November, 1981] © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***54****, 3265—3270 (1981)* 3265

Mechanisms of Light-initiated Redox Reactions of Copper(II)-Cyclic Polyamine Surfactant Assemblies

Yoshikiyo Moroi
Department of Chemistry, Faculty of Science, Kyushu University,
Higashi-ku, Fukuoka 812

(Received March 2, 1981)

Photo-induced reduction of Cu^{2+} ion by organic electron donors was studied, main attention being paid to the decay kinetics of the cationized donor using two kinds of Cu^{2+} ions; one is free to move around the micellar surface of copper(II) dodecyl sulfate($Cu(DS)_2$), the other being fixed in a cyclic polyamine, Cu^{2+} complex of 2-tetradecyl-1,4,7,10-tetraazacyclododecane (CPA). Sodium 12-(10-phenothiazinyl)dodecanesulfonate (PTHDS) functions quite similarly to *N*-methylphenothiazine (MPTH) in an electron transfer reaction in $Cu(DS)_2$ micelles, and the reduced Cu^+ is ejected from the micelles.[1] In the MPTH–CPA system, $MPTH^+$ is completely ejected from the host micelle in the CPA micellar system. In consequence, the decay of the cationized donor obeys a second-order rate law, while the rate constant becomes much less. In PTHDS–CPA micellar system, on the other hand, the kinetics of the cationized donor is a superposition of two first-order decays of different rate constants, which suggests that the cationized donor can not escape into an intermicellar bulk phase due to the hydrophobic interaction between the long alkyl chain and its host micelle. A similar decay was also observed in the mixed micelles of the polyamine and hexadecyltrimethylammonium bromide.

Considerable effort has been expended on attempts to convert light energy to chemical energy,[2,3] and as a result mechanisms of photochemical reactions in micellar systems have become quite clear.[4–7]

Macrocyclic compounds with a long alkyl chain have been prepared for use as phase-transfer catalysts.[8] Micelle formation and surface activity of these compounds, as well as their cation transfer reaction[9] and complex formation with Cu^{2+} or Ag^+,[10] have been reported in recent publications. As described in our previous paper,[11] micellar aggregates of macrocyclic surfactant containing Cu^{2+} ion were found to exhibit a high efficiency in quenching the excited state of fluorophores such as cyanine dyes and pyrene. In the light of our previous discussion from the view point of the reaction mechanism concerning the light-induced reduction of Cu^{2+} ion by *N*-methylphenothiazine followed by the back electron transfer from the Cu^+ to the cationized *N*-methylphenothiazine in copper(II) dodecyl sulfate micelles,[12] it is worth carrying out an experimental investigation in pursuit for the effect of substitution of Cu^{2+} in the cyclic polyamine cage on the reaction sequence. Another interest is in the effect of the variation of electron donors, which would possibly cause some alteration of the decay mechanism.

The object of the present study is to make clear the mechanism of photo-redox reactions in the micellar system, *i.e.*, to derive kinetic equations capable of accounting for experimental results obtained from laser photolysis studies. Our first attention was concentrated on the difference in effects on reaction mechanism caused by two kinds of electron donors: one has a long hydrocarbon chain attached to the phenothiazine ring and the other has none. The former, even when positively charged, cannot escape into the intermicellar bulk phase due to hydrophobic interaction which is stronger than electrostatic repulsion with positively charged micelle. On the contrary, the latter, when positively charged, has the possibility of being ejected from the micelle. Our first interest was then shifted from the electron donors to electron acceptors, *i.e.*, two kinds of Cu^{2+} ions: one is free to move around the micellar surface and the other is fixed in the polyamine cage as a complex.

Experimental

Materials. The Cu^{2+} complex of 2-tetradecyl-1,4,7,10-tetraazacyclododecane (CPA) was kindly given us by Dr. P. Tundo of the Institute de Chimica Organica, University di Trino, and used as supplied. The *N*-methylphenothiazine (MPTH) and sodium 12-(10-phenothiazinyl)dodecanesulfonate (PTHDS) were synthesized by Dr. A. M. Braun in Dr. Grätzel's laboratory. The hexadecyltrimethylammonium bromide (HTAB) of certified grade was obtained from E. Merck, Darmstadt, and purified by repeated recrystallization from acetone–ethanol mixture. The copper(II) dodecyl sulfate($Cu(DS)_2$) was prepared by the method described previously.[13] The deionized water was distilled first from alkaline permanganate and then twice with a quartz still. All samples were deoxygenated by passage of nitrogen of high purity.

Apparatus. Time-resolved experiments were run by the laser photolysis technique; laser photolysis experiments employed a frequency doubled KJ-2000 ruby or neodymium laser with pulsewidth of 25 ns and energy output of *ca.* 20 mJ.

Analysis. In the cases where $PTHDS^+$ decay kinetics in PTHDS–cationic micellar systems can result from superposition of two kinds of first-order decays, the rate parameter (α_2) for slower decay was first determined from an oscilloscope trace of longer-time scale. The rate parameter(α_1) for faster decay was then evaluated from the difference between the total optical density and the extraporated optical density of the shorter-time scale which had been calculated from the optical density of longer-time scale with the aid of the rate parameter α_2.

Results and Discussion

The light-initiated redox reaction in question is represented as

$$A + D \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} A^- + D^+, \qquad (1)$$

where A and D stand for an electron acceptor and

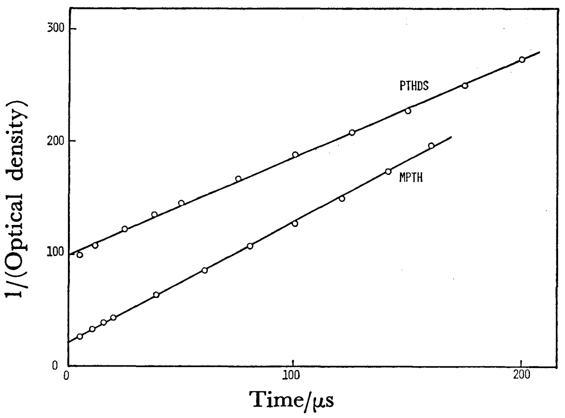


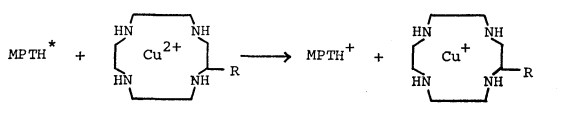
Fig. 1. Second-order plots of the 516 nm absorbance decay for MPTH (1.0×10^{-4} M†) and PTHDS (1.0×10^{-4} M) in $Cu(DS)_2$ (2.0×10^{-2} M) micellar systems.

donor, respectively, corresponding to Cu^{2+} ion and MPTH or PTHDS for the present experiment. The first requirement for analyzing the reaction mechanism is to pursue the decay rate of the cationized electron donor with absorption maximum at 516 nm on an oscilloscope screen. Quantum yields of the cationized and triplet states of the donors are given in our previous paper.[11] Figure 1 shows second-order plots of the 516 nm absorption decay for the MPTH- and PTHDS-$Cu(DS)_2$ micellar solutions. It can be seen that, down to 30 percent or less of the initial optical density, a good linear relation exists between the inverse of optical density and time, *i.e.*, that the cationized donor decays according to a second-order rate law. The slopes which are almost the same with each other give the following estimates:

$$k_{\text{obsd}} = 9.3\times10^{9}\ \text{M}^{-1}\,\text{s}^{-1}\ \text{for MPTH},$$

$$k_{\text{obsd}} = 7.9\times10^{9}\ \text{M}^{-1}\,\text{s}^{-1}\ \text{for PTHDS}.$$

This close equality indicates similar decay mechanism in operation. PTHDS plays the same role as MPTH in reduction of Cu^{2+} and subsequent reaction mechanism. That is to say, on the analogy of the MPTH case, the reduced electron acceptor Cu^{+} is detached from its host micelle not only by electrostatic substitution with Cu^{2+} but also *via* a hopping process before recombination with the oxidized donor.[12] With this view, attempt will be made to probe further into the effect of variation of electron acceptor on the decay mechanism of the cationized donor: one is free to move around the micellar surface and the other is fixed in the polyamine cage. For the latter acceptor, the hydrophobic electron donor, MPTH, is incorporated in the polyamine aggregate. The excited state of MPTH has such a propensity for strong reduction[1] as to be expected to react with Cu^{2+} in the complex as follows:



(2)

where R refers to $C_{14}H_{29}$ and MPTH* is the excited singlet state.[11] Figure 2 shows an oscilloscope trace illustrating a transient absorption at 516 nm for MPTH^{+}, together with plots of the inverse of optical density against time. The apparent decay process obeys the second-order kinetics in this case, too. The slope is, however, much less than those in the $Cu(DS)_2$ micellar assemblies.

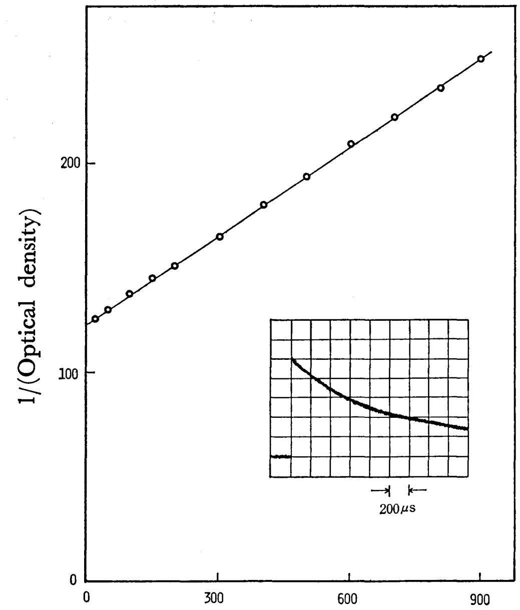


Fig. 2. Second-order plots of the 516 nm absorbance decay for MPTH (1.0×10^{-4} M) in Cu^{2+}-polyamine complex (5.0×10^{-3} M) micellar system. Insert: Oscilloscope traces showing the long-time MPTH^{+} decay.

$$k_{\text{obsd}} = 1.26\times10^{9}\ \text{M}^{-1}\,\text{s}^{-1}.$$

The discussion presented above leads to a possibility that either the oxidized MPTH^{+} or the reduced Cu^{+} is ejected from its host micelle by electrostatic repulsion before the backward reaction occurs. If not, the decay should obey a first-order rate law because the cationized electron donor and the reduced electron acceptor ought to be paired in their host micelle. Another possibility is that both MPTH^{+} and Cu^{+} leave the micelle. In this case, however, the k_{obsd} value should be larger than those for the MPTH- and PTHDS-$Cu(DS)_2$ systems because neither of the cations is trapped in the cationized micelle for a long time, resulting in a higher chance for them to come closer to each other for the backward electron transfer. In addition, not only Cu^{2+} but also Cu^{+} ions can form a stable complex with macrocyclic tetramine.[14-16] Hence, the chance that Cu^{+} leaves its mother micelle is very low.

In order to examine whether MPTH^{+} is ejected, we succeeded in using PTHDS as an electron donor, since PTHDS, even when charged positively, cannot be detached from its host micelle. It will be discussed more in detail from an energy point of view. If MPTH is assumed to be twice as strong as benzene in hydrophobic interaction because of a presence of two benzene rings in the molecule, the free energy change of transfer of MPTH from aqueous bulk into micellar core is 6—7 kT.[17,18] A location of solubilized

---

† 1 M=1 mol dm^{-3}.

aromatic molecules in the micellar phase is generally a palisade layer of micelle,[19] and the phenothiazine molecule is really solubilized in the palisade layer of alkyl sulfate micelles.[20] Accordingly, the free energy change for the present case is less than that value. On the other hand, the electrical surface potential is calculated[22] as 6.6 and 4.9 $e\Psi/kT$ for 1.0 and 0.2 of dissociation degree of the micelle, respectively, by using 50 A^2 for molecular surface area at the micellar surface, its CMC value for the counter-ion concentration, and 40 for the dielectric constant.[21] Suppose now that the free energy change of MPTH due to hydrophobic interaction is $6.5\,kT$. Then, a fraction of $MPTH^+$ ejected from the micelle is more than 50 and 16 percent for 1.0 and 0.2 of dissociation degree of the micelle, respectively. On the other hand, PTHDS has a longer alkyl chain of twelve carbon atoms and a free energy change of transfer per methylene group from aqueous bulk into micellar core is $1.1\,kT$.[22] Thus, the total free energy change due to hydrophobic interaction is about $22\,kT$, whereas the gross electrostatic repulsive energy due to micellar surface potential is zero even when the electron donor group is cationized, because the molecule has an SO_3^- group. Hence, just after the electron transfer reaction has taken place, some fraction of cationized donor groups is detached from its host micelle by electrostatic repulsion. However, the whole molecule cannot escape into the bulk phase, because the cationized group is anchored to the host micelle through the hydrophobic interaction between its alkyl chain and the hydrophobic micellar core.

The absorbance signal at 516 nm on the oscilloscope screen for the PTHDS–CPA system decays apparently in two steps, where the first component amounting to 55 percent of the total signal corresponds to the decay of the triplet of PTHDS. The kinetics obeys the first-order rate law with a time constant of $1.7\times10^7\ s^{-1}$.[11] The slow second component can be produced by neither the first nor the second-order kinetics but only by a superposition of two kinds of first-order decays (Fig. 3). Another difference in behavior between $MPTH^+$ and $PTHDS^+$ is that the latter decays much faster than the former as far as the apparent decay of the second component is concerned. This may be expected if the slow component is associated with the $MPTH^+$ which leaves the micellar aggregate and escapes into the intermicellar bulk phase. In contrast to $MPTH^+$ the detachment of $PTHDS^+$ will be incomplete, since the cation remains anchored to its mother micelle as mentioned above. Eventually, the charge recombination of $PTHDS^+$ and Cu^+ occurs giving rise to a faster decay process, and variation of laser intensity did not cause any change of this decay pattern, although two rate parameters, α_1 and α_2, altered in small amount (Table 1).

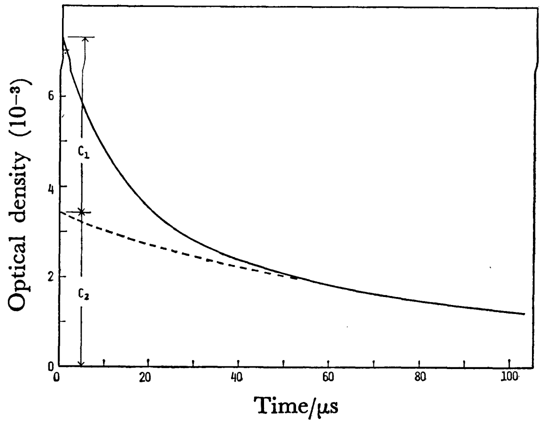


Fig. 3. The slower second-component decay of the absorbance at 516 nm for PTHDS (1.0×10^{-4} M) in Cu^{2+}–polyamine complex (5.0×10^{-3} M) micellar system.

In the light of the above discussion, it will be inquired whether the schematic diagram for the decay processes assists us in explaining the decays of both $MPTH^+$ and $PTHDS^+$ in the Cu^{2+}–polyamine micellar systems. As was mentioned above, the forward electron transfer from the photoexcited MPTH or PTHDS (electron donor D) to Cu^{2+} in a complex form (electron acceptor A) occurs within the duration of the laser pulse. Hence, the $D^+\cdots A^-$ pairs produced at the end of the pulse are the starting state of the decay processes. The kinetic parameters in the present study are quite similar to those used in our previous paper.[12]

With the solution containing PTHDS in the micelle, $PTHDS^+$ cannot be ejected into the intermicellar phase for the above reasons. Therefore, the whole molecule of $PTHDS^+$ cannot be detached from its host micelle even during the completion of the cation decay; the relaxation time of the gross rate of micelle association reaction is more than a millisecond order.[23,24] This means that the decay of D^+ is associated with the electron transfer to D^+ either inside or outside the micelle. Thus, we have the decay processes depicted in the scheme of Fig. 4, where the rate parameter k_b^i refers to the electron back transfer of D^+ inside the micelle, k_b^o that of D^+ outside the micelle, k_e the reaction of D^+ escape from the micellar interior, and k_r the reaction of D^+ return into the micellar interior.

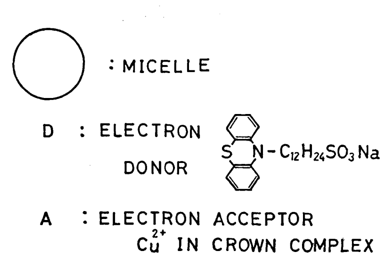


Fig. 4. Schematic illustration of the elementary processes for the decay kinetics of $PTHDS^+$ in Cu^{2+}–polyamine complex micellar system.

On the basis of the schematic diagram for the decay processes, we shall now develop kinetic equations to analyze the results. The following notations will be used for concentration terms: C_{D^+i} for micelles associated with D^+ inside the micelle; C_{D^+o} for micelles associated with D^+ outside the micelle.

$$\frac{dC_{D^+i}}{dt} = -(k_b^i+k_e)C_{D^+i} + k_rC_{D^+o}, \tag{3}$$

$$\frac{dC_{D^+o}}{dt} = -(k_b^o+k_r)C_{D^+o} + k_eC_{D^+i}. \tag{4}$$

From Eqs. 3 and 4, the decay rate of the total amount of the oxidized donor which is an experimentally observable quantity can be expressed as

$$\frac{d(C_{D^+i}+C_{D^+o})}{dt} = -k_b^iC_{D^+i} - k_b^oC_{D^+o}. \tag{5}$$

Introduction of Eqs. 3 and 4 into the time derivative equation of Eq. 3 gives

$$\frac{d^2C_{D^+i}}{dt^2} + \alpha\frac{dC_{D^+i}}{dt} + bC_{D^+i} = 0, \tag{6}$$

where

$$a = k_b^i + k_b^o + k_e + k_r \tag{7}$$

and

$$b = k_b^ik_b^o + k_b^ik_r + k_b^ok_e. \tag{8}$$

The solution of Eq. 6 becomes

$$C_{D^+i} = A_1e^{-\alpha_1t} + A_2e^{-\alpha_2t}, \tag{9}$$

where $\alpha_1+\alpha_2=a$ and $\alpha_1\alpha_2=b$. Here, we assume $\alpha_1>\alpha_2$. The boundary condition that the cation at time zero is totally C_{D^+i}, reduces Eq. 9 to

$$A_1 + A_2 = C_0, \tag{10}$$

where C_0 is the total cationized donor concentration at time zero and A_1 and A_2 are integration constants. Introducing Eq. 9 into Eq. 3, C_{D^+o} can be obtained as

$$C_{D^+o} = \frac{A_1(k_b^i+k_e-\alpha_1)}{k_r}e^{-\alpha_1t} + \frac{A_2(k_b^i+k_e-\alpha_2)}{k_r}e^{-\alpha_2t}. \tag{11}$$

As C_{D^+o} should be zero at time zero, we obtain for A_1 and A_2

$$A_1 = \frac{(k_b^i+k_e-\alpha_2)C_0}{\alpha_1-\alpha_2}, \tag{12}$$

and

$$A_2 = \frac{(k_b^i+k_e-\alpha_1)C_0}{\alpha_1-\alpha_2}. \tag{13}$$

Thus, the total decay of the cationized donor can be expressed as

$$C_{D^+i} + C_{D^+o} = C_1e^{-\alpha_1t} + C_2e^{-\alpha_2t}, \tag{14}$$

where

$$C_1 = \frac{A_1(k_b^i+k_e+k_r-\alpha_1)}{k_r}, \tag{15}$$

and

$$C_2 = \frac{A_2(k_b^i+k_e+k_r-\alpha_2)}{k_r}. \tag{16}$$

Hence, Eq. 14 indicates that the total decay is a superposition of the fast 1st-order decay on the slow 1st-order decay, which is the case with the present experiment. Now, we have to find a way to determine the rate parameters. Introducing Eqs. 9 and 11 into Eq. 5 and adopting the above two boundary conditions at time zero give k_b^i in the form,

$$k_b^i = \alpha_1\frac{C_1}{C_0} + \alpha_2\frac{C_2}{C_0}. \tag{17}$$

Using α_1, α_2, C_1, and C_2 which can be evaluated from the decay curves, k_b^i can be determined without any assumption and any mathematical approximation. Similarly, k_e value can also be determined by introducing Eqs. 9 and 11 into Eq. 4 and using the same boundary conditions in the following form,

$$k_e = \alpha_1\left(\frac{k_b^i+k_e-\alpha_2}{\alpha_1-\alpha_2}-\frac{C_1}{C_0}\right) + \alpha_2\left(\frac{k_b^i+k_e-\alpha_1}{\alpha_2-\alpha_1}-\frac{C_2}{C_0}\right). \tag{18}$$

As $k_b^i+k_e$ is nearly equal to α_1 (see Appendix), the third term cancels out and Eq. 18 can be rearranged using Eq. 17 into

$$k_e = \alpha_1 - k_b^i, \tag{19}$$

which means that Eq. 18 is consistent with the contents in the Appendix. Elimination of k_r term, using Eqs. 7 and 8, gives

$$k_b^o = \frac{k_b^{i2}+k_b^ik_e-(\alpha_1+\alpha_2)k_b^i+\alpha_1\alpha_2}{k_e}. \tag{20}$$

Introducing k_b^i, k_b^o, and k_e thus obtained into Eq. 7, we obtain k_r value (Table 1). The k_r values for the systems are almost zero, if the experimental error is taken into account. Thus, the initial fast kinetics can be eventually represented by the equations in the Appendix. If the preceding reaction mechanisms are correct, the similar kinetic decay must be observed in the CPA–HTAB mixed micellar system. In fact, a superposition of two kinds of first-order decays took place in this system, too (Table 1), which assists the decay mechanism to be correct. A brief mention should be made of the difference in numerical values of the reaction parameters between the CPA and CPA–HTAB mixed micellar assemblies. Going back again to Table 1, we see that the k_b^i and k_e values in the mixed micellar system are much larger than those in the CPA micelle. It is highly likely, therefore, that the polyamine cage is much more mobile in the mixed micelle leading to higher k_b^i value and that the electrostatic surface potential is more positive in the mixed micelle, as reflected in the higher k_e value. The surface potential of HTAB is 9.4 $e\Psi/kT$ by a similar calculation, whereby a dissociation degree of the micelle is assumed to be 0.2, so that the value of 9.4 becomes less for the present mixed micellar system where a ratio of CPA to HTAB is 0.09. On the other hand, k_b^o is much less in the mixed system. This too is owing to higher surface potential which causes larger separation between Cu^+ and D^+ outside micelle.

Next, we proceed to the $MPTH^+$ cation decay in the Cu^{2+}–polyamine micellar system. As mentioned before, the decay kinetics obeys the 2nd-order law and $MPTH^+$, not Cu^+, escapes into an intermicellar phase due to an electrostatic repulsion between $MPTH^+$ and the positive micellar charge. This can be verified by 1) very large k_e value of the PTHDS–cationic

Table 1. Rate parameters for PTHDS (1.0×10^{-4} M) in Cu^{2+}–polyamine complex (5.0×10^{-3} M) and Cu^{2+}–polyamine complex/HTAB ($1.0\times10^{-3}/1.0\times10^{-2}$ M) mixed micellar systems

	α_1 / 10^4 s^{-1}	α_2 / 10^4 s^{-1}	k_b^i / 10^4 s^{-1}	k_b^o / 10^4 s^{-1}	k_e / 10^4 s^{-1}	k_r / 10^4 s^{-1}
CPA	8.10 ± 0.36	1.04 ± 0.10	4.82	1.04	3.28	$\simeq0$
	$C_1/C_0=0.536$,	$C_2/C_0=0.464$				
CPA/HTAB	135 ± 10	0.261 ± 0.019	94.0	0.261	40.5	$\simeq0$
	$C_1/C_0=0.698$,	$C_2/C_0=0.302$				

The standard deviation for the numerical values of rate parameter is less than 10%.

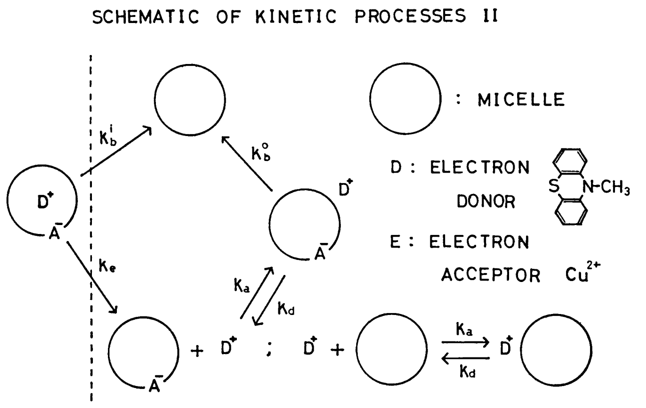


Fig. 5. Schematic illustration of the elementary processes for the decay kinetics of MPTH$^+$ in Cu^{2+}–polyamine complex micellar system.

micellar systems and 2) that the higher the surface potential of micelles, the larger the k_e value (see Table 1). In addition, as mentioned earlier, the k_r value was found to be almost zero. That is, the probability that the ejected cation donor goes back again into a micellar interior should be extremely small. Hence, the decay processes after the initial fast back electron transfer and after the cation ejection can be illustrated schematically in Fig. 5, where the reaction parameter k_a refers to the association reaction of D$^+$ with the micellar aggregate and k_d to the dissociation reaction of D$^+$ from the micellar aggregate. Now that the schematic diagram has been given, we can develop the kinetic equations for the decay processes. Following notations will be used for the concentration terms: $C_{D^+A^-}$ for micelles with simultaneous D$^+$ and A$^-$ association (location of D$^+$ association is micellar surface); C_{D^+} for D$^+$ in the intermicellar bulk phase; C_{MD^+} for micelles with D$^+$ association; C_{MA^-} for micelles with A$^-$ association; C_M for empty and D-containing micelles.

$$\frac{dC_{D^+A^-}}{dt} = -(k_b^o+k_d)C_{D^+A^-} + k_aC_{MA^-}C_{D^+}, \tag{21}$$

$$\frac{dC_{D^+}}{dt} = -k_aC_{D^+}(C_{MA^-}+C_M) + k_d(C_{D^+A^-}+C_{MD^+}), \tag{22}$$

$$\frac{dC_{MD^+}}{dt} = -k_dC_{MD}{}^+ + k_aC_{D^+}C_M, \tag{23}$$

$$\frac{dC_{MA^-}}{dt} = -k_aC_{MD^-}C_{D^+} + k_dC_{D^+A^-}. \tag{24}$$

What we can observe experimentally is the sum of $C_{D^+A^-}+C_{D^+}+C_{MD^+}$. Hence, the decay rate of the total cationized donor is

$$\frac{d(C_{D^+A^-}+C_{D^+}+C_{MD^+})}{dt} = -k_b^oC_{D^+A^-}. \tag{25}$$

After the initial fast back electron transfer reaction, the concentration of D$^+$A$^-$ becomes negligibly small and the system reaches a steady state for the concentration of $C_{D^+A^-}$ and for the partitioning of D$^+$ between the intermicellar phase and the micellar surface.$^{12)}$

$$\frac{dC_{D^+A^-}}{dt} = 0. \tag{26}$$

$$k_aC_{D^+}C_M = K_dC_{MD^+}. \tag{27}$$

An additional relationship is from the electroneutrality of the solution:

$$C_{MA^-} = C_{D^+} + C_{MD^+}. \tag{28}$$

Two equations which are derived by the introduction of Eq. 26 into Eqs. 21 and 25 give the total decay in the form,

$$\frac{d(C_{D^+}+C_{MD^+})}{dt} = -\frac{k_b^ok_aC_{MA^-}C_{D^+}}{k_b^o+k_d}. \tag{29}$$

Introducing Eqs. 27 and 28 into Eq. 29 gives

$$\frac{d(C_{D^+}+C_{MD^+})}{dt} = -k_{obsd}(C_{D^+}+C_{MD^+})^2, \tag{30}$$

where

$$k_{obsd} = \frac{k_b^ok_ak_d}{(k_b^o+k_d)(k_d+k_aC_M)}. \tag{31}$$

Thus, it has become clear that the cationized donor MPTH$^+$ is detached from the host micelle and that the decay rate of the total cation obeys the 2nd-order (Fig. 2). Namely, the mechanism depicted in Fig. 5 is consistent with the experimental results. Unfortunately, however, an evaluation of each rate parameter of this reaction system, unlike the system of MPTH in sodium dodecyl sulfate–europium decyl sulfate mixed micellar solution, can not be made only by increasing surfactant concentration,$^{12)}$ because the micellar aggregation number of CPA increases with the surfactant concentration.$^{10)}$ When the k_{obsd} value of MPTH$^+$ decay in the CPA micellar assembly is compared with that in the Cu(DS)$_2$ micellar assembly, we find that the former is as small as one-seventh of the latter. This is mainly attributable to the smaller k_a value for the former system which involves the repulsive force between MPTH$^+$ and the positive surface potential of CPA micelles, while, in the latter system, the negative surface potential gives rise to an attractive force between Cu^+ and micellar surface.

The author is grateful to Professor M. Grätzel of École Polytechnique Fédérale de Lausanne in Switzerland for his helpful comments and generous permission to publish this work which was partly done during my stay there.

Appendix

In the schematic diagram of Fig. 4, the returning reaction of D^+ outside the micelle into micellar core must be very slow, because the probability that the cationized donor repelled from the micelle by an electrostatic repulsion goes back again into the micellar core must be very small. Therefore, especially when we are discussing the short-time decay just after the laser pulse, $k_r C_{D^+o}$ term can be neglected in Eqs. 3 and 4. Hence they become

$$\frac{dC_{D^+i}}{dt} = -(k_b^i + k_e)C_{D^+i}, \tag{32}$$

$$\frac{dC_{D^+o}}{dt} = -k_b^o C_{D^+o} + k_e C_{D^+i}. \tag{33}$$

Integration of Eq. 32 yields

$$C_{D^+i} = C_0 e^{-(k_b^i + k_e)t}. \tag{34}$$

Introducing Eq. 34 into Eq. 33 and the subsequent integration give

$$C_{D^+o} = \frac{k_e C_0}{k_b^o - (k_b^i + k_e)} \{e^{-(k_b^i + k_e)t} - e^{-k_b^o t}\}. \tag{35}$$

The total cation concentration then becomes

$$C_{D^+i} + C_{D^+o} = \frac{k_b^i - k_b^o}{k_b^i + k_e - k_b^o} C_0 e^{-(k_b^i + k_e)t} \tag{36}$$

$$+ \frac{k_e}{k_b^i + k_e - k_b^o} C_0 e^{-k_b^o t}. \tag{36}$$

Comparing Eq. 36 with Eq. 14 as respects the first part, we have the following equation concerning just the initial decay rate:

$$\alpha_1 = k_b^i + k_e. \tag{37}$$

References

1) Y. Moroi, A. M. Braun, and M. Grätzel, *J. Am. Chem. Soc.*, **101**, 567 (1979).

2) a) S. A. Alkaitis, G. Beck, and M. Grätzel, *J. Am. Chem. Soc.*, **79**, 5723 (1975); b) S. A. Alkaitis and M. Grätzel, *ibid.*, **98**, 3549 (1976).

3) D. Meisil, M. S. Matheson, and J. Rabani, *J. Am. Chem. Soc.*, **100**, 1679 (1978).

4) P. P. Infelta, M. Grätzel, and J. K. Thomas, *J. Phys. Chem.*, **78**, 190 (1974).

5) F. H. Quina and V. G. Toscano, *J. Phys. Chem.*, **81**, 1750 (1977).

6) M. Maestri, P. P. Infelta, and M. Grätzel, *J. Chem. Phys.*, **69**, 1522 (1978).

7) a) M. Almgren, F. Grieser, and J. K. Thomas, *J. Am. Chem. Soc.*, **101**, 279 (1979); b) **101**, 2021 (1979).

8) a) C. M. Starks and R. M. Owens, *J. Am. Chem. Soc.*, **95**, 3613 (1973); b) M. Cinquini, F. Montanari, and P. Tundo, *Gazz. Chim. Ital.*, **107**, 11 (1977); c) D. Landini, A. Maia, F. Montanari, and P. Tundo, *J. Am. Chem. Soc.*, **101**, 2526 (1979).

9) J. L. Moigne, P. Gramain, and J. Simon, *J. Colloid Interface Sci.*, **60**, 565 (1977).

10) Y. Moroi, E. Pramauro, M. Grätzel, E. Pelizzetti, and P. Tundo, *J. Colloid Interface Sci.*, **69**, 341 (1979).

11) R. Humphry-Baker, Y. Moroi, M. Grätzel, E. Pelizzetti, and P. Tundo, *J. Am. Chem. Soc.*, **102**, 3689 (1980).

12) Y. Moroi, P. P. Infelta, and M. Grätzel, *J. Am. Chem. Soc.*, **101**, 573 (1979).

13) Y. Moroi, T. Oyama, and R. Matuura, *J. Colloid Interface Sci.*, **60**, 103 (1977).

14) J. M. Palmer, E. Papaconstantinou, and J. F. Endicott, *Inorg. Chem.*, **8**, 1516 (1969).

15) N. E. Tokel, V. Katovic, K. Farmery, L. B. Anderson, and D. H. Bush, *J. Am. Chem. Soc.*, **92**, 400 (1970).

16) D. C. Oslon and J. Vasilevskis, *Inorg. Chem.*, **10**, 463 (1971).

17) I. J. Lin, J. P. Friend, and Y. Zimmels, *J. Colloid Interface Sci.*, **45**, 378 (1973).

18) S. G. Dick, D. W. Fuerstenau, and T. W. Healy, *J. Colloid Interface Sci.*, **37**, 595 (1971).

19) P. Mukerjee, "Solution Chemistry of Surfactants," ed by K. L. Mittal, Plenum Publishing Corp., New York (1979), Vol. 1, p. 135.

20) Y. Moroi, M. Saito, and R. Matuura, *Nippon Kagaku Kaishi*, **13**, 483 (1980).

21) P. Mukerjee and J. R. Cardinal, *J. Phys. Chem.*, **82**, 1620 (1978).

22) Y. Moroi, K. Motomura, and R. Matuura, *J. Colloid Interface Sci.*, **46**, 111 (1974).

23) B. C. Bennion and E. M. Eyring, *J. Colloid Interface Sci.*, **32**, 286 (1970).

24) T. Yasunaga, K. Takeda, and S. Shirahama, *J. Colloid Interface Sci.*, **42**, 457 (1973).