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Effects of EDTA Derivatives on the Photoreduction of Methyl Viologen by a Thiacarbocyanine Sensitizer in a Micellar Solution

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The photoinduced reduction of Methyl Viologen (MV^{2+}) by ethylenediaminetetraacetate (EDTA), 1,2-propanediamine-*N,N,N′,N′*-tetraacetate (MeEDTA), and *trans*-1,2-cyclohexanediamine-*N,N,N′,N′*-tetraacetate (CyDTA) was investigated by using 3,3′-dioctadecylthiacarbocyanine (C^{+}_{18-18}) as a sensitizer in a micellar solution of a nonionic surfactant, heptaethylene glycol monododecyl ether. The production rate of reduced Methyl Viologen ($MV^{+\cdot}$) decreased with the light-irradiation time, while the deceleration increased in the order of: CyDTA<MeEDTA<EDTA. The concentration of the EDTA derivatives at the micellar surface was estimated to be in the order of EDTA<MeEDTA<CyDTA, this difference in the concentration being attributed to such hydrophobic groups as methyl group and cyclohexane ring in the EDTA-derivative molecules. The high concentration of the EDTA derivatives at the surface accelerated the reaction of the sensitizer divalent cation radical ($C^{2+\cdot}_{18-18}$) with the EDTA derivatives, prevented the consumption of $MV^{+\cdot}$ through the back reaction of $C^{2+\cdot}_{18-18}$ with $MV^{+\cdot}$, and facilitated the efficient photoproduction of $MV^{+\cdot}$. It was demonstrated that the hydrophobic interaction between the EDTA-derivative molecules and the micellar surface is an important factor in determining the efficiency of the photoinduced $MV^{+\cdot}$ production.

The phtotoreduction of an electron acceptor (A) by a photoexcited sensitizer (S*) has received much attention in recent years (Reaction 1).[1–4] One common feauture of such a reaction is the high efficiency of the dark reaction of recombination (Reaction 2), which is facilitated by the energetics and the initial proximity of the reactants:

$$S^{*} + A \longrightarrow S^{+} + A^{-} \tag{1}$$

$$S^{+} + A^{-} \longrightarrow S + A \tag{2}$$

It is often desirable to maximize the yield of photoreduction, and techniques to minimize the recombination have been much studied. Such techniques have generally involved physically separating the products of the photoreaction and then removing one of them by means of an added substance. In order to separate the products, charged micellar,[5] charged vesicular[6] or colloidal SiO_2 surfaces[7] and vesicular bilayers[8,9] have been used. The additives used to remove S^+ from the systems are generally good reducing agents or electron donors (D).[10] Thus,

$$D + S^{+} \longrightarrow D^{+} + S. \tag{3}$$

The overall reaction in such a three-component system is given as follows:

$$D + S^{*} + A \longrightarrow D^{+} + S + A^{-}. \tag{4}$$

In the system involving S in the micellar phase and D and A in the bulk aqueous phase, the high concentration of D at the micellar surface prevents the recombination (Reaction 2) and leads to the high efficiency of the photoreduction. Accordingly, the efficient photoreduction can be expected to be realized by the use of a substance as D, which can be strongly bound to the micellar surface. To demonstrate the above concept, we investigated the photoinduced reduction of Methyl Viologen by means of three kinds of ethylenediaminetetraacetate derivatives as a reducing agent in an aqueous phase sensitized by 3,3′-dioctadecylthiacarbocyanine incorporated in a nonionic micelle, composed of heptaethylene glycol monododecyl ether. The difference in the reaction rate between the ethylenediaminetetraacetate derivatives is examined. The results obtained are discussed in terms of the binding between the ethylenediaminetetraacetate derivatives and the micellar surface.

Experimental

The 3,3′-dioctadecyl-2,2′-thiacarbocyanine (C^{+}_{18-18}) bromide (the structure is shown in Fig. 1a) and 3,3′-diethyl-2,2′-thiacarbocyanine (C^{+}_{2-2}) bromide were purchased from the Japan Research Institute for Photosensitizing Dye Co., Ltd., and were used without further purification. The disodium ethylenediaminetetraacetate (EDTA), 1,2-propanediamine-*N,N,N′,N′*-tetraacetate (MeEDTA), and *trans*-1,2-cyclohexanediamine-*N,N,N′,N′*-tetraacetate (CyDTA) (the structures of these EDTA derivatives are shown in Fig. 1) were obtained from Dojindo Laboratories. The Methyl Viologen (1,1′-dimethyl-4,4′-bipyridinium, MV^{2+}) dichloride was received from the Sigma Chemical Company. The nonionic surfactant, heptaethylene glycol monododecyl ether (HED), was obtained from the Nikko Chemicals Co., Ltd.; the reported value of the critical micelle concentration is 8×10^{-5} M ($1\ M=1\ mol\ dm^{-3}$).[11] The monoethylene glycol monohexyl ether (MEH) was purchased from the Tokyo Chemical Industry Co., Ltd. The water was doubly distilled from a quartz still.

The preparation of HED micellar solutions containing a sensitizer has been described elsewhere.[12] C^{+}_{18-18} is insoluble in water[13] and may be considered to be incorporated in the micellar phase. The sample solution (5×10^{-7} M C^{+}_{18-18}, 2×10^{-3} M MV^{2+}, 2×10^{-2} M HED in a buffered solution with 2×10^{-3} M EDTA derivatives and 2×10^{-3} M tris(hydroxymethyl)aminomethane, Tris, at pH 7.0) was placed in a quartz cell

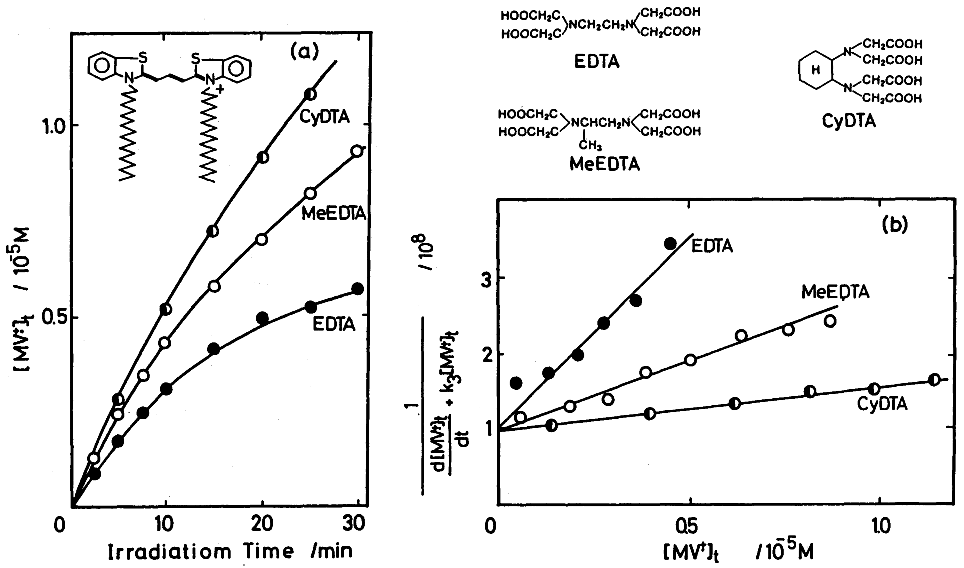

Fig. 1. (a) Built-up of $MV^{+\cdot}$ as a function of irradiation time at 25 °C. 5×10^{-7} M of C^{+}_{18-18} is solubilized in 2×10^{-2} M HED micellar solution (2×10^{-3} M EDTA derivatives, 2×10^{-3} M MV^{2+} and 2×10^{-3} M Tris at pH 7.0). Chemical structure of a sensitizer (C^{+}_{18-18}) is shown in the margin. (b) Variation of $1/(d[MV^{+\cdot}]_t/dt+k_3[MV^{+\cdot}]_t)$ as a function of $[MV^{+\cdot}]_t$ according to Eq. 8, and chemical structures of EDTA derivatives.

(1X1X4 cm) fitted with a stopcock was freed of oxygen by bubbling a nitrogen gas for 15 min, and was then degassed by aspiration at 2700 Pa (20 mmHg) prior to irradiation.

Irradiations were carried out using a Kondo-Sylvania 1 kW tungsten halogen lamp. A Toshiba KL-56 interference filter was used to obtain monochromic light, $\lambda=560\pm5$ nm (the absorption maximum of C^{+}_{18-18} in the HED micellar phase was about 560 nm). The intensity of light incident upon the cell was 3.26×10^{15} quanta s^{-1} as determined by trisoxalateferrate(III) actinometry.[14]

The production of reduced Methyl Viologen ($MV^{+\cdot}$) after intervals of irradiation was monitored by means of the absorption spectra on a Shimadzu UV-180 spectrophotometer. The concentration of $MV^{+\cdot}$ was calculated from the absorbance of the solution at 395 nm by taking $\varepsilon_{395\text{nm}}=3.8\times10^{4}$ M^{-1} cm.[15]

The measurements of the partition coefficient of EDTA derivatives from aqueous to water-saturated MEH phases were performed by the following procedure. The mixture of MEH solution, previously saturated with water, and a 2×10^{-3} M EDTA-derivative buffer solution was stirred well. After the centrifugation of the mixture, the aqueous phase was collected. Then, the decrease in the concentration of the EDTA derivatives in the aqueous phase was measured by chelatometry using magnesium chloride.

All the measurements were carried out at 25 °C.

Results

Photoreduction of MV^{2+}. A deoxygenated solution containing C^{+}_{18-18} in the HED micellar phase and MV^{2+} in the aqueous phase was irradiated with green light. As a result, the solution turned dark blue; a development of absorption maxima at about 395- and 603-nm was observed in the presence of EDTA derivatives. The development of the absorption maxima is characteristic of the formation of $MV^{+\cdot}$.[15] The subsequent introduction of air into the cuvette resulted in the prompt reoxidation of $MV^{+\cdot}$ to MV^{2+}, as manifested by decolorization.[16] In the dark or in the absence of the EDTA derivatives, no $MV^{+\cdot}$ was produced.

In Fig. 1a, the concentrations of $MV^{+\cdot}$ formed by irradiation with light are plotted against the irradiation time. In all the EDTA derivatives, the production rate of $MV^{+\cdot}$ decreased with the increase in the irradiation time. The degree of the deceleration increased in this order: CyDTA<MeEDTA<EDTA.

After the removal of the light, the concentration of $MV^{+\cdot}$ gradually decreased with the increase in the time as a result of the reoxidation of $MV^{+\cdot}$ to MV^{2+} by the small amount of oxygen dissolved in the solution.[17] In a previous study,[12] it was found that this reoxidation in the dark followed pseudo first-order kinetics and that the rate constant (k_3) was 5.4×10^{-5} s^{-1} under our conditions. Such a reoxidation of $MV^{+\cdot}$ to MV^{2+} may be considered to proceed not only after the removal of light, but also during irradiation with light.

The mechanism of the reaction which was proposed in a previous report[12] is depicted in Fig. 2. Assuming that the concentration of the sensitizer cation radical ($C^{2+\cdot}_{18-18}$) is constant in a stationary state and that the moles of MV^{2+}, $MV^{+\cdot}$, and EDTA derivatives in the HED micellar phase are much smaller than the total moles of the respective components in the solution, the measureable production rate of $MV^{+\cdot}$ during irradiation with light may be described by:

$$\frac{d[MV^{+\cdot}]_t}{dt} = \frac{k_1k_2[{}^3C^{+*}_{18-18}]_m[MV^{2+}]_m[EDTAd^{3-}]_m^{1/2}}{k_{-1}(P_{MV+}[MV^{+\cdot}]_t)+k_2[EDTAd^{3-}]_m^{1/2}} - (k_3'P_{MV+}[O_2]_m+k_3''[O_2]_a)[MV^{+\cdot}]_t, \qquad (5)$$

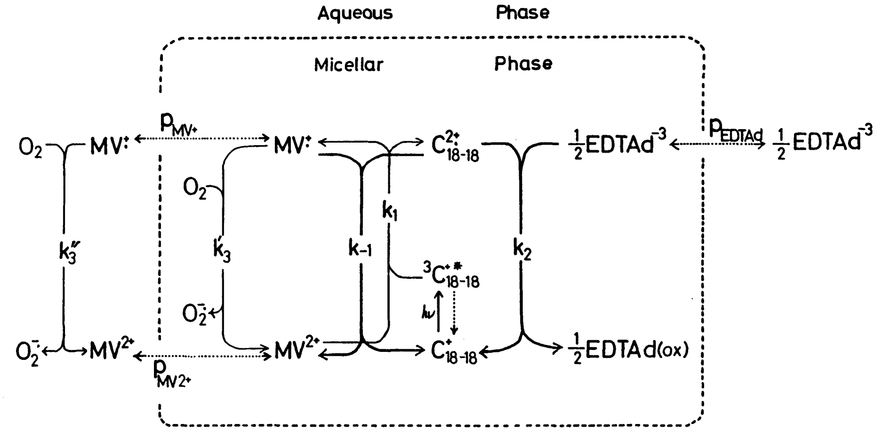

Fig. 2. The proposed mechanism of the photoreduction of MV^{2+} by EDTA derivatives. C^{+}_{18-18} and $^3C^{+*}_{18-18}$, sensitizers in the ground and the triplet excited states in the micellar phase; $C^{2+\cdot}_{18-18}$, sensitizer cation radical; EDTAd and EDTAd(ox), EDTA derivatives and the oxidated form of EDTAd; P_{MV2+}, P_{MV+}, and P_{EDTAd}, partition coefficients of MV^{2+}, $MV^{+\cdot}$, and $EDTAd^{3-}$ from the aqueous phase to the micellar pseudophase; k_1, k_{-1}, k_2, k'_3 and k''_3, the rate constants of each reaction.

where $^3C^{+*}_{18-18}$ and $EDTAd^{3-}$ represent the sensitizer in the triplet excited state and the EDTA derivatives respectively. P_{MV+} stands for the partition coefficient of $MV^{+\cdot}$ from the bulk aqueous phase to the micellar pseudophase, defined as $P_{MV+}=[MV^{+\cdot}]_m/[MV^{+\cdot}]_a$. The subscripts a and m denote the concentration at the aqueous phase and at the micellar pseudophase, while the subscript t denotes the total concentration in the micellar solution. The initial rate of $MV^{+\cdot}$ production (V_{init}), which can be obtained from Eq. 5 at $[MV^{+\cdot}]_t \rightarrow 0$, is given as follows:

$$V_{init} = k_1[^3C^{+*}_{18-18}]_m[MV^{2+}]^0_m. \tag{6}$$

Here, $[MV^{2+}]^0_m$ is the initial value of $[MV^{2+}]_m$. Since, in this experiment, $[MV^{2+}]_t \gg [MV^{+\cdot}]_t$, and $[MV^{2+}]_m$ in Eq. 5 is nearly equal to $[MV^{2+}]^0_m$ and is a constant, Eq. 5 becomes:

$$\frac{d[MV^{+\cdot}]_t}{dt} = \frac{V_{init}k_2[EDTAd^{3-}]^{1/2}_m}{k_{-1}(P_{MV+}[MV^{+\cdot}]_t)+k_2[EDTAd^{3-}]^{1/2}_m} - k_3[MV^{+\cdot}]_t, \tag{7}$$

where $k_3=k'_3P_{MV+}[O_2]_m+k''_3[O_2]_a$. The second term on the right-hand side of Eq. 7 corresponds to the reoxidation rate of $MV^{+\cdot}$ to MV^{2+} in the dark after the removal of the light. Equation 7 indicates that the deceleration in the production rate of $MV^{+\cdot}$ with the increase in the time arises from the decrease in the first and the second terms on the right-hand side of the equation with the increase in $[MV^{+\cdot}]_t$.

Equation 7 may be transformed to:

$$\frac{1}{\frac{d[MV^{+\cdot}]_t}{dt}+k_3[MV^{+\cdot}]_t} = \frac{k_{-1}P_{MV+}}{V_{init}k_2[EDTAd^{3-}]^{1/2}_m}[MV^{+\cdot}]_t + \frac{1}{V_{init}}. \tag{8}$$

Plots of $1/(d[MV^{+\cdot}]_t/dt+k_3[MV^{+\cdot}]_t)$ vs. $[MV^{+\cdot}]_t$ according to Eq. 8 are shown in Fig. 1b. Here, the observed values evaluated from Eqs. 9 and 10 were substituted for the values of $d[MV^{+\cdot}]_t/dt$ and $[MV^{+\cdot}]_t$ respectively:

$$\frac{d[MV^{+\cdot}]_t}{dt} = \frac{[MV^{+\cdot}]_{t(n+1)}-[MV^{+\cdot}]_{t(n)}}{t(n+1)-t(n)} \tag{9}$$

and

$$[MV^{+\cdot}]_t = \frac{[MV^{+\cdot}]_{t(n+1)}+[MV^{+\cdot}]_{t(n)}}{2}. \tag{10}$$

Here, $[MV^{+\cdot}]_{t(n)}$ and $[MV^{+\cdot}]_{t(n+1)}$ are $[MV^{+\cdot}]_t$ at the measuring time $t=t(n)$ and at $t=t(n+1)$ respectively. These plots give straight lines, and the slope and the intercept lead to values for V_{init} and $(k_2[EDTAd^{3-}]^{1/2}_m)/(k_{-1}P_{MV+})$ respectively, as is shown in Table 1.

The values of V_{init} in all the EDTA derivatives are the same, but the values of $(k_2[EDTAd^{3-}]^{1/2}_m)/(k_{-1}P_{MV+})$ increase in this order; EDTA<MeEDTA<CyDTA. In the case of EDTA, the value of V_{init} with monochromic light ($\lambda=560\pm5$ nm, percent transmission of the filter at 560 nm, $T_{560nm}=25\%$) is smaller than that with visible light ($\lambda>460$ nm, using Y-46 cut-off filter, $T_{560nm}=90\%$). The values of $(k_2[EDTAd^{3-}]^{1/2}_m)/(k_{-1}P_{MV+})$ are, however, the same in both irradiation intensities. These results correspond to the expectation that V_{init} is dependent on the intensity of the incident light, which is propotional to $[^3C^{+*}_{18-18}]$, but is independent of the kind of EDTA derivatives, as may be seen from Eq. 6, and that $(k_2[EDTAd^{3-}]^{1/2}_m)/(k_{-1}P_{MV+})$ is affected by the kind of EDTA derivatives, but not by the light intensity.

Absorption Maxima of Sensitizer Dye in Various Solvents. Previously,[18] it was demonstrated that C^{+}_{2-2} and C^{+}_{18-18} showed considerably large shifts in their absorption maxima in various aliphatic alcohols used as solvents; the wave numbers at their absorption

Table 1. Experimental Values on Photoreduction of MV^{2+}

EDTAd	$\frac{V_{init}}{M\,s^{-1}}$	$\frac{k_2[EDTAd^{3-}]_m^{1/2}}{k_{-1}P_{MV^+}} \Big/ M^{1/2}$	P^*_{EDTAd}	Irradiation light
EDTA	1.00×10^{-8}	0.20×10^{-5}	1.2×10^{-2}	Monochromic[a]
	12.71×10^{-8}	0.19×10^{-5}		Visible[b]
MeEDTA	1.02×10^{-8}	0.56×10^{-5}	2.4×10^{-2}	Monochromic[a]
CyDTA	1.02×10^{-8}	1.45×10^{-5}	3.0×10^{-2}	Monochromic[a]

a) Monochromic, monochromic light (λ=560 nm, percent transmission at 560 nm, $T_{560\,nm}$=25%); b) visible, visible light (λ>460 nm, $T_{560\,nm}$=90%).

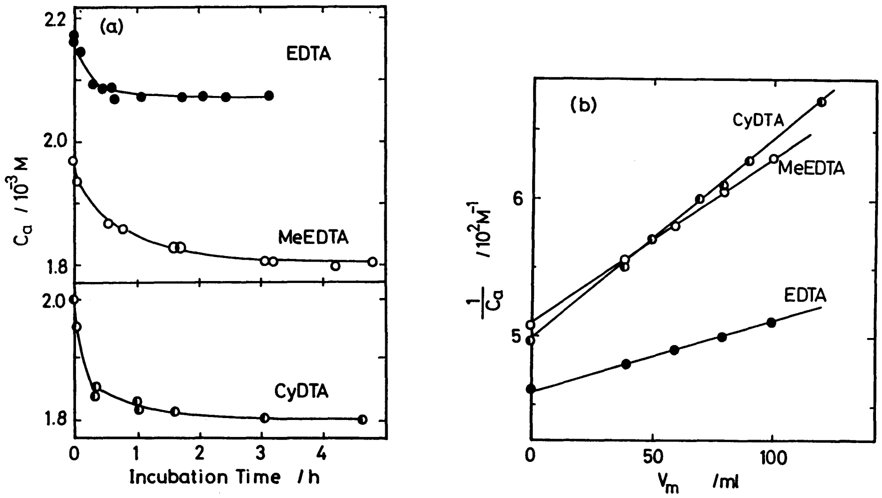

Fig. 3. (a) Time course of partition of $EDTAd^{3-}$ from aqueous to water-saturated MEH phase in the case of V_a=10 ml and V_m=40 ml at 25 °C. (b) Plots of $1/C_a$ versus V_m according to Eq. 12 in the case of V_a=10 ml. C_a, the concentration of $EDTAd^{3-}$ in the aqueous pase; V_a and V_m, the volumes of the aqueous and the water-saturated MEH phases.

maxima ($\tilde{\nu}_{max}$) increase with the dielectric constant (D) of alcohols. The value of D in the vicinity of the chromophore of C^+_{18-18} in the HED micellar phase, which has been defined as the effective dielectric constant (D_{eff}), was estimated as D_{eff}=20.0 using the values of $\tilde{\nu}_{max}$ and D for alcohols.[18] Similar procedures led to the D_{eff} value of 19.4 for C^+_{2-2} in a water-saturated MEH solution. These D_{eff} values correspond to the polarity of 1-propanol or 1-butanol, and indicate that the chromophore of C^+_{2-2} in the water-saturated MEH solution is dissolved in an environment with a micropolarity similar to that of C^+_{18-18} in the HED micellar phase.

Partition of EDTA Derivatives from Aqueous to Water-Saturated MEH Phases. The time course of the partition of EDTA derivatives between aqueous and water-saturated MEH phases was investigated; the results are shown in Fig. 3a. The partition equilibrium was established after about 3 h under our conditions. The partition coefficient of the EDTA derivatives from the aqueous to the water-saturated MEH phases (P^*_{EDTAd}) is given by:

$$P^*_{EDTAd} = \frac{C_m}{C_a} = \frac{V_a}{V_m}\left(\frac{C^0_a}{C_a} - 1\right), \tag{11}$$

where C_a, C_m, and C^0_a are the concentration of the EDTA derivatives in the aqueous and water-saturated MEH phases, and the initial concentration of the EDTA derivatives in the aqueous phase respectively. Here, V_a and V_m are the volumes of the aqueous and water-saturated MEH phases respectively. Equation 11 may be rewritten as:

$$\frac{1}{C_a} = \frac{P^*_{EDTAd}}{C^0_a V_a} V_m + \frac{1}{C^0_a}. \tag{12}$$

Plots of $1/C_a$ versus V_m according to Eq. 12 are shown in Fig. 3b in the case of V_a=10 ml. These plots give straight lines, and their slopes and intercept lead to the values for P^*_{EDTAd} shown in Table 1. These results indicate that the concentrations of the EDTA derivatives in the water-saturated MEH phase increase in the order of EDTA<MeEDTA<CyDTA at the partition equilibrium.

Discussion

The photoinduced reduction of MV^{2+} by EDTA has been carried out with various sensitizer dyes such as tris(2,2′-bipyridine)ruthenium,[1–6,8] porphyrins,[1–7,9,10,19] and phatalocyanines[20] by numerous workers, and every effort has been made to maximize the efficiency of the photoinduced production of $\mathrm{MV}^{+\cdot}$, for $\mathrm{MV}^{+\cdot}$ is capable of generating hydrogen from water when platinum dioxide is used as a catalyst.[21] In our studies, 3,3′-dioctadecylthiacarbocyanine in a nonionic micelle has been adopted as a sensitizer.[12,13] This dye has been known as a probe for investigating the membrane potentials of erythrocyte membranes[22] and cell membranes of bacteria[23] and as a strong inhibitor of the endogeneous respiration of Ehrlich ascites tumor cells.[24]

In this study, in order to minimize the recombination of photoproducts (Eq. 13, corresponding to Eq. 2), EDTA derivatives are used as reducing agents, resulting in the removal of $\mathrm{C}_{18-18}^{2+\cdot}$ from the system (Eq. 14, corresponding to Eq. 3) and in the prevention of the recombination of $\mathrm{C}_{18-18}^{2+\cdot}$ with $\mathrm{MV}^{+\cdot}$ (Eq. 9):

$$(\mathrm{C}_{18\text{-}18}^{2+\cdot})_m + (\mathrm{MV}^{+\cdot})_m \xrightarrow{k_{-1}} (\mathrm{C}_{18\text{-}18}^{+})_m + (\mathrm{MV}^{2+})_m, \tag{13}$$

$$(\mathrm{C}_{18\text{-}18}^{2+\cdot})_m + (\mathrm{EDTAd}^{3-})_m \xrightarrow{k_2} (\mathrm{C}_{18\text{-}18}^{+})_m + (\mathrm{EDTAd(ox)})_m. \tag{14}$$

It can be expected that the faster the process shown as Eq. 14 is, that is, the higher $[\mathrm{EDTAd}^{3-}]_m$ and/or the rate constant (k_2) of this process is, the larger is the efficiency of the $\mathrm{MV}^{+\cdot}$ production. As may be seen from Fig. 1, the production rates of $\mathrm{MV}^{+\cdot}$ decrease with the increase in the time, and the deceleration is the smallest in CyDTA and the largest in EDTA. Equation 7, showing the production rate of $\mathrm{MV}^{+\cdot}$, indicates that the deceleration of the $\mathrm{MV}^{+\cdot}$ production arises from the decrease in the first and second terms on the right-hand side of Eq. 7 with the increase in $[\mathrm{MV}^{+\cdot}]_t$. Furthermore, since V_{init}, k_3, k_{-1}, and $P_{\mathrm{MV+}}$ are independent of the kind of the EDTA derivatives and constant, Eq. 3 indicates that the larger $[\mathrm{EDTAd}^{3-}]_m$ and/or k_2 is, the smaller is the deceleration of the $\mathrm{MV}^{+\cdot}$ production.

As may be seen from the proposed mechanism, $\mathrm{MV}^{+\cdot}$ is produced through the following process:

$$({}^3\mathrm{C}_{18\text{-}18}^{+*})_m + (\mathrm{MV}^{2+})_m \xrightarrow{k_1} (\mathrm{C}_{18\text{-}18}^{2+\cdot})_m + (\mathrm{MV}^{+\cdot})_m. \tag{15}$$

On the other hand, $\mathrm{MV}^{+\cdot}$ disappears through the processes shown by Eqs. 13, 16, and 17:

$$(\mathrm{MV}^{+\cdot})_m + (\mathrm{O}_2)_m \xrightarrow{k_3'} (\mathrm{MV}^{2+})_m + (\mathrm{O}_2^{-\cdot})_m \tag{16}$$

$$(\mathrm{MV}^{+\cdot})_a + (\mathrm{O}_2)_a \xrightarrow{k_3''} (\mathrm{MV}^{2+})_a + (\mathrm{O}_2^{-\cdot})_a \tag{17}$$

Therefore, by using the reaction rate of these processes, the efficiency of $\mathrm{MV}^{+\cdot}$ production (E) is introduced as follows:

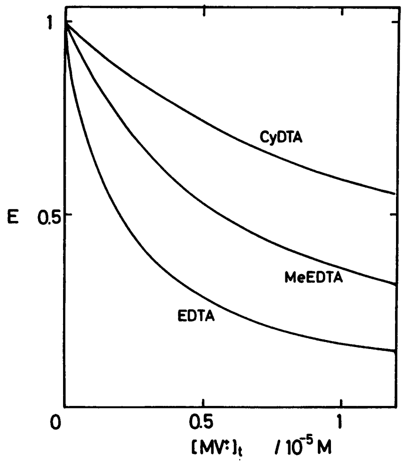

Fig. 4. Comparison of the efficiency of $\mathrm{MV}^{+\cdot}$ production (E) between the three EDTAd^{3-} as a function of $[\mathrm{MV}^{+\cdot}]_t$. The values of E were evaluated using Eq. 19 and the values in Table 1.

$$E = \frac{k_1[{}^3\mathrm{C}_{18\text{-}18}^{+*}]_m[\mathrm{MV}^{2+}]_m - k_{-1}[\mathrm{C}_{18\text{-}18}^{2+\cdot}]_m[\mathrm{MV}^{+\cdot}]_m - k_3[\mathrm{MV}^{+\cdot}]_t}{k_1[{}^3\mathrm{C}_{18\text{-}18}^{+*}]_m[\mathrm{MV}^{2+}]_m}$$
$$= 1 - \frac{k_3}{V_{\mathrm{init}}}[\mathrm{MV}^{+\cdot}]_t - \frac{1}{1+\left(\dfrac{k_2[\mathrm{EDTAd}^{3-}]_m^{1/2}}{k_{-1}P_{\mathrm{MV+}}}\right)\dfrac{1}{[\mathrm{MV}^{+\cdot}]_t}} \tag{18}$$

Here, $[\mathrm{C}_{18-18}^{2+\cdot}]_m$ is constant and is equal to $V_{\mathrm{init}}/(k_{-1}P_{\mathrm{MV+}}[\mathrm{MV}^{+\cdot}]_t+k_2[\mathrm{EDTAd}^{3-}]_m^{1/2})$ in a stationary state (see Fig. 2). Since the value of k_3 is 10^{-5}-order and since the values of V_{init} are 10^{-8}-order, it may be considered that $k_3[\mathrm{MV}^{+\cdot}]_t/V_{\mathrm{init}} \ll 1$ at $[\mathrm{MV}^{+\cdot}]_t$ below about 1×10^{-5} M. Therefore, Eq. 18 may reduce to:

$$E = \frac{1}{1+[\mathrm{MV}^{+\cdot}]_t\Big/\left(\dfrac{k_2[\mathrm{EDTAd}^{3-}]_m^{1/2}}{k_{-1}P_{\mathrm{MV+}}}\right)}. \tag{19}$$

Figure 4 compares the E values between the three EDTA derivatives as a function of $[\mathrm{MV}^{+\cdot}]_t$. The values of E were calculated using the values of $(k_2[\mathrm{EDTAd}^{3-}]_m^{1/2})/(k_{-1}P_{\mathrm{MV+}})$ in Table 1. As may be seen from Fig. 4, the value of E for CyDTA decreases gradually with the increase in $[\mathrm{MV}^{+\cdot}]_t$. On the other hand, the value of E for EDTA decreases rapidly in the region of small values of $[\mathrm{MV}^{+\cdot}]_t$. Equation 19 indicates that the slower decrease of E for CyDTA with the increase in the $[\mathrm{MV}^{+\cdot}]_t$ may be ascribed to the relatively high value of $[\mathrm{EDTAd}^{3-}]_m$, i.e. $[\mathrm{CyDTA}^{3-}]_m$ and/or k_2.

The binding between the EDTA derivatives and the HED micelle (P_{EDTAd}) was measured with the ultrafiltration method. However, the binding was slight and was not clearly detected. As has been mentioned before, the D_{eff} for C_{18-18}^{+} in the HED micellar phase is 20.0 and corresponds to the polarity of 1-propanol or 1-butanol. This indicates that the chromophore of C_{18-18}^{+} accommodated in the HED micellar phase is pro-

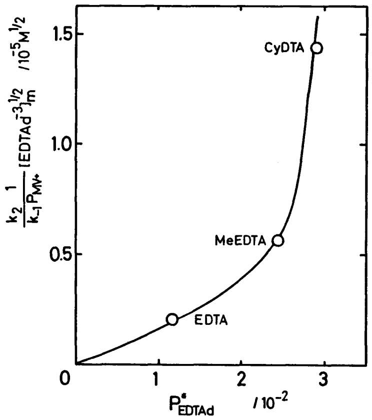

Fig. 5. Plots of $(k_2[EDTAd^{3-}]_m^{1/2})/(k_{-1}P_{MV+})$ versus P^*_{EDTAd}.

vided with a remarkably less polar environment than that in the aqueous phase, but it seems to be in a more polar environment than in a liquid hydrocarbon. These results indicate that the chromophore is located in the surface region of the HED micelle,[12] probably in its ethylene glycol mantle. The D_{eff} value for C_{2-2}^{+}, which has the same chromophore as C_{18-18}^{+}, in a water-saturated MEH solution is 19.4; this indicates that C_{2-2}^{+} is dissolved in a micropolarity similar to that of C_{18-18}^{+} in the HED micellar phase. Therefore, the concentration of the EDTA derivatives at the HED micellar surface (the binding between the EDTA derivatives and the HED micelle) was estimated from the partition coefficient (P^*_{EDTAd}) of the EDTA derivatives from the aqueous to the water-saturated MEH phases. As a result, the concentration of CyDTA in the water-saturated MEH phase is the highest,while that of EDTA is the lowest, in the three EDTA derivatives. These differences in the concentration of the EDTA derivatives in the water-saturated MEH phase may be attributed to the hydrophobic groups, such as the methyl group and cyclohexane ring in the EDTA-derivative molecules. The order of the concentration of EDTA derivatives in the water-saturated MEH phase coincides with that of the efficiency of $MV^{+\cdot}$ production (E), indicating that the local concentration of the EDTA derivatives at the HED micellar surface ($[EDTAd^{3-}]_m$) is an important factor in determining E.

Figure 5 shows the plots of the values of $(k_2[EDTAd^{3-}]_m^{1/2})/(k_{-1}P_{MV+})$ versus P^*_{EDTAd}. These plots suggest the close correlation between E and P^*_{EDTAd}. The difference in the value of k_2 in the three EDTA derivatives is probably a result of difference in the oxidation potential of the EDTA derivatives, their proximity to $C_{18-18}^{2+\cdot}$ in the micellar surface, which are also associated with their partition coefficient (P_{EDTAd}). Thus, though the k_2 values are somewhat different in the three EDTA derivatives, the agreement in the order in the EDTA derivatives between the ease of the partition to the MEH phase and the efficiency of $MV^{+\cdot}$ production indicates that the local concentration of the EDTA derivatives at the HED micellar surface is an important factor in determining the efficiency of $MV^{+\cdot}$ production.

In conclusion, it seems that the high concentration of EDTA derivatives at the micellar surface is essential for the efficient photoproduction of $MV^{+\cdot}$. It is also suggested that not only the electrostatic interaction, demonstrated by many workers, but also the hydrophobic interaction between EDTA derivatives and the micellar surface is important for the achievement of a high concentration of EDTA derivatives at the micellar surface and for the effective production of $MV^{+\cdot}$.

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