July, 1984] © *1984 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 57, 2033—2034 (1984)* 2033

Dependence of Efficiency of Photoinduced Electron Transfer from Pyrene to Copper(II) Ion on Copper(II)-Ion Fraction on Dodecyl-Sulfate-Micelle Surface

Takashi NAKAMURA, Akira KIRA,* and Masashi IMAMURA
The Institute of Physical and Chemical Research Wako-shi, Saitama 351-01

(Received November 24, 1983)

Synopis. In quenching of the pyrene fluorescence by copper(II) ions in dodecyl sulfate micelles whose surface is covered by sodium and copper(II) ions, the pyrene-cation quantum yield decreases, after reaching a certain maximum yield, with increasing copper(II)-ion fraction. The decrease suggests that the micellar structure becomes unfavorable for electron transfer quenching as copper(II) ions displace sodium ions on the micellar surface.

Pyrene cations are produced in quenching of the pyrene singlet excited state by copper(II) ions in sodium dodecyl sulfate (SDS) micelle solutions.[1)] Previous studies of fluorescence measurement[2)] as well as our early laser photolysis study[1)] have been made at low concentrations of both surfactant and quencher in order to avoid possible complexities caused by the change in the micellar size and shape. Recently, remarkable surfactant-concentration effects have been found in this electron transfer at SDS concentrations of 0.05—1 M (1 M=1 mol dm^{-3}).[3)] The present note deals with the seemingly unusual dependence of the pyrene-cation quantum yield on the fraction of copper(II) dodecyl sulfate (CUDS) in mixed solutions of SDS and CUDS. This mixture provides dodecyl sulfate micelles covered by sodium and copper(II) ions. Considering the importance of comparison of the data for the same total dodecyl sulfate (DS$^-$) concentration, it is convenient to define the copper(II)-ion fraction on the micellar surface, $F(\mathrm{Cu}^{2+})$, by

$$F(\mathrm{Cu}^{2+}) = 2[\mathrm{CUDS}]/(2[\mathrm{CUDS}]+[\mathrm{SDS}]) \qquad (1)$$

where the denominator represents the total dodecyl sulfate concentration, and the value of $F(\mathrm{Cu}^{2+})$ thus defined equals unity for CUDS solutions without SDS.

Experimental

Deaerated solutions containing 0.2 mM pyrene were subjected to laser photolysis, where a 20-ns pulse of a frequency-doubled ruby laser (347 nm) was used for excitation.[1,3)] In order to prevent biphotonic ionization, the excitation intensity was adjusted so that the sample absorbed an energy of about 2 mJ cm^{-2} per pulse. The numbers of absorbed photons were estimated using the anthracene T-T absorption as a reference.[1)]

Results

The pyrene fluorescence lifetime in the presence of 10 mM CUDS is 43 ns for an SDS concentration of 1.0 M and becomes shorter with decreasing SDS concentration.[3)] In CUDS micelles the pyrene fluorescence vanishes within the duration of the laser pulse, indicating a lifetime shorter than 20 ns. These lifetimes are much shorter than the natural fluorescence lifetime in SDS micelles, 340 ns for SDS concentrations of 0.05 to 1.0 M. Thus, practically all the excited pyrene molecules were quenched by copper(II) ions under the present experimental conditions. The absorption spectra of pyrene cations with a peak at 450 nm were practically unchanged in shape and position under various conditions used in the experiments. The cation quantum yield, Φ, was determined from the absorbance at 450 nm where the molar absorption coefficient is 20500 M^{-1} cm^{-1}.[4)]

Figure 1A exhibits the cation quantum yield as a function of the copper(II)-ion fraction in SDS/CUDS mixture solutions where the total dodecyl sulfate concentraion was kept at 0.5 M. The cation yield increases as expected with the CUDS concentration up to Φ=0.56 at a copper(II)-ion fraction of 0.2 (the data in such a region are presented elsewhere[3)]) but then decreaes to converge finally to about 0.45. Such decrease in the cation yield with increasing reactant concentration is rather unusual in the chemical-kinetic point of view. The cation quantum yields in CUDS solutions containing no SDS are plotted in Fig. 2A for several CUDS concentrations. The dependence of the yield on the CUDS concentration in this plot cannot be ascribed to the difference in the copper(II)-ion fraction on the micellar surface, for $F(\mathrm{Cu}^{2+})$=1 for all these solutions, but to the change in the micellar size, as has been discussed in our preceding paper.[3)] The cation quantum yields in mixture solutions of SDS (0.05—1.0 M) and

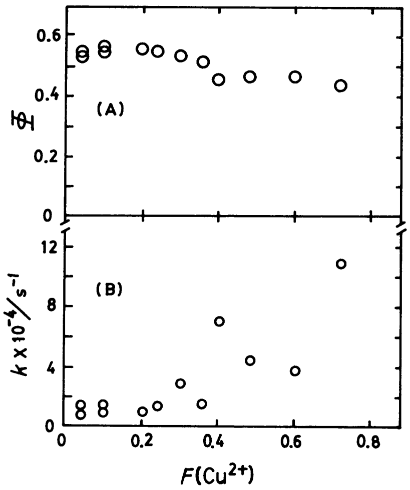

Fig. 1. The pyrene cation quantum yields (A) and the decay rate constants (B) plotted as a function of the copper(II)-ion fraction in CUDS/SDS mixture solutions where the total DS$^-$ concentration is kept at 0.5 M.

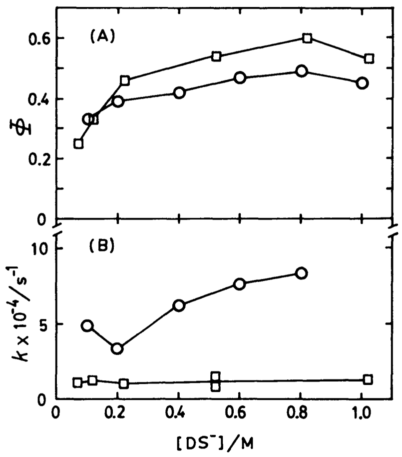

Fig. 2. The pyrene cation quantum yields (A) and the cation decay rate constants (B) in CUDS solutions (○) and in SDS solutions containing 10 mM CUDS (□) plotted as a function of the DS^- concentration.

CUDS (10 mM) are also plotted, for comparison, as a function of the total dodecyl sulfate concentration in Fig. 2A. When the two plots are compared at the same DS^- concentration, the yield for a CUDS solution is lower than that for a SDS/10 mM-CUDS mixture solution, that is, the decrease in the cation yield in the region of high copper(II)-ion fraction occurs, except in the low DS^- concentration region near 0.05 M.

The decay of pyrene cations obeyed the first-order rate law in contrast to a previous result for *N*-methylphenothiazine ions in CUDS micelles.[5] The apparent decay rate constants as plotted in Fig. 1B and 2B indicate that the decay is too slow to compete with the cation formation whose apparent rate constants exceed $2\times10^7\ \mathrm{s}^{-1}$ (=1/(43 ns)) and that it does not affect the observed cation yield. It is interesting that the cation decay is not affected by sodium ions but enhanced by copper(II) ions, as suggested by the results shown in Fig. 2B, although this finding will not be subjected to discussion in this note.

Discussion

Phenomenologically, the pyrene cation quantum yield is given by

$$\Phi = \frac{k_{qe}[\mathrm{CUDS}]}{k_s + (k_{qe} + k_{qd})[\mathrm{CUDS}]} \tag{2}$$

where k_s is the rate constant for the spontaneous fluorescence decay in the absence of copper(II) ions, k_{qe} is the one for electron transfer on quenching, and k_{qd} is the one for quenching processes other than the electron transfer. The electron-transfer efficiency defined by $k_{qe}/(k_{qe}+k_{qd})$ practically equals the observed cation yield, if $k_s \ll (k_{qe}+k_{qd})[\mathrm{CUDS}]$. The fluorescence decay data indicate that this condition is met in CUDS solutions. In SDS/10-mMCUDS mixture solutions, certain portions, which is less than 13% (=43 ns/340 ns), of the singlet excited pyrene molecules fail to react with copper(II) ions; therefore, the electron-transfer efficiency is higher than the observed cation yield. Thus, the decrease in the cation yield observed at high CUDS concentrations indicates the decrease in the electron-transfer efficiency. The concentration dependence of the electron-transfer efficiency is most likely connected with the change in the micellar structure, as will be discussed below.

In our preceding paper on surfactant concentration effects on electron transfer,[3] we have proposed a hypothesis that the electron-transfer efficiency is larger for a densely packed structure of the surfactant layer than for a porous structure. According to this hypothesis, the decrease in the cation yield in the region of high copper(II)-ion fraction is interpreted as that the increase in the copper(II)-ion fraction disturbs a densely packed structure attained in SDS micelles. The densely packed structure is probably peculiar to large rod-like micelles which are believed to exist in solutions of high (above about 0.5 M for SDS) surfactant concentrations.[6] The finding that the decrease in the cation yield at high copper(II)-ion fractions occurs for DS^- concentrations above 0.2 M supports the above explanation based on the densely packed structure of rod-like micelles. The exceptional agreement in the cation yield between a 50 mM-SDS/10 mM-CUDS solution and a 50 mM CUDS solution as shown in Fig. 2A is understood, if it is assumed that porous spherical micelles which lack the densely packed structure are mainly involved in the reaction at these low surfactant concentrations. Incidentally, spherical micelles of CUDS and SDS are similar in size, as suggested by the aggregation numbers (of dodecyl sulfate ions): 85 for CUDS[7] and 62 for SDS.[8]

References

1) T. Nakamura, A. Kira, and M. Imamura, *J. Phys. Chem.*, **87**, 3122 (1983).

2) M. A. J. Rodgers and M. E. DaSilva e Wheeler, *Chem. Phys. Lett.*, **53**, 165 (1978); F. Grieser and R. Tausch-Treml, *J. Am. Chem. Soc.*, **102**, 7258 (1980); J. C. Dederen, M. Van der Ausweaer, and F. C. DeSchryver, *J. Phys. Chem.*, **85**, 1198 (1981).

3) T. Nakamura, A. Kira, and M. Imamura, *J. Phys. Chem.*, in press.

4) G. E. Hall and G. A. Kenney-Wallace, *Chem. Phys.*, **32**, 313 (1978).

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

6) For example, J. K. Thomas, *Chem. Rev.*, **80**, 23 (1980).

7) I. Satake, I. Iwamatsu, S. Hosokawa, and R. Matuura, *Bull. Chem. Soc. Jpn.*, **36**, 204 (1963).

8) K. J. Mysels and L. H. Princen, *J. Phys. Chem.*, **63**, 1696 (1959).