

Figure 3. Change in Franck–Condon overlap with change in the outof-plane deformation angle (qualitative picture). (a) shows a small Franck–Condon overlap for a small out-of-plane angle in the equilibrium geometry of the  $T_1$  state. In (b) the Franck–Condon overlap (shaded area) is larger than in (a) due to the larger out-of-plane angle which brings the  $T_1$  and  $S_0$  potential energy curves closer together.

The seemingly small deuterium effects for the aldehydes propynal and glyoxal (see Table II) are probably due to their planar  $T_1$ -state configurations for which the Franck–Condon terms for  $T_1 \rightarrow S_0$  intersystem crossing would be determined by the overlap between vibrational wave functions in two single-minimum potential energy surfaces. Therefore, enhancement of intersystem crossing by out-of-plane modes (as in Figure 3) would be relatively small. In conclusion, some factors can be stated that are responsible for the transition from small- to intermediate- to large-sized deuterium effects on  $T_1 \rightarrow S_0$  intersystem crossing in alkyl carbonyl compounds.

1. Molecules with a small deuterium effet have  $T_1$ -state geometries that are either planar or pyramidal about the carbonyl group. Planar molecules have only a single-minimum potential energy surface with respect to inversion through the molecular plane, which reduces the enhancement of intersystem crossing by out-of-plane modes.

Pyramidal molecules have a smaller out-of-plane deformation angle than do molecules with intermediate- and large-sized deuterium effects. The carbonyl substituents are both larger than hydrogen atoms and dampen the efficiency of out-of-plane modes in enhancing intersystem crossing.

2. Molecules with an intermediate-sized deuterium effect have a pyramidal configuration which produces a double-minimum potential energy surface with respect to inversion through the molecular plane and increases the enhancement of intersystem crossing by out-of-plane modes. The presence of one small carbonyl substituent and one large carbonyl substituent produces an intermediate-sized dampening of out-of-plane modes and an intermediate-sized deuterium effect.

3. Molecules with a large-sized deuterium effect have a pyramidal configuration. Both substituents are small. This makes the out-of-plane deformation angle the largest possible and reduces the dampening of the out-of-plane mode. Both effects make  $k_{\rm TS}$ very large and very sensitive to deuteration.

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# Surfactant-Concentration Effects in Photoinduced Electron Transfer from Pyrene to Cupric Ions in Sodium Dodecyl Sulfate Micelle Solutions

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The decay of pyrene fluorescence and the quantum yield of pyrene cations were measured by using the laser photolysis method in sodium dodecyl sulfate (SDS) micelle solutions containing both pyrene and cupric dodecyl sulfate at 40 °C. The decay curve of the pyrene fluorescence deviates from the first-order rate law at SDS concentrations below 0.2 M, as already known, but becomes first order at higher SDS concentrations. The rate shows incontinuity between 0.2 and 0.5 M SDS. The cation quantum yield remarkably increases with the SDS concentration: For 10 mM of cupric ion, the quantum yields were 0.25 and 0.60 at SDS concentrations of 0.05 and 0.8 M, respectively. These results can be explained in terms of involvement of large rodlike micelles in which the portion of the net electron transfer in quenching is larger than in usual spherical micelles.

## Introduction

Photochemical reactions in micellar solutions are influenced by the properties of a micelle such as the critical micelle concentration (cmc) and the aggregation number,<sup>1,2</sup> which depend on temperature, surfactant concentration, and added salt or cosurfactant. In most experiments these factors are adjusted carefully so that one type of micelle, viz., a spherical one, dominates the system in order to avoid complexity in analysis. In experiments of sodium dodecyl sulfate (SDS) micelles, the surfactant concentration has been kept at 0.05-0.2 M, although it has not been experimentally assured that the above condition is fulfilled over this concentration range. The present study is

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<sup>(1)</sup> As to micelles, see, for example: (a) Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems"; Academic Press: New York, 1975; Chapter 2A. (b) Mittal, K. L.; Mukerjee, P. In "Micellization, Solubilization, and Microemulsions"; Plenum Press: New York, 1977; Vol. 1.

<sup>(2)</sup> As to photochemical aspects, see, for example: (a) Thomas, J. K. Chem. Rev. 1980, 80, 283. (b) Graetzel, M.; Thomas, J. K. In "Modern Fluorescence Spectroscopy"; Wehry, E., Ed.; Plenum Press: New York, 1976.

concerned with the contribution of another type of micelle, probably a rodlike one, in reactions of the excited singlet pyrene with cupric ions in concentrated SDS solutions with special attention to net electron transfer from pyrene to cupric ions. The highest SDS concentration examined was 1.0 M, which seemed almost maximum in the liquid phase. An attempt to prepare a 1.5 M SDS solution resulted in production of a jelly at 25 °C.

The use of pyrene enables us to follow directly the kinetics of the excited singlet pyrene by using a nanosecond laser apparatus owing to its long-lived fluorescence. The cupric ion is, to our knowledge, the only metal-ion quencher that causes net electron transfer from pyrene to a cupric ion in SDS solutions.<sup>3</sup> Comparative measurements were also done with the thallous ion, one of the quenchers that are known to induce enhancement of intersystem crossing.4-6

Surfactant-concentration effects on pyrene fluorescence quenching have been observed at SDS concentrations below 0.2 m<sup>4,7,8</sup> and attributed to exchange of quenchers between the micellar and aqueous phases<sup>9,10a</sup> and between micelles.<sup>7,8,10b</sup> However, it seems difficult to explain the present results, especially the increase in the pyrene-cation quantum yield, solely in terms of quencher exchange. A reasonable explanation is provided on the assumption of involvement of large rodlike micelles which are believed to predominate in concentrated SDS solutions.<sup>1,2a</sup> Current theories of reaction kinetics in micellar solutions<sup>7-10</sup> are formally applicable to solutions containing rodlike micelles, provided that their concentration is known. However, kinetic analysis in the present paper is rather qualitative or semiquantitative, since no definite quantitative information is available concerning micelle formation at SDS concentrations as high as 0.5-1.0 M.

#### **Experimental Section**

The laser photolysis apparatus with a frequency-doubled ruby laser is the same as the one reported previously<sup>5</sup> except for the modification that the analyzing light beam crosses the sample cell in the opposite direction along the identical axis. The incident photon numbers were calibrated by using the absorption of the anthracene triplet state in cyclohexane solution for which the quantum yield is 0.75<sup>11</sup> and the extinction coefficient at 422 nm is 64 700  $M^{-1}$  cm<sup>-1</sup>.<sup>12</sup> The laser beam was attenuated so that the energy absorbed by a sample was kept about 2 mJ/cm per pulse.

Pyrene was purified by silica gel column chromatography. Sodium dodecyl sulfate of biochemical grade (Wako) was used without further purification, as atomic absorption analysis showed that the contents of heavy metal elements were below the detection limit (<10 ppb). The pyrene concentration was  $2 \times 10^{-4}$  M in all the samples. Cupric ions were added in the form of cupric dodecyl sulfate, which was precipitated from a solution of SDS and cupric sulfate, and recrystallized from water. Cupric sulfate (Koso), sodium chloride (Junsei), and thallous nitrate (Wako) were used as received. The sample solutions except those containing thallous ions were degassed by freeze-pump-thaw cycles, since the usual method of nitrogen bubbling foams too much in concentrated (above 0.5 M) SDS solutions. The measurements were done at 40 °C unless otherwise stated.

#### Results

Quenching of Pyrene Fluorescence. The decay of the pyrene fluorescence was monitored at 400 nm. The natural lifetime was

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Figure 1. SDS-concentration dependence of pyrene fluorescence decay measured at 400 nm on quenching by 2 mM cupric ion. SDS concentrations (M): ( $\Delta$ ) 0.05, (**\blacksquare**) 0.1, ( $\Box$ ) 0.2, (**\bullet**) 0.5, (**\circ**) 0.8, (+) 1.0. The intensities are not normalized among measurements.



Figure 2. Decay of pyrene fluorescence at 400 nm in 0.05 M SDS solutions. Cupric ion concentrations (mM): (O) 0.50, ( $\Delta$ ) 1.1, ( $\Box$ ) 2.1, **(●)** 4.7.



Figure 3. Decay of pyrene fluorescence at 400 nm in 0.5 M SDS solutions. Cupric ion concentrations (mM): (O) 0.49, ( $\Delta$ ) 1.0, ( $\Box$ ) 2.2, ( $\bullet$ ) 5.1.

 $340 \pm 20$  ns, being practically independent of the SDS concentration. In the presence of cupric ions, the fluorescence decay depends on the SDS concentration as shown in Figures 1-3. In solutions with 2 mM cupric ions, the semilog plot of the decay



**Figure 4.** SDS-concentration dependence of the quenching rate constants  $(k_q, \Box)$ , ET rate constants  $(k_{qe}, \blacksquare)$ , and ET efficiencies  $(f_e, O)$  in quenching by cupric ions.

at 0.05 M SDS deviates from a straight line, and the deviation gradually diminishes as the SDS concentration increases, and finally the seeming decay follows the first-order rate law above 0.5 M of SDS, as shown in Figure 1. The decay curves for other cupric ion concentrations are also shown for 0.05 M SDS (Figure 2) and 0.5 M SDS (Figure 3). The same tendency in the SDSconcentration dependence seems to occur at other cupric ion concentrations, although the plots are almost straight at high quencher concentrations in dilute SDS solutions. The curves in 0.05 M SDS solutions as shown in Figure 2 are typical for quenching in dilute micellar solutions.<sup>3,7–9,13</sup> Linear semilog plots are obtained for SDS concentrations above 0.5 M even at low cupric ion concentrations, as shown in Figure 3. The kinetic data in Figure 1 indicate that the decay rate suddenly increases somewhere between 0.2 and 0.5 M SDS, contrary to a decreasing tendency seen below 0.2 M SDS, and decreases again with the SDS concentration above 0.5 M SDS. This peculiar change in the decay rate suggests the occurrence of remarkable change in the properties of a micellar solution.

The deviation in the semilog plot of the fluorescence decay is essentially due to distribution of quenchers among micelles.<sup>8,10,13</sup> The exchange of a quencher as mentioned above<sup>7-10</sup> also affects the decay. A few elaborate theoretical formulas have been presented on the basis of these schemes.<sup>7,10b</sup> However, an essential parameter, micelle concentration, cannot be estimated correctly for such high SDS concentrations as 0.5 M; therefore, analysis cannot help being semiquantitative, and simplified approximations will be used. Previous analyses of SDS micelle systems have rested on the assumption that reactions involve only the spherical micelle whose concentration, [M], is given by eq 1 with an aggregation number of 62 and a cmc of 8.2 mM.<sup>14</sup>

$$[M] = ([SDS] - cmc)/N_g$$
(1)

The second-order quenching rate constant,  $k_q$ , was calculated in terms of

$$\ln (I/I_0) = -(k_q[Q] + k_s)t$$
 (2)

where  $I/I_0$  denotes the fluorescence intensity divided by that at t = 0, [Q] denotes the quencher concentration, and  $k_s$  is the spontaneous decay rate constant, being  $(2.9 \pm 0.2) \times 10^6 \text{ s}^{-1}$  irrespective of the SDS concentration. Equation 2 is a very crude approximation to refined expressions for micellar kinetics,<sup>10b</sup> although it is seemingly identical with an equation for kinetics in usual solutions. In the data plots, ln  $(I/I_0)$  is substituted by

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  - (14) Mysels, K. J.; Princen, L. H. J. Phys. Chem. 1959, 63, 1696.



**Figure 5.** Plots of pyrene cation quantum yields,  $\Phi(P^+)$ , and triplet-state quantum yields,  $\Phi(P^T)$ , at SDS concentrations of (O) 0.8, ( $\oplus$ ) 0.5, ( $\Box$ ) 0.2, ( $\blacksquare$ ) 0.1, ( $\Delta$ ) 0.05 M. The curves show simulations based on eq 8 and 9 with the parameter values shown in Figure 4.

In *I*; therefore, the plots are not normalized with respect to the intensity, and only the slope and curvature can be compared with one another. When the observed decay deviated from the first-order rate law, eq 2 was applied to the initial decay for which the approximation holds. The observed pseudo-first-order rate constants were plotted against the cupric ion concentration to evaluate  $k_q$  from its slope (plots not illustrated). The values of  $k_q$  thus calculated for several SDS concentrations are plotted in Figure 4 as a function of the SDS concentration.

Yields of Pyrene Cations and Triplet States. The observed transient spectra include the bands of pyrene cations with a principal peak at 450 nm where  $\epsilon = 20500 \text{ M}^{-1} \text{ cm}^{-1}$  (ref 15 and 16) and the bands of pyrene triplet states with a main peak at 414 nm where  $\epsilon = 35000 \text{ M}^{-1} \text{ cm}^{-1.17}$  The absorption spectra of both cation and triplet state were independent of the SDS concentration under the present conditions. The quantum yields of the cation and triplet state were determined from the absorbances at 450 and 414 nm, respectively, at the time when they reached maxima. The absorbance was corrected for the overlap of the bands whenever necessary. The quantum yields at several SDS concentrations are plotted against the cupric ion concentrations in Figure 5. At every SDS concentration, the cation yield increases and the triplet-state yield decreases with increasing cupric ion concentration. The decay of the pyrene cation was independent of the SDS concentration, being first order with a rate constant of  $(1.2 \pm 0.3) \times 10^4 \text{ s}^{-1}$ ; therefore, its competition with the cation formation does not practically affect the measurement of the cation yield.

Reactions and rate constants concerned are denoted as follows:

$$\mathbf{P}^* \xrightarrow{k_{\rm sd}} \mathbf{P} \tag{3}$$

$$\mathbf{P}^* \xrightarrow{k_{\mathrm{si}}} \mathbf{P}^{\mathrm{T}}$$
(4)

$$P^* + Q \xrightarrow{k_{qd}} P + Q \tag{5}$$

$$\mathbf{P}^+ + \mathbf{Q} \xrightarrow{k_{qi}} \mathbf{P}^{\mathsf{T}} + \mathbf{Q} \tag{6}$$

$$P^* + Q \xrightarrow{k_{qe}} P^+ + Q \tag{7}$$

(15) Hall, G. E.; Kenney-Wallace, G. A. Chem. Phys. **1978**, 32, 313. (16) Our preliminary measurement gave a value of  $3.1 \times 10^4 \, M^{-1} \, cm^{-1}$  for the extinction coefficient of the pyrene cation in 2-chlorobutane matrix at 77 K without correction for the bandshape, which was sharper in this matrix than in the micelle solution.

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**Figure 6.** SDS-concentration dependence of quenching rate constants  $(k_q, \square)$ , isc rate constants  $(k_{qi}, \blacksquare)$ , and isc efficiencies  $(f_i, O)$  in quenching by thallous ions.

Note that  $k_s = k_{sd} + k_{si}$  and  $k_q = k_{qd} + k_{qi} + k_{qe}$ . The quantum yields of the cation,  $\Phi(P^+)$ , and the triplet state,  $\Phi(P^T)$ , are represented by

$$\Phi(P^{+}) = k_{ae}[Q] / (k_{s} + k_{a}[Q])$$
(8)

$$\Phi(\mathbf{P}^{\mathrm{T}}) = \frac{k_{\mathrm{si}} + k_{\mathrm{qi}}[\mathbf{Q}]}{k_{\mathrm{s}} + k_{\mathrm{q}}[\mathbf{Q}]}$$
(9)

Since both  $k_s$  and  $k_q$  are obtained from the fluorescence decay data, the electron-transfer (ET)<sup>18</sup> rate constant,  $k_{qe}$ , can be determined in terms of eq 8. Its values thus calculated are also plotted in Figure 4 and the quantum yields simulated by using these values are shown by the curves in Figure 5. The calculated quantum yield is slightly higher than the experimental one at cupric ion concentrations below 2 mM. This small discrepancy is due to the deviation of the fluorescence decay from the first-order rate law. Examples of better simulations for such a case have been shown;<sup>3</sup> however, precise analysis seems rather meaningless in the present study for the reason mentioned previously. The ET rate constant can be estimated satisfactorily from the data for high cupric ion concentrations.

The intersystem-crossing (isc)<sup>18</sup> enhancement rate constant,  $k_{qi}$ , can also be calculated in terms of eq 9. The spontaneous isc rate constants,  $k_{si}$ , were determined from  $k_s$  and the spontaneous triplet-state quantum yield at every SDS concentration, being (7.2  $\pm 0.6$ )  $\times 10^5 \text{ s}^{-1}$  without particular tendency. The experimental data indicate that  $k_{qi}$  should be negligible compared with  $k_q$  within the experimental accuracy. The triplet-state quantum yields simulated for  $k_{qi} = 0$  are shown in Figure 5.

We define the ET efficiency  $f_e$  by

$$f_{\rm e} = k_{\rm qe} / k_{\rm q} \tag{10}$$

which is the same as the ultimate quantum yield defined in our previous reports.<sup>3-5</sup> Terminology was altered because it was found that the real quantum yield converges upon a lower value than this in solutions where surfactant is added in the form of cupric dodecyl sulfate.<sup>19</sup> The values of ET efficiency are plotted in Figure 4, where the errors in  $f_e$  indicated by bars do not include those caused by a possible error in the extinction coefficient of pyrene cations. The ET efficiency increases with the SDS concentration until somewhere between 0.2 and 0.5 M SDS and reaches a plateau. Such a change in the ratio of rate constants is unusual for ordinary chemical reactions and suggests involve-



**Figure 7.** Plots of pyrene cation quantum yields in 0.05 M SDS solutions containing 0.6 M sodium chloride ( $\mathbf{O}$ ) and plots for the same solutions without sodium chloride ( $\mathbf{O}$ ). The curve is a simulation based on eq 8.



Figure 8. Decay of pyrene fluorescence at 400 nm in 0.05 M SDS solutions containing 0.6 M sodium chloride. Cupric ion concentrations (mM): ( $\Delta$ ) 1.1, ( $\Box$ ) 2.1, ( $\blacksquare$ ) 5.0.

ment of something peculiar, which is probably a reaction in rodlike micelles in the present systems, as will be discussed later. The peculiarity in the concentration dependence of the ET efficiency will be clarified by comparison with the results of quenching by thallous ions, which will be described below.

The experiments on quenching by thallous nitrate were done with nitrogen-bubbled samples at 22-25 °C. Thallous nitrate enhances intersystem crossing<sup>4-6</sup> without causing net electron transfer.<sup>4</sup> Figure 6 shows the rate constants and the isc enhancement efficiencies,  $f_i = k_{qi}/k_q$ , as a function of the SDS concentration. The spontaneous triplet-state quantum yield,  $\Phi_T^0$ , increases from 0.19 for 0.05 M SDS to 0.23 for 0.2 M SDS. The rate constant decreases with increasing SDS concentration, but the isc enhancement efficiency is constant within the experimental accuracy. The decrease in  $k_q$  with increasing SDS concentration is essentially due to the decrease in the average quencher number per micelle, although there is a secondary effect of an equilibrium:<sup>4</sup>  $Tl_a^+ + SDS \rightarrow Tl_m^+$ , where subscripts a and m denote the aqueous and micellar phases, respectively. Although the apparent quenching rate constant changes, the isc enhancement efficiency is unchanged. Such is the ordinary behavior expected from usual chemical kinetics.

Effects of 0.6 M Sodium Chloride. Sodium chloride was added at 0.6 M in 0.05 M SDS solutions containing 0.2 mM pyrene and various concentrations of cupric ions. Mazer et al.<sup>20</sup> claim that this condition leads to the formation of rodlike micelles even at an SDS concentration as low as 0.05 M. Other authors have reported aggregation numbers smaller than 200 for lower sodium chloride concentrations.<sup>14,21</sup> The cation quantum yields in the

<sup>(18)</sup> The abbreviations ET and isc are used when the words are used as adjectives.

<sup>(19)</sup> Nakamura, T.; Kira, A.; Imamura, M. Bull. Chem. Soc. Jpn., in press.

<sup>(20)</sup> Mazer, N. A.; Benedek, G. B.; Carey, M. C. J. Phys. Chem. 1976, 80, 1075.



Figure 9. Simulations of decay using eq 13 for some parameter values of  $\bar{n}$  and  $k_q'$  as indicated in the figure.

presence of sodium chloride are plotted against the cupric ion concentration in Figure 7, where the data in the absence of sodium chloride are also shown. The cation yield is obviously enhanced by addition of sodium chloride. The simulation shown in Figure 7 was made for the following parameter values:  $k_q = 7.8 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> and  $f_e = 4.9$ . The isc enhancement was negligible. Incidentally, the spontaneous isc rate constant was  $5.6 \times 10^5$  s<sup>-1</sup>, being slightly smaller than that in the solution without sodium chloride. Figure 8 exhibits semilog plots of the fluorescence decay in the presence of 0.6 M sodium chloride, which do not bend as markedly as those in its absence. Although the plot is almost linear, its slope is much steeper than that of the corresponding linear plot for the same cupric ion concentration obtained in a 0.5 M SDS solution without sodium chloride.

#### Discussion

Fluorescence Quenching Kinetics. A first-order rate constant,  $k_q'$ , of quenching in a micelle containing one quencher molecule is calculated from the observed second-order rate constant in terms of

$$k_{q}' = k_{q}[M] \tag{11}$$

The rate in a micelle accommodating *n* quencher molecules is given by  $nk_q' = k_q[Q]$ . Since *n* follows a distribution like the Poisson distribution, the rate differs among micelles. The observed decay, therefore, is the sum of first-order components with different rates and accordingly deviates in general from the first-order rate law.<sup>6-10,13</sup> Other factors affecting the rate include the quencher exchange between the micellar and aqueous phases<sup>6,9,13</sup> and between micelles.<sup>7,8,10</sup> The exchange enhances the decay of the excited pyrene at long time dominated by slow components for small *n*. An explanation assuming a restricted quencher occupation number in a micelle has also been proposed as an alternative for the quencher exchange scheme.<sup>10b</sup> The initial decay is governed by the average quencher number per micelle,  $\bar{n}$ , given by

$$\bar{n} = [\mathbf{Q}] / [\mathbf{M}] \tag{12}$$

We will use an approximation for the initial decay<sup>13</sup>

$$\ln (I/I_0) = -\bar{n}(1 - \exp(k_a')) - k_s t$$
(13)

which is derived on the assumption of the Poisson distribution and no contributions of the quencher exchange nor the restricted occupation number. Note that eq 2 is a further approximation of eq 13 for small t.

Some curves calculated by using eq 13 are drawn in Figure 9. Note that the intensity is normalized in Figure 9 but not in the data plots in Figures 1–3 and 8. Micelle concentrations were tentatively estimated by using eq 1, and they led to values of  $\bar{n}$  of 3.0, 0.64, and 0.25 for SDS concentrations of 0.05, 0.2, and 0.5 M, respectively. Curves A–C in Figure 9 represent calculations for these values of  $\bar{n}$ , where  $k_q'$  is set at  $1.0 \times 10^7 \text{ s}^{-1}$ , which is an approximation for the values of  $k_q'$  estimated by using eq 11:  $6.7 \times 10^6$  and  $9.3 \times 10^6 \text{ s}^{-1}$  for 0.05 and 0.2 M SDS, respectively. Curves A and B for 0.05 and 0.2 M SDS, respectively, reproduce semiquantitatively the corresponding experimental curves in Figure 1, but curve C for 0.5 M SDS does not. Failure of the calculation for 0.5 M SDS probably results from the use of eq 1, viz., assumption of the spherical micelle.

If rodlike micelles predominate at SDS concentrations above 0.5 M, other values may be associated with  $\bar{n}$  and  $k_{q'}$ . Curve D in Figure 9 represents another calculation for 0.5 M SDS where the parameters are set as  $\bar{n} = 5.0$  and  $k_q' = 1.0 \times 10^6 \text{ s}^{-1}$ . Curve D reproduces the features of the reactions in the concentrated SDS solutions where the decay approaches first order and its rate is faster than that for 0.2 M SDS. The preceding value of  $\bar{n}$  means that the rodlike micelle is 20 times as large as the spherical one, and the value of  $k_q'$  indicates that  $k_q'$  is reduced by a factor of 10 in this rodlike micelle. The approach of the decay to the first-order rate law results from the decrease in  $\bar{n}$ . As to the enhancement of the decay rate, however, success in the above simulation is owed to the assumption of a particular ratio between two factors associated with parameter setting, although it seems quite reasonable to assume a smaller value of  $k_{q'}$  in a larger micelle: The calculation gives close results insofar as the factor for the increase in the size is kept twice as large as the factor for the decrease in the quenching rate constant, as done above. No separate material to examine this assumption is available at present.

Dederen et al.<sup>7a</sup> have briefly referred to their observation of first-order decay in concentrated (up to 0.5 M) SDS solutions and attributed it to predominance of quencher exchange resulting from the decrease in  $k_q'$  ( $k_{qm}$  in their notation) in rodlike micelles, which occurs under the condition

$$k^{-} + k_{\rm x}[{\rm M}] > k_{\rm q}'$$
 (14)

where  $k^-$  and  $k_x$  denote the rate constants for the micellar-aqueous interphase exchange and the intermicellar exchange of a quencher, respectively. For instance, if the rodlike micelle in 0.5 M SDS solutions is 20 times as large as the spherical one in 0.1 M solutions and  $k_q'$  is smaller in the former by a factor of 10, then the micelle concentration reduces by a factor of 2.5 with the change in the SDS concentration from 0.1 to 0.5 M. Thus, the dependence of the terms in inequality 14 on the micelle size also seems to be qualitatively consistent with the results. More precise calculation based on elaborate formulas would enable us to evaluate contributions of the above two mechanisms in real situations. Such calculations were not carried out because of the lack of knowledge concerning the aggregation number of the rodlike micelle or its equilibrium with the spherical micelle or the possible change in the size in each of these micelles.

The effects of 0.6 M sodium chloride are explicable with the increase in the micelle size which accompanies the decrease in '. For instance, if the aggregation number increases by a factor of 5 as has been suggested,  $20 \bar{n}$  for 0.05 M SDS will be 15. In order for calculation using eq 13 with this value to be consistent with the above calculations,  $k_q'$  should be about  $1 \times 10^6$  s<sup>-1</sup>; viz., the rate constant is reduced by a factor of 10. The above ratio between the increase in  $\bar{n}$  and the decrease in  $k_0'$  differs from that assumed tentatively for 0.5 M SDS in the absence of sodium chloride. This difference suggests that a large micelle induced by addition of sodium chloride may not necessarily be the same as rodlike micelles formed at high SDS concentrations. Grieser and Tausch-Treml<sup>8</sup> have observed first-order decay in pyrene fluorescence quenching by cupric ions in SDS solution containing 0.05-0.1 M sodium chloride and explained it in terms of quencher exchange between micelles enhanced by reduction in intermicellar repulsion. This type of quencher exchange cannot be ruled out in the decay enhancement in solutions with 0.6 M sodium chloride,

<sup>(21) (</sup>a) Granath, K. Acta. Chem. Scand. 1953, 7, 297. (b) Coll, H. J. Phys. Chem. 1970, 74, 520. (c) Turro, N. J.; Yekta, A. J. Am. Chem. Soc. 1978, 100, 5951.



Figure 10. Schematic illustration of spherical and rodlike micelles containing a pyrene molecule and a metal-ion quencher. Two different positions are distinguished in the rodlike micelle as cases S and C.

although the micelle size is probably larger there.

Electron-Transfer Efficiency. The present experiments revealed that the ET efficiency increases with the SDS concentration. The ET efficiency is recast as eq 15 in terms of the first-order rate

$$f_{\rm e} = k_{\rm qe'} / (k_{\rm qe'} + k_{\rm qd'})$$
(15)

constants of electron transfer and deactivation defined as done in eq 11. Note that isc enhancement is negligible in quenching by cupric ions. These first-order rate constants reflect the properties of micelles in which reactions occur. If rodlike micelles predominate in the high-SDS region as discussed above, the experimental results require that the ratio of the ET rate constant,  $k_{qe'}$ , to the deactivation rate constant,  $k_{qd'}$ , should be larger in rodlike micelles than in spherical ones.

The difference between the spherical and rodlike micelles is not only in the size but also in the structure. Surfactant molecules must be more densely packed in the rodlike micelle than in the spherical ones, since the ratio of the repulsion energy to the cohesive energy decreases with increasing micelle size (otherwise the micelle size does not increase). Thus, the spherical micelle is rather porous and the rodlike micelle consists of a main region consisting of a densely packed cylinder and a porous spherical region at either end, as shown in Figure 10. In the porous regions of either micelle, a cupric ion can permeate inside to some extent,<sup>13,22</sup> and short reaction distance can be attained, as shown in Figure 10 (case S for the rodlike micelle). In the cylindrical region, it is rather hard for a cupric ion to penetrate deeply into the surfactant layer, and the average reaction distance will be larger than that in the porous region, indicated as case C in Figure 10.

On the assumption of such micelle structures, the difference in the ET efficiency between the spherical and rodlike micelles can be explained by the different dependences of the ET and deactivation rate constants on the reaction distance, R, as schematically illustrated in Figure 11: the ET rate constant weakly and the deactivation rate constant strongly depend on the reaction distance. The former is smaller than the latter at an average reaction distance of the spherical region,  $R_s$ , and larger at the distance of the cylindrical region,  $R_c$ . Incidentally, the logarithms of the rate constants are plotted in Figure 11 because of the exponential distance dependence of the rate constant at long distance, as will be mentioned later.

The first-order rate constants can be written as

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$$k_{\rm qe'} = W_{\rm e} \tau_{\rm e} \xi_{\rm e} \tag{16}$$

$$k_{\rm qd}' = W_{\rm d} \tau_{\rm d} \xi_{\rm d} \tag{17}$$

$$\kappa_{\rm qd} = W_{\rm d} \tau_{\rm d} \xi_{\rm d} \tag{17}$$



Figure 11. Distance dependence of the rate constants.  $R_s$  and  $R_c$  denote average distances in the spherical and cylindrical regions, respectively.

where W denotes the intrinsic rate constant at the reaction distance,  $\tau$  is the duration during which both pyrene molecule and cupric ion are located within the reaction distance, and  $\xi$  denotes the rate constant  $(in s^{-1})^{23}$  for diffusion of both cupric ion on the micelle surface and pyrene molecule inside the micelle.

Currently, electron transfer, intersystem crossing, and radiationless deactivation are treated in common in terms of nonadiabatic radiationless transition theory,<sup>24</sup> in which the rate constant, which corresponds to W above, is given as the product of a frequency associated with electronic interaction and the Franck-Condon factor. The electronic interaction depends on the intermolecular distance and the dependence is believed to be exponential with respect to the distance at large distance.<sup>25</sup> The electronic interaction is the only explicit distance-dependent factor in  $k_{qe'}$  and  $k_{qd'}$ . The diffusion rate constant,  $\xi$ , is not necessarily sensitive to the reaction distance in the particular cases of micellar systems where the reaction distance is governed by the structure as shown in Figure 10, although it may slightly depend on the distance. The diffusion rate constant decreases with increasing micelle size in general; however, the ET efficiency is hardly affected by this change because both  $k_{qe'}$  and  $k_{qd'}$  undergo a similar effect. The duration,  $\tau$ , is determined by the stability of the encounter state, which is not a simple function of the distance. Complex formation will increase the duration. The predominance of the deactivation rate constant at short distance may relate to formation of a relatively long-lived transient complex. Our previous results<sup>4</sup> suggest that isc enhancement and deactivation caused by various metal-ion quenchers occur via a complex.

The results of quenching by thallous ions indicate that the ratio of isc enhancement rate constant to the deactivation rate constant is unchanged. Both intersystem crossing and deactivation are intramolecular processes in the sense that no net chemical change occurs; therefore, perturbations concerned with these processes can be regarded as similar. The present results demand that the interactions governing these intramolecular processes be of short range and also that the interactions concerned with the intermolecular electron transfer be of long range. It should be remarked that this conclusion is based on only the present results, which are the only material available currently concerning the micelle dependence of the transient products.

Although the above discussion deals with distance, mutual orientation is important as well. Brocklehurst<sup>26</sup> has pointed out that the energy of the electronic exchange interaction can differ by about a factor of 1000 depending on the angle, if  $\pi$  orbital is involved in it; the exchange interaction is believed to be responsible for intermolecular electron transfer. In spherical micelles, the angular dependence will be easily averaged, for a quencher can go anywhere on the micelle surface. In rodlike micelles, however, if a pyrene molecule is oriented in a particular direction, e.g., perpendicular to the rod axis of the micelle, then electronic interactions are limited to those allowed for this geometry. Such

<sup>(23)</sup> The dimension of reciprocal time results from the use of the number per micelle instead of the molar concentration.

<sup>(24)</sup> For example, see: Ulstrup, J.; Jortner, J. J. Chem. Phys. 1975, 63, 4358.

 <sup>(25)</sup> Dexter, D. E. J. Chem. Phys. 1953, 21, 863.
 (26) Brocklehurst, B. J. Phys. Chem. 1979, 83, 536.

restriction in geometry may also serve to select a certain mode of reaction.

So far, only one size of each type of micelle has been considered; however, the size may change even in the same type of micelle. The increase in the ET efficiency observed in the region of 0.05–0.5 M SDS can relate to the increase in the micelle size as follows: If the micelle size increases in the fashion that the length of the cylinder increases with the SDS concentration, the ET efficiency will increase with the portion of the cylindrical region in a micelle. If this explanation is correct, the assumption of eq 1 in the above SDS concentration region should be reconsidered. It should be remarked that participation of quencher exchange has been proposed on the basis of the analysis assuming eq  $1.^7$  As discussed in the preceding section, the quenching kinetics can be explained, without invoking quencher exchange, in terms of micelle-size change, if certain conditions regarding the size and the first-order rate constant are met. The large micelle formed in the presence of sodium chloride may also be spherical or disklike as suggested by small aggregation numbers reported by a majority of authors.<sup>14,21</sup> If surfactant molecules are also very densely packed in such a large micelle, reactions will be similar to those in the cylindrical region of the rodlike micelle, viz., the ET efficiency will be enhanced.

Registry No. SDS, 151-21-3; Cu(DS)<sub>2</sub>, 7016-47-9; Cu<sup>2+</sup>, 15158-11-9; pyrene, 129-00-0; pyrene cation, 34506-93-9; sodium chloride, 7647-14-5.

# Molecular Mechanics of Kink Formation in Lipid Monolayers

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The energetics of formation of kink disorders in lipid monolayers is studied by using empirical energy functions and a detailed atomic model of the monolayer. Hydrocarbon chains are induced to undergo transitions from an all-trans conformation to kink conformations at various chain positions. The surrounding layers of chains are allowed to relax adiabatically in response to the induced disorders, and potential energy profiles and other structural aspects of kink disorders are determined. The lowering of activation barriers to kink formation and increased stability of the kink state are found for kink formation in the presence of existing kinks in the same and in adjacent chains.

## Introduction

Lipid bilayers, along with proteins, are the primary constituents of cell membranes. A large body of evidence exists which indicates that lipid assemblies exhibit a fairly pronounced phase transition from a highly ordered gel state, with hydrocarbon chains in an all-trans conformation, to a more disordered liquid crystalline state, in which many chain bonds are rotated into gauche conformations.<sup>1</sup> The role of this transition in biological function and control is under widespread investigation.

A complete understanding of both structural and dynamical aspects of lipid bilayers requires knowledge on the detailed molecular level. A number of theoretical descriptions of lipid bilayer phase transitions recognize the existence of kinks or related phenomena as a fundamental manifestation of disorder in the hydrocarbon chains.<sup>2-4</sup> In the transition of a hydrocarbon chain from an all-trans (t) conformation to kink conformation, two gauche  $(g_{\pm})$  rotations occur in the opposite direction, symbolized by the usual notation

$$..ttt... \rightarrow ...g_{+}tg_{-}...$$
(1)

This "crankshaft" rotation preserves the overall direction of the chain, allowing it to remain packed essentially parallel to neighboring chains and perpendicular to the plane of the bilayer. Isolated gauche rotations may occur at the chain terminus.

A number of molecular mechanics studies have provided information on the energetics of various conformations available to lipid assemblies.<sup>5</sup> Several theoretical studies have calculated interaction energies between packed all-trans hydrocarbon chains.<sup>6-8</sup> Others have explored the interaction between hydrocarbon chain packing and the polar region.<sup>9-11</sup> This paper provides a more detailed look at the hydrocarbon region. By using empirical energy functions, we study the energetics of stacking of hydrocarbon chains in a monolayer, including not only the preferred all-trans conformation but a number of specific disordered states. These include isolated kinks at various chain locations and kinks occurring in pairs in the same and in adjacent chains. This is carried out by selective adiabatic deformation of a monolayer of hexagonally packed hydrocarbon chains.

Potential energy profiles are calculated in this fashion for the formation of isolated kinks and the cooperative formation of neighboring kinks in the same and in adjacent chains. Several important and useful quantities are thus obtained. For example, information is obtained on the interaction energy between neighboring chains which are respectively trans-trans, trans-kink, and kink-kink, energy differences between all-trans and kink states for isolated and dovetailed kinks, the internal degrees of freedom to which the disorder strain is disposed, adherence to crankshaft cooperative behavior, and the spatial distances over which disorder perturbations occur. The above information, particularly the energy data, may be immediately incorporated into explicit empirical biomembrane phase transition models.<sup>2-4</sup> Perhaps more importantly, the potential energy profiles yield activation barriers to the elementary mechanistic steps associated with the nucleation and propagation kinetics of phase transitions in lipids  $^{12-18}$  and

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