Light-Initiated Redox Reactions in Functional Micellar Assemblies. 2. Dynamics in Europium(III) Surfactant Solutions

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Abstract: The light-induced reduction of Eu^{3+} ions by *n*-methylphenothiazine (MPTH) and the subsequent back electron transfer from Eu^{2+} to $MPTH^+$ were examined in anionic surfactant aggregates in which Eu^{3+} together with Na^+ or Zn^{2+} constituted the micellar counterion atmosphere. In the back reaction two well-separated kinetic components can be distinguished arising from a fast intramicellar and a much slower intermicellar reaction. The rapid process obeys first-order kinetics and is competing with the escape of Eu^{2+} from its native micelle into the solution bulk. Two escape modes have been detected which can be attributed to simple surface detachment of Eu^{2+} (rate independent of micellar concentration) and direct transfer (hopping) to an adjacent aggregate (rate dependent on micellar concentration). The slower process obeys second-order kinetics, with the rate constant decreasing with increasing micellar concentration. A phenomenological kinetic model is developed which allows us to evaluate the rate constants for the elementary processes involved in the back reaction and to design ways to prevent the intramicellar as well as to retard the intermicellar process.

Introduction

In the preceding paper,[1] a first report was given on photoredox processes in functional surfactant assemblies. The counterion of the micelle constituted by Cu^{2+} ions served as an electron acceptor and was reduced by the excited state of a hydrophobic donor incorporated in the interior of the aggregates. An important outcome of this work concerned the fate of the cuprous ion produced in the photoredox reaction. It was claimed that Cu^+ through a cooperative effect escaped from its native micelle before back reaction with the oxidized donor could occur.

In the present study, we pursue our research on light-induced electron reactions in functional micellar units. The trivalent lanthanide ion Eu^{3+} is introduced in the counterion atmosphere of the surfactant aggregates and is reduced by the excited state of the donor *N*-methylphenothiazine (MPTH) solubilized in the micellar interior:

$$MPTH^* + Eu^{3+} \rightarrow Eu^{2+} + MPTH^+ \quad (1)$$

Particular interest in this system arises from the fact that bivalent lanthanide ions in a thermal[2] or photoassisted[3] reaction can evolve hydrogen from water. However, the utilization of such a process in a light energy conversion system is only feasible if the electron back transfer

$$Eu^{2+} + MPTH^+ \rightarrow Eu^{3+} + MPTH \quad (2)$$

which in homogeneous solution occurs at a very rapid rate, can be prevented or at least retarded considerably. The elucidation of the kinetics of this reaction in europium(III) surfactant solutions is the main goal of the present investigation. It will be shown that the back electron transfer in the micellar system consists of two components arising from a very rapid intramicellar and a slower intermicellar process. Pathways will be explored to avoid the first reaction channel and to retard the second one. Also, from the results of the kinetic analysis, the earlier conclusions[1] will be vindicated regarding the escape mechanism of Cu^+ ions from copper(II) lauryl sulfate micelles.

Experimental Section

Zinc lauryl sulfate ($Zn(LS)_2$) and europium decyl sulfate ($Eu(DS)_3$) were prepared as described earlier.[4] All other substances as well as the apparatus employed were specified before. The Krafft point of $Eu(DS)_3$ is too high to allow for the preparation of micellar solution at room temperature. Therefore, mixed micelles of $Eu(DS)_3$ with NaLS and $Eu(DS)_3$ with $Zn(LS)_2$ containing Eu^{3+} ions were used for the studies at ambient temperature. They were prepared by dissolving the europium surfactant into either the $Zn(LS)_2$ or the NaLS solutions. The micellar concentration was varied by evaporating water in order to maintain the same composition in the sample. The concentration of mixed micelles was determined by the solubilization method[5] using MPTH as a probe. Experimental details concerning the composition of the mixed micellar solutions employed are summarized in Table I. All samples were deoxygenated by flushing with high purity grade nitrogen.

Results

The photoinduced reduction of Eu^{3+} by MPTH (eq 1) incorporated into $Eu(DS)_3/NaLS$ or $Eu(DS)_3/Zn(LS)_2$ mixed micelles is an extremely rapid process. In analogy to the $Cu(LS)_2$ solutions, reaction 1 is completed within the laser pulse and occurs with a quantum yield of unity. The $MPTH^+$ cation radical produced in the Eu^{3+} surfactant solution is unstable and undergoes the back reaction with Eu^{2+} ions described in eq 2. Kinetic spectroscopy experiments showed that this electron transfer reaction is characterized by two stages occurring in well-separated domains.

(a) A rapid process which is terminated within a few microseconds after the laser pulse. This phase is illustrated in Figure 1 which shows oscilloscope traces obtained from the laser photolysis of MPTH in Eu^{3+}/Na^+ and Eu^{3+}/Zn^{2+} surfactant solutions. The absorbance-time curves were recorded at 516 nm, where $MPTH^+$ has its characteristic absorption maximum.[1] The signal is deflected upward during the laser pulse indicating the formation of $MPTH^+$. It decays thereafter until a plateau is attained. As $MPTH^+$ cation radicals are stable for many hours in anionic micellar solution in the absence of reducing cations such as Cu^+ or Eu^{2+}, the decrease in the 516-nm absorbance must be attributed to the back electron transfer reaction (2). A careful analysis of this rapid component of the $MPTH^+$ decay for various conditions of initial $MPTH^+$ and micellar concentrations revealed the following three important features: (1) The decay kinetics follow strictly an *exponential time law.* (2) The rate of the 516-nm absorbance decay as well as the fraction of $MPTH^+$ disappearing in this rapid process are affected by the *concentration of mixed micelles.* It is readily seen from Figure 1 that both in the $NaLS/Eu(DS)_3$ and $Zn(LS)_2/Eu(DS)_3$ systems, an increase in the micellar concentration enhances the kinetics of the decay and reduces its relative magnitude, i.e., the ratio of transient absorbances A_0/A_p measured immediately after

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Table I. Experimental Details Concerning the Composition of the Micellar Solutions Employed

system	metal ion concn, 10^{-2} M		total surfactant ion concn, 10^{-2} M	micellar concn, 10^{-4} M	no. of surfactant ions per micelle
NaLS/Eu(DS)$_3$	Na^+	3.13	8.5	2.7	
$Eu^{3+}/Na^+ = 0.6$		5.56	15.1	6.1	270 ± 25
		7.99	21.8	7.6	($\alpha = 2.0$)
Zn(LS)$_2$/Eu(DS)$_3$	Zn^{2+}	1.56	6.3	1.4	
$Eu^{3+}/Zn^{2+} = 0.7$		2.99	12.2	2.3	500 ± 40
		4.42	18.0	3.3	($\alpha = 3.7$)
Cu(LS)$_2$	Cu^{2+}	0.73	1.45	1.27	
		1.45	2.90	2.80	95 ± 10
		2.42	4.84	4.83	($\alpha = 1.0$)
		3.38	6.76	6.87	
		4.07	8.14	8.31	

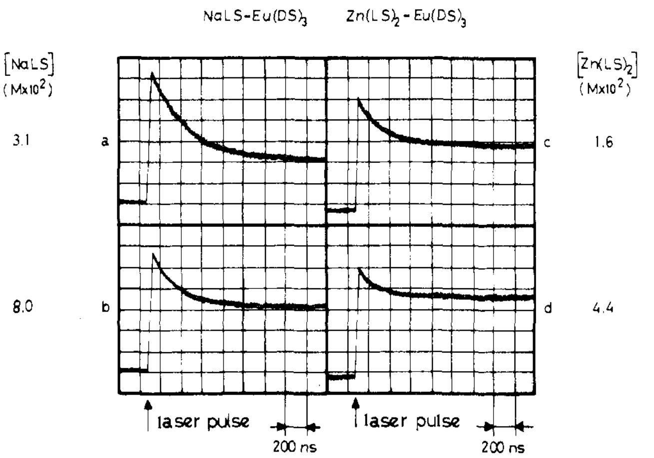

Figure 1. Oscilloscope traces obtained from the laser photolysis of 5×10^{-5} M MPTH in europium surfactant solutions.

the pulse and in the plateau region. (3) The characteristics of the fast component depend on the *charge of the counterion,* which, together with Eu^{3+}, forms the ionic atmosphere of the micelle. For example, each of the two sets of pictures a-c and b-d in Figure 1 corresponds to solutions with about the same mixed micelle concentration. From a comparison of these oscilloscope traces, it is apparent that the replacement of Na^+ by Zn^{2+} as a counterion induces an enhancement of the $MPTH^+$ decay and simultaneously decreases the absorbance ratio A_0/A_p.

(b) The initial fast decrease in the $MPTH^+$ absorption is followed by a much slower decay process occurring in the millisecond time range. This second component distinguishes itself from the first one by two crucial kinetic facts: (1) The slower part decays according to a *second-order rate law.* This is documented in Figure 2, which shows the temporal behavior of the optical density at 516 nm in the long time range for the NaLS/Eu(DS)$_3$ solutions. The inserted oscilloscope traces display a smooth decrease of the transient signal until the original base line level is attained. At 100 µs/div the time scale is too long to allow for a resolution of the initial fast absorbance decrease. Thus, the plots of reciprocal optical density vs. time included in the figure for three surfactant concentrations yield straight lines illustrating the second-order character of the decay process. (2) The rate constant for the slower $MPTH^+$ reaction decreases with increasing concentration of mixed micelles. This parameter k_{obsd} is obtained from the slope of the straight lines such as displayed in Figure 2 and the extinction coefficient of $MPTH^+$ at 516 nm,[1] ϵ_{516} ($MPTH^+$) (9.18×10^3 cm^{-1} M^{-1}):

$$k_{obsd} = \text{slope} \times \epsilon_{516}\,(MPTH^+)$$

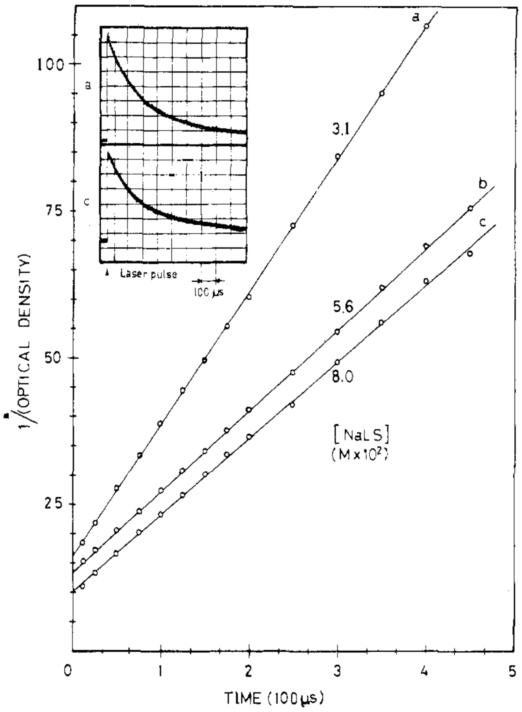

Figure 2. Second-order plots of the 516-nm absorbance decay in the long-time domain for NaLS/Eu(DS)$_3$ mixed micellar solutions. Effect of concentration of mixed micelles. Insert: oscilloscope traces showing the long-time $MPTH^+$ decay for two concentrations of mixed micelles: a, [NaLS] = 3.1×10^{-2} M; c, [NaLS] = 8×10^{-2} M.

Table II lists specific rates of the long time $MPTH^+$ decay for the micellar systems investigated. Also included in this collection are data obtained from the Cu(LS)$_2$ surfactant solutions. There, only the slow second-order decay process was observed which was attributed to the reduction of $MPTH^+$ by Cu^+ via intermicellar migration of the latter ion.[1] From the results presented in Table II we note similar trends for the three surfactant systems investigated, the value of k_{obsd} decreasing with increasing concentration of micelles.

Discussion

In the following section we shall first develop a kinetic model that provides the basis for a quantitative evaluation of our results. As was pointed out above, the forward electron transfer from photoexcited MPTH to Eu^{3+} in the europium surfactant solutions occurs within the duration of the laser pulse. This reaction time is too short to allow for any significant diffusional displacement of the reduced acceptor Eu^{2+} (A^-) and oxidized donor $MPTH^+$ (D^+) produced in the photoredox process. Hence, at the end of the laser pulse, the $D^+ \cdots A^-$ pairs are ex-

Table II. Parameters Obtained from the Short- and Long-Time Analysis of the MPTH$^+$ Decay in Eu^{3+} and Cu^{2+} Surfactant Solutions

system	αc_M, 10^{-4} M	k_1, 10^6 s^{-1}	k_b, 10^6 s^{-1}	k_d, 10^6 s^{-1}	k_h, 10^9 M^{-1} s^{-1}	k_{obsd}, 10^9 M^{-1} s^{-1}	k_a, 10^9 M^{-1} s^{-1}	α
NaLS/Eu(DS)$_3$	5.38	3.3	2.2			2.1		
	10.30	4.0	2.2	0.45	2.6		5.2	2.0
	15.2	4.5	2.1			1.3		
Zn(LS)$_2$/Eu(DS)$_3$	5.18	4.7	1.8			3.5		
	8.66	5.0	1.5	2.1	5.7	2.4	12.0	3.7
	12.30	5.35	1.4			2.0		
Cu(LS)$_2$	1.27					15.5		
	2.80					12.3		
	4.83		10.0	$\simeq 10^2$		11.0		1.0
	6.87					7.8		
	8.31					7.7		

pected to still be associated with those aggregates where the electron transfer events initially took place. The subsequent back reaction according to eq 2 is constituted by several elementary processes which are illustrated schematically in Figure 3.

A. Intramicellar Electron Back Transfer. This involves geminate ion pairs D$^+\cdots$A$^-$ that have remained on their native micelle where they were originally produced. Such a process is different from a conventional electron transfer reaction in homogeneous solutions in that reactive interactions take place between groups of only two molecules. The D$^+\cdots$A$^-$ pairs are compartmentalized in their host micelles and hence are isolated from each other. In analogy with intramolecular processes, such intramicellar events may be described by first-order kinetics. The rate parameter k_b then is expressed in units of s^{-1} and corresponds to the mean reciprocal time required for the electron transfer from A$^-$ to D$^+$.

B. Intermicellar Electron Transfer. The reduced acceptor A$^-$ may dissociate from the micellar surface and escape into the bulk solution before the electron transfer to D$^+$ has occurred. An exit of D$^+$ from the micelle is very unlikely to take place on our time scale of observation since organic cations such as MPTH$^+$ are tightly bound to anionic surfactant aggregates. Two possible escape routes may be envisaged. The first involves detachment of A from the surface of its host micelles *without the aid of neighboring aggregates*. The reduced metal ion diffuses away into the solution thereby leaving the attractive potential field of its native micelle. The rate constant k_d is expressed in s^{-1} since this process obeys a first-order rate law.

The second escape pathway to be considered involves the direct transfer of A$^-$ from its host to an adjacent aggregate. Such a process requires that, during their random motion, the two micelles approach each other sufficiently close to assure a significant overlap of their respective potential fields. Under this condition, it is conceivable that A$^-$ changes its host aggregate via a hopping process, rate constant k_h (M^{-1} s^{-1}). The empty circles in Figure 3 stand for micelles with or without D association which are both treated as kinetically equivalent. This second pathway of A$^-$ escape from its original host aggregate is *assisted by neighboring micelles*. It is expected to follow second-order kinetics, the hopping rate increasing linearly with micellar concentration.

Once the reduced acceptor has left the sphere of influence of its native micelle, it will undergo random motion through the solution which involves association with and dissociation from the surfactant aggregates. The specific rates of these two processes are given by the parameters k_a and k_d, respectively. It is assumed that the rate of Eu^{2+} association or dissociation is the same for micelles containing no donor, donor, or donor cation.

During this migration A$^-$ will eventually be trapped by a micelle with D$^+$ association where the back electron transfer can occur. Thus, two kinds of electron transfer processes are distinguished in this kinetic model. In the intramicellar reaction A$^-$ reduced the cation of the same donor molecule from which it originally had received the electron. The intermicellar process, on the other hand, arises from reduced acceptor ions which were able to escape from their native micelle into the solution bulk. The back reaction is accomplished via diffusion of A$^-$ to *any D$^+$* containing aggregate to which the electron is returned.

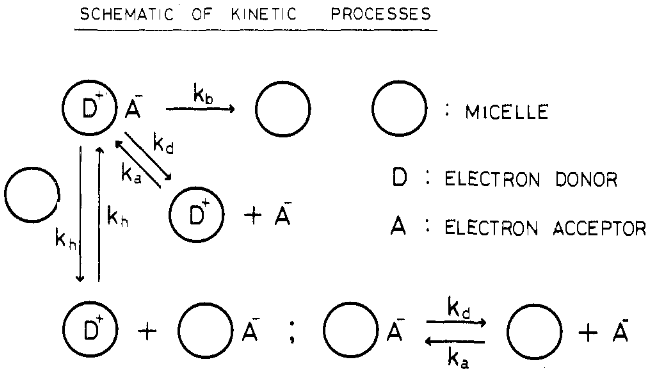

Figure 3. Schematic illustration of the elementary processes contributing to the back transfer of an electron from a reduced acceptor to an oxidized donor in a micellar solution.

On the basis of the concepts outlined above, we shall now develop the kinetic equations needed to analyze the results. The following notations will be used for the concentration terms: c_M = empty and D-containing micelles; c_{D^+} = micelles with D$^+$ association; c_{A^-} = micelles with A$^-$ association; $c_{D^+A^-}$ = micelles with simultaneous D$^+$ and A$^-$ association. The parameter observed experimentally is the transient optical density at 516 nm, which is related to the MPTH$^+$, i.e., total D$^+$ concentration: $[\mathrm{MPTH}^+] = [\mathrm{D}^+] = A_{516}/\epsilon_{516}(\mathrm{MPTH}^+) \times l$, where l is the cell length. The latter may be expressed as the sum of the two concentration terms:

$$[\mathrm{D}^+] = c_{D^+} + c_{D^+A^-} \tag{3}$$

comprising all the micelles with D$^+$ association. From Figure 3 we find the following differential time laws:

$$\frac{\mathrm{d}c_{D^+A^-}}{\mathrm{d}t} = -(k_b + k_d + k_h c_M)c_{D^+A^-} + k_h c_{D^+} c_{MA^-} + k_a c_{D^+} c_{A^-} \tag{4}$$

$$\frac{\mathrm{d}c_{D^+}}{\mathrm{d}t} = (k_d + k_h c_M)c_{D^+A^-} - k_a c_{D^+} c_{A^-} - k_h c_{D^+} c_{MA^-} \tag{5}$$

$$\frac{\mathrm{d}c_{MA^-}}{\mathrm{d}t} = k_h c_M c_{D^+A^-} - k_d c_{MA^-} + k_a c_M c_{A^-} - k_h c_{D^+} c_{MA^-} \tag{6}$$

$$\frac{dc_{A^-}}{dt} = k_d(c_{D^+A^-} + c_{MA^-}) - k_a(c_M c_{A^-} + c_{D^+} c_{A^-}) \quad (7)$$

The last two terms in eq 4 and 5 contain the products of the concentrations of the transient species $c_{D^+}c_{MA^-}$ and $c_{D^+}c_{A^-}$. In the short-time domain, these second-order expressions do not contribute significantly to the reaction rate. Hence, for the initial fast component of the back reaction, the differential time laws (4) and (5) may be approximated as

$$\frac{dc_{D^+A^-}}{dt} = -(k_b + k_d + k_h c_M)c_{D^+A^-} \quad (4a)$$

$$\frac{dc_{D^+}}{dt} = (k_d + k_h c_M)c_{D^+A^-} \quad (5a)$$

Integration of eq 4a yields

$$c_{D^+A^-} = c^0 \exp[-(k_b + k_d + k_h c_M)t] \quad (8)$$

Inserting this expression for $c_{D^+A^-}$ in eq 5a and integrating gives

$$c_{D^+} = c^0 \frac{k_d + k_h c_M}{k_b + k_d + k_h c_M} \times [1 - \exp[-(k_b + k_d + k_h c_M)t]] \quad (9)$$

Using eq 3, we thus obtain the integral rate law for D^+ in the short-time domain:

$$[D^+] = \frac{c^0}{k_b + k_d + k_h c_M} \times [k_d + k_h c_M + k_b \exp[-(k_b + k_d + k_h c_M)t]] \quad (10)$$

Within the longer time domain, the system reaches a steady state for the concentration $c_{D^+A^-}$:

$$\frac{dc_{D^+A^-}}{dt} \simeq 0 \quad (11)$$

The partitioning of reduced acceptor between the aqueous bulk phase and the micellar surface is also stationary:

$$k_d c_{MA^-} \simeq k_a c_M c_{A^-} \quad (12)$$

The condition of electroneutrality of the solution gives us an additional relationship:

$$c_{D^+} = c_{MA^-} + c_{A^-} \quad (13)$$

Using eq 4, 11, 12, and 13, it is possible to express all transient concentrations in terms of c_{D^+}:

$$c_{A^-} = \frac{c_{D^+}}{1 + \frac{k_a c_M}{k_d}} \quad (14)$$

$$c_{MA^-} = \frac{k_a c_M}{k_d} \frac{c_{D^+}}{1 + \frac{k_a c_M}{k_d}} \quad (15)$$

$$c_{D^+A^-} = \frac{1 + \frac{k_h c_M}{k_d}}{1 + \frac{k_a c_M}{k_d}} \frac{k_a}{k_b + k_d + k_h c_M} {c_{D^+}}^2 \quad (16)$$

Equations 14, 15, and 16 may be inserted into (5) to obtain

$$\frac{dc_{D^+}}{dt} = -k_{obsd} {c_{D^+}}^2 \quad (17)$$

where

$$k_{obsd} = \frac{k_a k_b}{k_b + k_d + k_h c_M} \frac{1 + \frac{k_h c_M}{k_d}}{1 + \frac{k_a c_M}{k_d}} \quad (18)$$

Finally, under the present conditions, $c_{D^+A^-} \ll c_{D^+}$ in the long-time region: hence

$$[D^+] \simeq c_{D^+} \quad (19)$$

and

$$\frac{d[D^+]}{dt} = -k_{obsd}[D^+]^2 \quad (20)$$

The evaluation of the short-time data was performed by first plotting the logarithm of the absorbance difference $A(t) - A_p$ from oscilloscope traces such as shown in Figure 1 as a function of time. From the slope of the straight lines obtained, the first-order rate constant k_1 of the fast MPTH$^+$ decay was determined. The values listed in Table II show that in both the Eu^{3+}/Na$^+$ and Eu^{3+}/Zn^{2+} systems k_1 increases with micellar concentration.[12] According to eq 10 k_1 is defined by the sum of three terms:

$$k_1 = k_b + k_d + k_h c_M \quad (21)$$

the last containing the concentration of mixed micelles. Thus, the observed trends in k_1 provide strong support for the hopping mechanism that assists the escape of the Eu^{2+} ion from its original host aggregate.

In the further analysis of the short-time data, it was attempted to find the individual values for the rate constants k_b, k_d, and k_h. Two different procedures of evaluation were employed. First, the slope of the MPTH$^+$ decay curves was determined at the onset of the back reaction, i.e., zero time. The starting point was taken as the middle of the exciting laser pulse which required a small extrapolation of the 516-nm absorbance decay functions. From eq 10 it is readily derived that

$$\left(\frac{dD^+}{dt}\right)_{t=0} = c_0 k_b \quad (22)$$

Hence, the initial slope is directly related to the specific rate of the back electron transfer. The values of k_b obtained from this analysis are included in Table II. They are somewhat smaller for the Zn^{2+}/Eu^{3+} as compared to the Na$^+$/Eu^{3+} solution and exhibit in the former system a small decrease with increasing micellar concentration. Subtraction of the k_b values from the decay rate constant k_1 yields the parameter $k_d + k_h c_M$, which is plotted as a function of micellar concentration in Figure 4. Straight lines are obtained in agreement with the predictions of the model whose intercept with the ordinate corresponds to k_d and the slope to k_h/α. The numerical values for these rate parameters are also listed in Table II whereby the α values used to calculate k_h were obtained from the numerical analysis of the long-time decay (see below). Both k_h and k_d are considerably larger for the Zn^{2+}/Eu^{3+} than for the Na$^+$/Eu^{3+} micelles. This explains why in the former system a much smaller fraction of Eu^{2+} undergoes intramicellar back reaction. The marked difference in k_d found for the two solutions may be rationalized in terms of the escape mechanism suggested to be operative for Cu$^+$ ions in the Cu(LS)$_2$ solutions.[1] The dissociation of reduced metal ion from the micellar surface was envisaged to proceed via the replacement by other metal ions present in the counterion atmosphere of the micelle. The probability of this exchange will crucially depend on the respective charge of the two ions and the potential decay curve in the electrical double layer around the micelle. Thus, the monovalent Na$^+$ is less efficient in replacing Eu^{2+} than the bivalent Zn^{2+} ion. Hence, within the mixed counterion atmosphere of a Eu(DS)$_3$/Zn(LS)$_2$ micelle, the Eu^{2+} escape is expected to be much faster than for the Eu(DS)$_3$/NaLS aggregates.

The conditions for the dissociation of reduced metal ion from the micellar surface are particularly favorable in the case of the functional Cu(LS)$_2$ assemblies.[1] Therefore, in this system

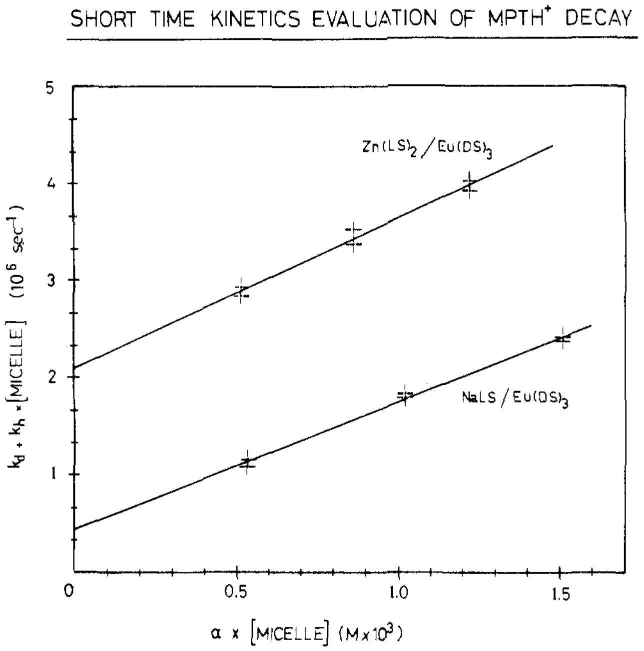

Figure 4. Kinetic evaluation of the fast component of the MPTH$^+$ decay for Zn(LS)$_2$/Eu(DS)$_3$ and NaLS/Eu(DS)$_3$ surfactant solutions, according to procedure 1 (see text).

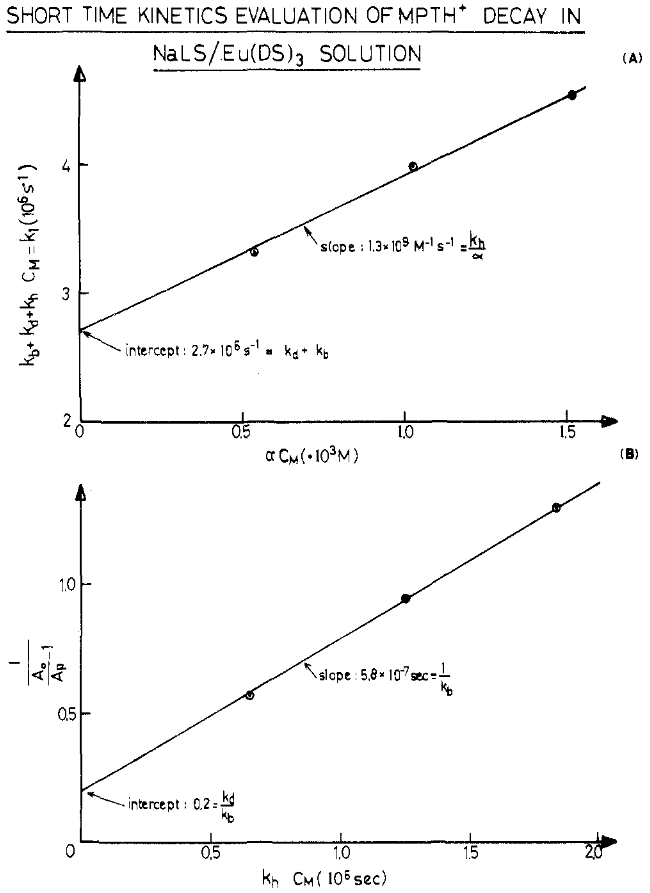

Figure 5. Kinetic evaluation of the fast component of the MPTH$^+$ decay for NaLS/Eu(DS)$_3$ surfactant solutions, according to procedure 2 (see text).

the intramicellar back transfer of an electron from Cu$^+$ to MPTH$^+$ is not at all observed since it cannot compete kinetically with the fast detachment of Cu$^+$ from the surface of the aggregates. Indeed, from the long-time analysis of the data it is possible to estimate that k_d in such a solution is approximately 10^2 times greater than for the mixed europium surfactant micelles, indicating a mean residence time of only a few nanoseconds for Cu$^+$ on the micellar surface. A similar residence time has been determined for hydrated electrons on cationic micelles.[6] (Interestingly, in this earlier pulse radiolysis study, first evidence was provided for a hopping mechanism to be operative in the intermicellar migration of hydrated electrons.)

In order to check the validity of the individual rate parameters k_b, k_d, and k_h listed in Table II, a second evaluation method of the short-time data was applied. This consisted in first plotting the MPTH$^+$ decay rate constants k_1 as a function of micellar concentration. As is shown for the NaLS/Eu(DS)$_3$ system in Figure 5A, a straight line is obtained whose intercept and slope give the values $k_d + k_b = 2.7 \times 10^6$ s^{-1} and $k_h/\alpha = 1.3 \times 10^9$ M^{-1} s^{-1}. Next, from the ratio of the absorbances A_0/A_p, measured at zero time and in the plateau region for different micellar concentrations, the expression $1(A_0/A_p - 1)$ was derived and is plotted in Figure 5B against $k_h c_M$. The latter quantity can be extracted directly from graph (A) in Figure 5. From eq 10, it is predicted that these variables should be related in a linear fashion:

$$\frac{1}{A_0/A_p - 1} = \frac{k_d}{k_b} k_h c_M \tag{23}$$

The experimental points plotted in Figure 5B fit indeed a straight line whose slope and intercept give us $k_b = 1.8 \times 10^6$ s^{-1}; $k_d/k_b = 0.2$ and therefore $k_d = 3.5 \times 10^5$ s^{-1}. We note that the sum of the rate parameters $k_d + k_b$ derived from graph (B) is 2.15×10^6 s^{-1} as compared to the value 2.7×10^6 s^{-1} obtained from plot (A). This discrepancy, which was found to be even larger in the Zn(LS)$_2$/Eu(DS)$_3$ system, is attributed to the choice of the variables made in the second diagram. Both $A_0/A_p - 1$ and $k_h c_M$ are calculated from the difference of two almost identical numbers. Hence, in graph (B) any error in the experimentally determined quantities A_0/A_p and k_1 is amplified considerably rendering this analysis less reliable than the other linear plots. As a whole, the results from this second procedure of evaluating the MPTH$^+$ short-time decay curves confirm the values for the rate parameters listed in Table II.

Turning now to the analysis of the long-time decay curves, we noted already above that these follow precisely a second-order rate law, the observed rate constant k_{obsd} decreasing with increasing micellar concentration. Such a behavior is entirely compatible with the predictions of eq 18 where the concentration of micelles appearing in the denominator is of dominant influence. The same equation may also be used to gain information on the magnitude of the parameters k_a and α. For this purpose, the rate parameters obtained from the short-time evaluation were inserted in eq 18 and the values of α and k_a adjusted to give an optimum fit with the measured k_{obsd} values. The results listed in Table II indicate that the Eu^{2+} association with the anionic aggregates occurs extremely rapidly, the rate being essentially controlled by the diffusion of the reactants. It appears that Eu^{2+} is trapped twice as fast by Zn(LS)$_2$/Eu(DS)$_3$ as by NaLS/Eu(DS)$_3$ mixed micelles. This is attributed to the fact that in the former surfactant system, owing to the presence of the bivalent counterion Zn^{2+}, the critical micelle concentration and hence the concentration of monomer electrolyte is smaller than in the latter. As a consequence, the Debye length of Zn^{2+}-containing micelles is greater than that of Na$^+$ aggregates allowing the electrostatic field which attracts the Eu^{2+} ion to protrude further into the bulk aqueous phase. A similar effect may account for the difference in the hopping rates between the two systems. In the case of Zn(LS)$_2$/Eu(DS)$_3$ micelles, the potential function decreases less sharply with the distance from the micellar surface than

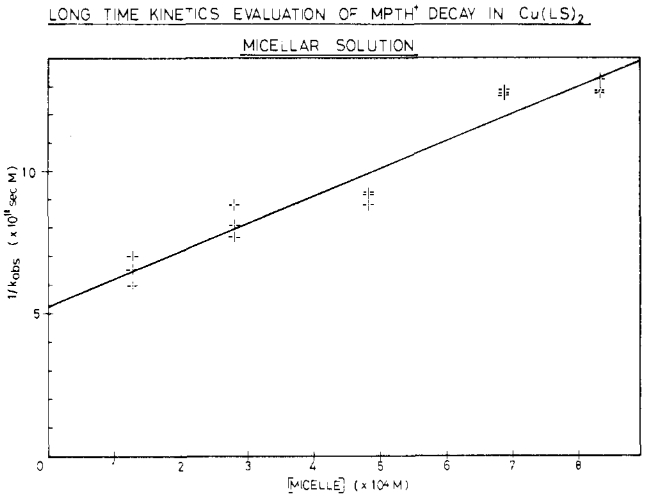

Figure 6. Kinetic evaluation of the long-time component of the $MPTH^+$ decay in $Cu(LS)_2$ solutions. Plot according to eq 25.

for $NaLS/Eu(DS)_3$ implying a spreading of the counterions including Eu^{2+} over a larger region of space. Hence, in the former system hopping can occur at a greater distance of approach of neighboring aggregates.

We note that the rate of Eu^{2+} association with the mixed micelles is higher than that for the hopping from one aggregate to another. This appears reasonable since the latter process may be retarded by intermicellar repulsion or an activation barrier for the surface detachment of the migrating ion. From the ratio k_a/k_b the association constant of Eu^{2+} with the mixed micelles may be calculated:

$$K_a = \frac{k_a}{k_d} = \frac{c_{MA^-}}{c_{A^-}c_M} \tag{24}$$

From the results in Table II we obtain

$$K_a = 1.0 \times 10^4 \text{ M}^{-1} \text{ for NaLS/Eu(DS)}_3$$

and

$$K_a = 5.7 \times 10^3 \text{ M}^{-1} \text{ for Zn(LS)}_2\text{/Eu(DS)}_3$$

The effect of micellar concentration on the k_{obsd} values observed in the two europium surfactant systems led us to examine whether similar phenomena would exist in the $Cu(LS)_2$ solutions, where Cu^+ ions acted as the reductant of $MPTH^+$. In particular, it is crucial to show that the k_{obsd} values follow here the same trends with micellar concentration as in the case of the europium surfactant solutions. The mathematical relation between the second-order rate constant and the concentration of surfactant aggregates c_M is expressed by eq 18. This may be rewritten in the form

$$\frac{1}{k_{obsd}} = \frac{k_d}{k_b k_a \beta} + \frac{1}{k_b \beta} c_M \tag{25}$$

where

$$\beta = \frac{k_d + k_h c_M}{k_b + k_d + k_h c_M} = 1 - \frac{k_b}{k_b + k_d + k_h c_M} \tag{26}$$

is a parameter which reflects the escape probability of reduced acceptor from its original host aggregate. A plot of the reciprocal k_{obsd} values listed in Table II for the $Cu(LS)_2$ system against c_M is presented in Figure 6. The experimental points lie on a straight line whose slope and intercept have the values 9.76×10^{-8} s and 5.25×10^{-11} s, respectively. Division of the former by the latter parameter yields the association constant for Cu^+ with $Cu(LS)_2$ micelles:

$$K_a = \frac{k_a}{k_d} = 1.85 \times 10^3 \text{ M}^{-1}$$

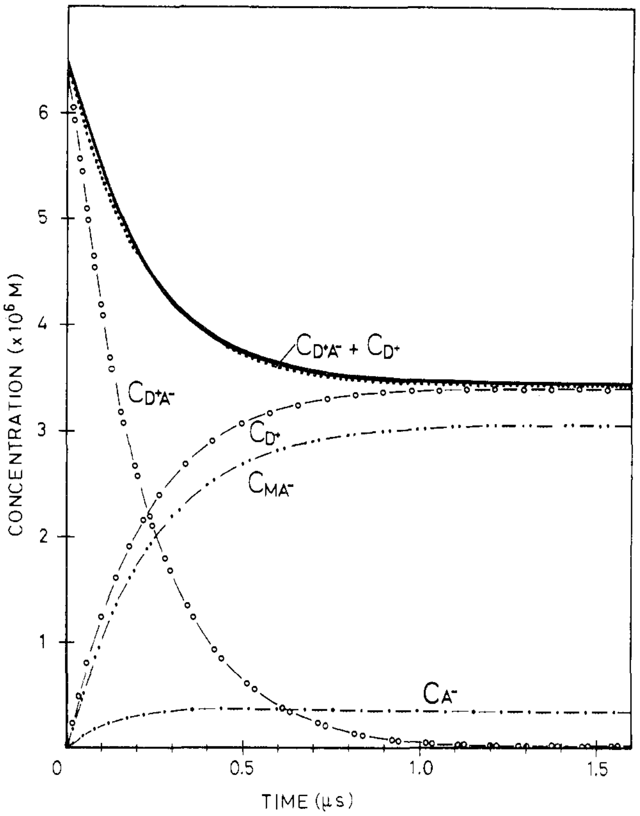

Figure 7. Numerical calculation of the transient concentration-time functions in the short-time domain from eq 4-7 and the rate constants k_d, k_h, and k_a listed for the $Na(LS)/Eu(DS)_3$ solution in Table 11. $k_b = 2.1 \times 10^6\ s^{-1}$, $c_M = 7.6 \times 10^{-4}$ M, initial concentration of oxidized donor $[D^+]_{t=0} = 6.42 \times 10^{-6}$ M. Notations: —, experimental decay curve for D^+; ········, calculated curve for $[D^+] = c_{D^+A^-} + c_{D^+}$; —●●—, c_{MA^-}; —●—, c_{A^-}; —○○—, $c_{D^+A^-}$; —○—, c_{D^+}.

The fact that the experimental points in Figure 6 show no systematic deviation from linearity implies that the slope of the function $1/k_{obsd} = f(c_M)$ defined by eq 25 as $1/k_b\beta$ does not change significantly over the range of micellar concentration investigated. The slope may be expressed as

$$\frac{1}{k_b \beta} = \frac{1}{k_d + k_h c_M} + \frac{1}{k_b} \tag{27}$$

It is concluded that under our experimental conditions $k_d \gg k_h c_M$, indicating that the hopping process practically does not contribute to the escape of Cu^+ ions from its native aggregate.

Apparently, the simple Cu^+ surface detachment (Figure 3) occurs so rapidly that it dominates over the hopping process. We find here the confirmation of the concept introduced earlier[1] that a cooperative effect, i.e., the fast exchange of Cu^+ with another Cu^{2+} ion present in the counterion atmosphere of the aggregate, renders this escape route particularly effective. In fact, from the lack of any indication of an intramicellar back electron transfer, it must be inferred that the escape probability, as defined by the parameter β, is practically unity in the $Cu(LS)_2$ system. The slope of the straight line in Figure 6 may therefore be identified to a good approximation with the reciprocal back transfer rate: slope $\simeq 1/k_b$ or $k_b \simeq 10^7\ s^{-1}$. The value obtained for k_b from this analysis appears reasonable. It is larger than in the europium surfactant systems since we deal here with micelles of considerably smaller size. The micellar radius is expected to have a decisive influence on k_b since it determines the mean distance over which the electron transfer has to occur. In this context, we note that the reduction of $MPTH^+$ by $Ru(bpy)_3{}^+$ in sodium tetradecyltrioxyethylene sulfate micelles, whose radius is almost twice as big as that of

$Cu(LS)_2$ aggregates, occurs with a specific rate of $6 \times 10^6\ s^{-1}$, i.e., almost exactly half as rapidly as the electron transfer in the Cu^{2+} surfactant system.[7]

The association constant for Cu^+ with its host aggregate is smaller than the two K_a values determined for Eu^{2+}. Evidently, this effect arises from the different charge of the two ions. In fact, K_a may be expressed as the product of two terms one of which contains the electrostatic contribution to the association constant:

$$K_a = A \exp(-z_{A^-} e\psi / kT)$$

Here, z_{A^-} is the charge of the reduced metal ion and ψ is the surface potential. In the case of the $Cu(LS)_2$ micelles, both K_a and ψ are known ($\psi = -79$ mV[11]) which allows us to evaluate the parameter A. Assuming that the same A value is valid for the europium surfactant solutions, we obtain $\psi(Zn(LS)_2/Eu(DS)_3) = -54$ mV and $\psi(NaLS/Zn(DS)_3) = -63$ mV.

The kinetic analysis of the Eu^{2+} reaction with $MPTH^+$ was concluded by a numerical simulation of the decay curves obtained in the $NaLS/Eu(DS)_3$ system. The results are presented in Figures 7 and 8 for the short- and long-time components, respectively. The temporal evolution of the concentration of the relevant intermediates, i.e., $c_{D^+A^-}$ (-○○-), c_{D^+} (-○-), c_{MA^-} (-●●-), and c_{A^-} (-●-), was calculated by numerical integration of the differential time laws formulated in eq 4 and 7, using the rate parameters listed in Table II. The concentration of D^+A^- pairs reaches a stationary level close to zero within a time period of less than 1.5 μs. This justifies the application of the steady-state condition in the long-time domain, eq 11. Within the same time region, the concentrations c_{MA^-} and c_{A^-} attain their respective maxima. In the subsequent decay of these species, the ratio c_{MA^-}/c_{A^-} maintains a constant value vindicating the application of the pseudoequilibrium condition (10). Furthermore, in the long-time domain, the total concentration of oxidized donor is practically identical with c_{D^+} and $c_{D^+A^-}$ gives the overall decay function for oxidized donor (. . . .) which is seen to merge almost with the experimentally determined concentration curve (solid line). Thus, in an encouraging fashion, the numerical construction of the $MPTH^+$ decay characteristics from the rate parameters in Table II and the mechanistic concepts developed in this article overlap with the data derived directly from the experiments.

Conclusions

During this investigation, the salient kinetic features of the reduction of an organic cation by Eu^{2+} in europium surfactant solution have been scrutinized. The reaction was found to occur in two steps: a fast intramicellar process obeying first-order kinetics, followed by a much slower intermicellar second-order electron transfer. A close analogy exists here with radical deactivation reactions in micellar solutions where the same clear separation of these two kinetic components was observed. Our results also confirm two earlier observations of intramicellar electron transfer between donor and acceptor pairs,[7,11] which were found to follow first-order kinetics, the specific rate being 10^6–$10^7\ s^{-1}$.

The intramicellar back electron transfer competes with the escape of Eu^{2+} from its native micelle into the solution bulk. Here the simple detachment of Eu^{2+} from the micellar surface has to be distinguished from a direct transfer to an adjacent aggregate (hopping). The escape process may be enhanced and as a consequence the intramicellar electron transfer suppressed by increasing the surfactant concentration and selecting a bivalent instead of a monovalent metal ion as the partner of Eu^{3+} in the mixed counterion atmosphere of the micelle. The same conditions produce a retardation of the intermicellar reaction of Eu^{2+} with the oxidized donor—an indispensable prerequisite for the utilization of such a photoredox reaction in a light energy conversion system.

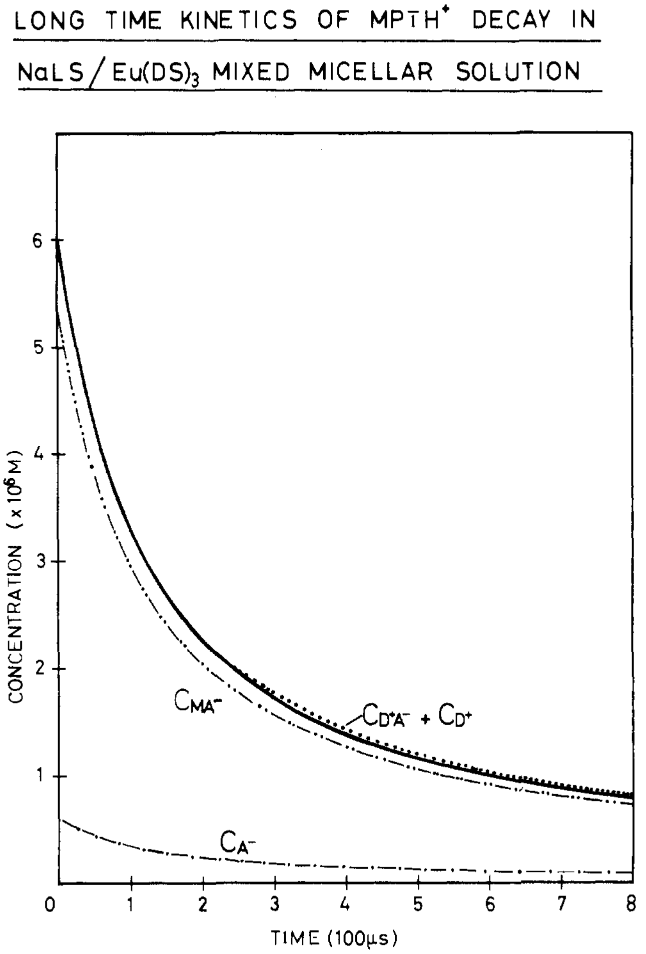

Figure 8. Numerical calculation of the transient concentration time functions in the long-time domain from eq 4–7. Notations as in Figure 7.

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(12) Instead of micellar concentrations Table II lists values for the quantity αc_M determined directly via the solubilization method. The parameter α represents the average number of solubilizate per micelle in a solution which is saturated by the solubilizate molecules.