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PHOTOREDUCTION OF METHYLENE BLUE BOUND TO SODIUM DODECYLE SULFATE MICELLES

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Photochemical reduction of methylene blue bound to sodium dodecyl sulfate micelles is inhibited in a given concentration range of a reductant (EDTA). The concentration dependence of EDTA on the quantum yield shows a sigmoidal type, which is explained by the mechanistic interpretations consisting of the ionic strength effect and the essential concentration effect of EDTA.

Recently several investigations have been reported on the photoionization of some compounds located in micelles.1-5) Paticular interest in this phenomenon and associated electron transfer reactions arises from their possible importance in photosynthesis.6,7) For some kinds of photochemical reactions the quantum yields may be affected by the environment of the micellar periphery, i.e., so-called micellar effect. We have observed that the photoreduction of methylene blue (MB) by sodium ethylenediaminetetraacetate (EDTA) was retarded by the addition of sodium dodecyl sulfate (SDS). Furthermore, an unusual sigmoidal dependence on the EDTA concentration was observed, where the maximum photoreduction quantum yield at high concentration of EDTA ($\sim$0.1 M) exceeded the value (0.156) provided from the equation representing the quantum yield in aqueous solution.8) Since this type of EDTA concentration dependence is quite different from that usually observed for the photochemical reduction in a homogeneous solutions, we have investigated the mechanism of photoreduction in the dye-micelle system.

From the results of an electrophresis experiment it has been reported that some ionic dyes bind to the oppositely charged micelles.9) In our typical condition ([MB]; 10 μM, [SDS]: 10 mM, pH:7.0), it was confirmed by means of electrophoresis that most of MB molecules was bound to SDS micelles.

The magnitude of fluorescence polarization (P) is the measure of the microscopic viscosity around fluorescer and the conditions of its binding situation.[10] The P-value of MB fluorescence in the presence of fresh SDS micelles was measured as 0.17 ± 0.04 compared with the value ($P = 0.06 \pm 0.02$) in aqueous solution. The former was not affected by the addition of 0.1 M EDTA and/or 0.1 M NaCl. By comparing these results with those for pyrene ($P \simeq 0$) which is dissolved in the micellar interior, and for 2-methylanthracene ($P \simeq 0.06$) which can exist at the micellar boundary with some restriction of molecular free rotation,[10,11] it is indicated that MB does not go into the hydrophobic core of SDS micelles as in the case of pyrene but is bound in the boundary zone of the micelles. The fluorescence of MB bound to the SDS micelle is hardly quenched by adding EDTA at concentration up to ~ 0.1 M or by adding 0.36 M of $S_2O_3^{2-}$ or 0.1 M of CNS^- ions which quench the MB fluorescence in aqueous solution efficiently. It is expected that the dynamic quenching of the MB fluorescence is inhibited because of the electrostatic repulsion between the anionic SDS micelles and the quencher anions.

At a high concentration of MB in aqueous solution, it has been reported that the decay constant of the excited triplet MB depends on the concentration of MB and that the photoreaction starts from the electron transfer between both of the triplet states and/or between the triplet and ground states of the dye (i.e., D-D mechanism).[12] At lower concentration of EDTA the quantum yield of the photoreduction of MB in aqueous solution is considerably influenced by the contribution of D-D mechanism.[8] If D-D mechanism were involved even in the micellar system the decay rate of the triplet MB would depend on the concentration of MB at higher concentration without EDTA, where the possibility of the reaction with free MB in aqueous phase is considered depending upon the concentration of MB and its equilibrium constant between both phases. However, by laser flash photolysis on the MB-micellar solution only one transient spectrum is observed and assigned to bound triplet MB ([MB]: 5.0×10^{-5} M). The decay constant is not affected by wide concentration change of MB from 10^{-6} to 10^{-4} M. This suggests that most of MB is bound to SDS micelles at these higher concentration and that the deactivation of bound triplet MB occurs dominantly without any other processes started from triplet MB as D-D mechanism. Thus the photoreduction of MB with EDTA occurs mostly in the bound triplet state in our reaction system.

The photoreduction of the bound MB by EDTA with stationary light irradiation proceeds at a rate which is proportional to the light absorption similarly to the case in aqueous solution. However the concentration effect of EDTA on the photoreduction quantum yield of bound MB (Φ^M) is quite different from that in aqueous solution.[8] As shown in Figure 1 the dependence follows a sigmoidal curve and the reaction at lower concentration of EDTA is suppressed in the SDS micellar system. Furthermore it is observed that Φ^M at a constant concentration of EDTA (5.0 mM, pH : 7.0) increases with the ionic strength (μ) in the aqueous phase by the addition of strong electrolytes such as NaCl, $NaNO_3$ and Na_2SO_4. In the μ -range of about 0.3, Φ^M at 5 mM EDTA reaches a limiting value which is about ten times larger than that in the case of $\mu \simeq 0$. Then using the relation of Φ^M against μ the contribution of ionic strength by EDTA itself was calculated on the values of Φ^M given in Fig. 1. The corrected dependence of Φ^M on the concentration of EDTA shows not the sigmoidal curve but the usual one of the saturation-type as noted in Reference (8). Since the ionic strength effect of EDTA ion (HY^{3-}) was superposed on the concentration dependence of EDTA for Φ^M value (i.e., $\Phi^M(\mu)$), the concentration effect of EDTA on $\Phi^M(\mu)$ was reexamined at a constant ionic strength. The results are expressed as a linear double reciprocal plot of $1/\Phi^M(\mu)$ against 1/[EDTA] in Figure 2. Thus, by referring to the analysis in the case of aqueous solution,[8] $\Phi^M(\mu)$ can be tentatively expressed at a constant ionic strength as follow;

$$\Phi^M(\mu) = \frac{\phi_{st}\, k^r(\mu)\,[\mathrm{EDTA}]}{k_d + k^s(\mu)\,[\mathrm{EDTA}]} \qquad (1)$$

where ϕ_{st} is the intersystem crossing probability of MB bound to SDS and $k^r(\mu)$ and $k^s(\mu)$ are the reactive and overall rate constants for the reaction of bound triplet MB with EDTA respectively. Incidentally, the concentration effect of EDTA on Φ^M does not follow the equation (1) at a constant concentration of electrolytes.

From the results in Figure 2 the usual reaction scheme of the competition between the spontaneous deactivation of the bound triplet MB and the reaction with EDTA seems to be expected. By substituting k_d ($4.1 \times 10^4\ s^{-1}$, Na_2HPO_4-KH_2PO_4 buffer; 10^{-3} M, pH: 7.0) measured by laser flash photolysis into the value of $k_d/k^s(\mu)$ obtained from an intercept and a slope of the line in Fig. 2, the values of $k^s(\mu)$ are estimated under a constant ionic strength and are shown in Table 1. Since the values of $k^s(\mu)$ decrease with the ionic strength, it shows that the product Z_AZ_B is negative when the equation of the neutral salt effect ($\ln k^s(\mu) = \ln k^s_0 + 1.02\, Z_AZ_B \sqrt{\mu}$) can be applied to $k^s(\mu)$. This suggests that EDTA anion reacts with the positively charged micellar particle of SDS containing MB. But in spite of the expectation that the decay constant of the bound triplet MB should be given by the expression of $k_d + k^s(\mu)[\mathrm{EDTA}]$, the decay constant measured by laser excitation was not linear to the analytical concentration of EDTA. Although this implies that the bound MB reacts not with the free EDTA in the bulk but with the molecule bound on the surface of the micelle, more kinetic investigations are required to identify the elementary processes at the micellar boundary.

Table 1. Effect of ionic strength on the values of $k^s(\mu)$

μ	$k^s(\mu)$ M^{-1} s^{-1}
0.010	1.8×10^8
0.025	1.8×10^7
0.100	8.5×10^5
0.200	5.1×10^5
0.400	3.6×10^5

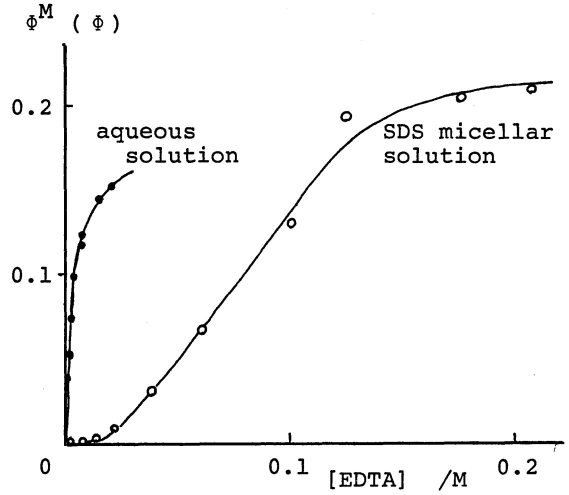

Figure 1. Effect of [EDTA] on Φ^M and Φ. Values of Φ in aqueous solution are plotted after Ref. (8).

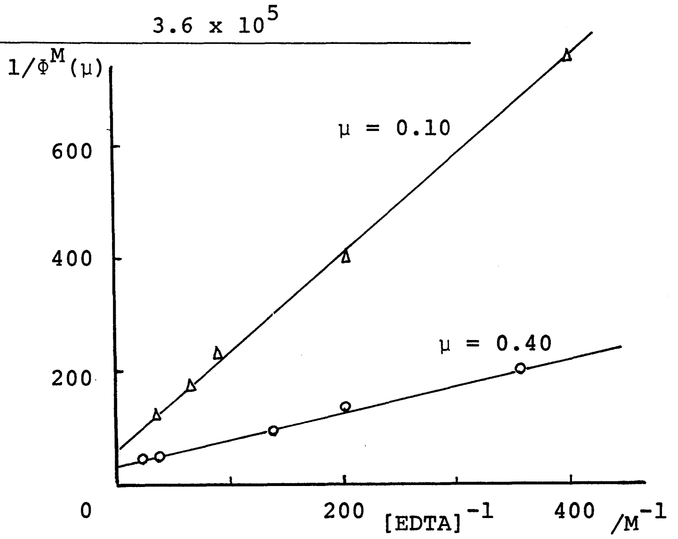

Figure 2. Plot of $1/\Phi^M(\mu)$ against 1/ [EDTA].

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$$\Phi = \frac{3.9 \times 10^6\ [EDTA]}{1.2 \times 10^4 + 2.5 \times 10^7 [EDTA]}$$ in aqueous solution, pH = 6.7.[13)]

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