $1 - \exp(-\langle q \rangle)$, Φ_1 and Φ^S for a micellar solution containing 10 μM 10-dodecyl(acridine orange) and 0.2 mM ascorbic acid in addition to methylene blue

$[MB^+]$ (μM)	$1 - \exp(-\langle q \rangle)$	Φ_1 (calculated)	Φ^S (observed)
5	0.05	0.0012	0.042
9	0.11	0.0027	0.056
15	0.16	0.0038	0.066
> 20	1	0.024	—

We can evaluate Φ_1 from the data shown in Figs. 1 - 3 as follows. The Φ value for the micellar solution containing 0.2 mM AA is 0.024 for MB^+ concentrations below 15 μM. The $1 - \exp(-\langle q \rangle)$ values are evaluated from Fig. 3 by assuming that $\langle q \rangle$ does not depend on the pH. Equations (8) and (11) are used to calculate the values for Φ_1 summarized in Table 1. These values for Φ_1 are much less than the observed values for Φ^S at MB^+ concentrations of 5, 9 and 15 μM. Therefore the results shown in Fig. 2 can be described as the sum of Φ_2 and Φ_3:

$$\Phi^S \approx \exp(-\langle q \rangle)\Phi_{\mathrm{isc}}{}^S \left(\frac{\zeta \delta k_r[AA]}{k_t + k_r[AA]} + \eta \right) \frac{\theta k_{\mathrm{qt}}{}'[MB^+]}{k_{\mathrm{dt}} + k_{\mathrm{qt}}{}'[MB^+]} \tag{12}$$

When k_{dt} is much less than $k_{\mathrm{qt}}{}'[MB^+]$ and $[AA]$ is kept constant, eqn. (12) is reduced to

$$\Phi_c{}^S \approx \exp(-\langle q \rangle)\Phi_{\mathrm{isc}}{}^S \left(\frac{\zeta \delta k_r[AA]}{k_t + k_r[AA]} + \eta \right) \theta \tag{13}$$

Putting $\psi \equiv \Phi^S \exp(\langle q \rangle)$ and $\psi_c \equiv \Phi_c{}^S \exp(\langle q \rangle)$ in eqns. (12) and (13) we obtain

$$\frac{\psi_c}{\psi} \approx 1 + \frac{k_{\mathrm{dt}}}{k_{\mathrm{qt}}{}'[MB^+]} \tag{14}$$

Figure 8 shows the plot of $1/\psi$ versus $1/[MB^+]$. As the plot is linear, we obtain $1/\psi_c \approx 10$ and $k_{\mathrm{dt}}/\psi_c k_{\mathrm{qt}}{}' \approx 6 \times 10^{-5}$ M from the intercept and slope of the plot respectively. The ratio of these values gives $k_{\mathrm{dt}}/k_{\mathrm{qt}}{}' \approx 6 \times 10^{-6}$ M which is in fair agreement with the results obtained in Section 3.2.3. One of
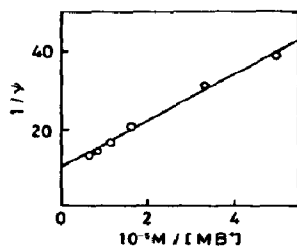

Fig. 8. Plot of $1/\psi$ vs. $1/[MB^+]$.

the reasons for the steady state and flash values of k_{qt} to differ by a factor of 2 is the low buffer concentration in the steady state experiments which may not produce an adequate decrease in the critical micelle concentration of SDS (8 mM) and may allow the formation of submicellar SDS aggregates or SDS–dye aggregates. Since both Φ and Φ^S change slightly in the pH range 5 - 8.5, it seems that the mechanisms for direct and sensitized reduction of MB^+ do not change in this pH range. Therefore it can be concluded that the photosensitized reduction of MB^+ in the micellar solution occurs through reaction pathways (ii) and/or (iii) in the pH range 5 - 8.5 and at MB^+ concentrations below 15 μM.

The ratio $\Phi_{isc}{}^S/\Phi_{isc}$ in the micellar solution at pH 6.2 was determined by an emission–absorption flash technique [11] to be 0.3. Since this value is close to the ratio in the 30vol.%ethanol–water mixture, it is assumed that neither Φ_{isc} nor $\Phi_{isc}{}^S$ changes in these solutions. Then the maximum value for Φ_2 can be evaluated using eqns. (9) and (11) and the data shown in Figs. 1 and 3. For example, the Φ_2 value for the micellar solution containing 0.2 mM AA is calculated as follows. The $\Phi_{isc}{}^S$ value is assumed to be 0.13. Putting $\Phi_{isc} = 0.52$ and $\Phi = 0.024$ in eqn. (11), we obtain

$$\frac{\theta \delta k_r [AA]}{k_t + k_r [AA]} = 0.046 \tag{15}$$

Consequently eqn. (9) is reduced to

$$\Phi_2 = 0.0060 \frac{\exp(-\langle q \rangle) \zeta k_{qt}{}' [MB^+]}{k_{dt} + k_{qt}{}' [MB^+]} \tag{16}$$

Since ζ is less than unity, the value for $\Phi_2 \exp(\langle q \rangle)$ does not exceed 0.0060 which is a factor of 17 less than that of ψ_c. Therefore it is concluded that the photosensitized reduction of MB^+ occurs mainly through reaction pathway (iii) at MB^+ concentrations below 15 μM in the pH range 5 - 8.5.

However, for the micellar solution containing 0.2 mM AA, eqn. (10) becomes

$$\Phi_3 = 0.13 \frac{\exp(-\langle q \rangle) \theta \eta k_{qt}{}' [MB^+]}{k_{dt} + k_{qt}{}' [MB^+]} \tag{17}$$

When k_{dt} is much less than $k_{qt}{}' [MB^+]$, we obtain from eqns. (16) and (17)

$$\psi_c \approx 0.0060 \zeta + 0.13 \theta \eta \tag{18}$$

Putting $\psi_c \approx 0.10$ and $\zeta \leqslant 1$ in eqn. (18) we obtain $\theta \eta \approx 0.7$. θ is less than unity so that η is larger than 0.7. Therefore the quenching of $^3DAO^+$ by MB^+ in the micellar solution is mainly due to electron transfer from $^3DAO^+$ to MB^+, in contrast with the mechanism in the 30vol.%ethanol–water solution. The fact that the efficiency of $MBH \cdot {}^+$ formation in the micellar solution containing 9.3 μM DAO^+ and 6.3 μM MB^+ is 0.05 can be attributed to back electron transfer. In the presence of AA, however, it is assumed that reactions of AA with semioxidized 10-dodecyl(acridine orange) ($DAO \cdot {}^{2+}$) and/or $MB \cdot$ retard back electron transfer.

When the MB^+ concentration is increased the participation of reaction pathway (i) increases. The limiting value of Φ^S for a higher concentration of MB^+ should be equal to Φ_1. Using eqns. (8) and (15) and assuming Φ_{1sc} to be 0.52 we calculated Φ^S to be 0.024. This value is less than Φ^S at an MB^+ concentration of 15 μM. Therefore it is expected that with increasing MB^+ concentration Φ^S increases up to the optimum concentration and then decreases gradually until Φ^S reaches a constant value of 0.024. This prediction was confirmed by the results obtained for a solution containing 8 mM SDS, 8 μM DAO^+ and 10 mM edta in addition to MB^+ [6].

Acknowledgments

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