CHEMISTRY LETTERS, pp. 529-532, 1986.

ENHANCED QUENCHING OF PYRENE FLUORESCENCE IN METHYLVIOLOGEN-INDUCED PREMICELLAR AGGREGATES AND INCLUSION EFFECT OF β-CYCLODEXTRIN ON THE QUENCHING

Yoshihumi KUSUMOTO,* Michiko SHIZUKA, and Iwao SATAKE†
Chemical Institute, College of Liberal Arts, Kagoshima University,
Korimoto, Kagoshima 890
†Department of Chemistry, Faculty of Science, Kagoshima University,
Korimoto, Kagoshima 890

The formation of methylviologen-induced premicelles was evidenced by an enhanced fluorescence quenching and the appearance of a new absorption band of pyrene in the premicellar region of sodium dodecyl sulfate. Addition of β-cyclodextrin to the above system led to less pronounced quenching.

The efficiency of electron transfer between solute molecules is enhanced by the presence of an appropriate surfactant. This effect has been the subject of recent intense research.1) The enhancement of the electron transfer in the premicellar region below the critical micelle concentration (CMC), has been attributed to the formation of premicellar (or submicellar) aggregates.1-6) The formation of such a premicelle is characteristic of solute-surfactant systems with the opposite charge. However, discrepancy remains as to whether 1,1'-dimethyl-4,4'-bipyridinium (methylviologen; MV^{2+}) cation really induces such premicelles in aqueous solution of sodium dodecyl sulfate (SDS), a typical anionic surfactant.1-5)

Cyclodextrins (CDx's) have received much attention because of their enzyme-like activity.7,8) The catalytic action of CDx's is associated with their ability to form inclusion compounds with various molecules.7) Recently, several multicomponent complexes of CDx's have been reported.9) More recent work has shown that the ternary complexes composed of pyrene, β-CDx and SDS are formed below CMC.10-12) The purpose of the present study is to elucidate the pyrene-MV^{2+} system in SDS and/or β-CDx solutions, on the basis of the absorption and fluorescence spectral change of pyrene with SDS concentration ([SDS]).

Materials and procedures were essentially the same as those described previously.12) MV^{2+} (dichloride, GR grade of Nakarai Chemicals) was used as received. [pyrene] and [MV^{2+}] were fixed at 5×10^{-7} and 1×10^{-5} mol dm^{-3} throughout whole experiments, respectively. Laboratory deionized water was doubly distilled. The excitation wavelength for fluorescence measurements was 337.1 nm. All measurements were made at 25 °C for aerated solutions.

The systematic studies were carried out for aqueous solutions of pyrene with and without MV^{2+} at varying molar fractions of β-CDx to SDS, x_β, defined by [β-CDx] /([β-CDx] + [SDS]). The degree of fluorescence quenching, E_Q, defined by $1 - I_Q/I_0$, was measured as a function of [SDS], where I_0 and I_Q are the fluorescence intensi-

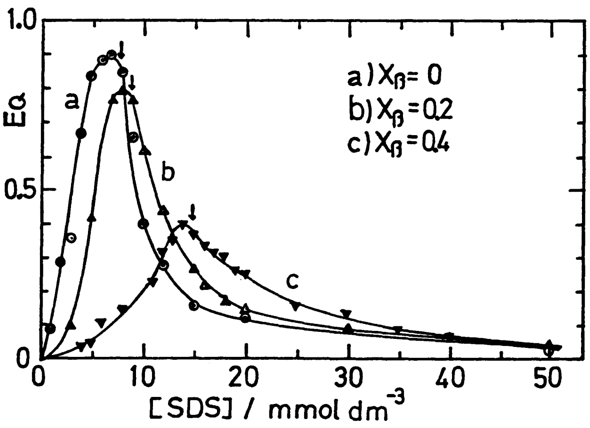

Fig. 1. Variation in the quenching efficiency (E_Q) vs. [SDS]. The respective values of CMC in the absence of pyrene and MV^{2+} are indicated by arrows.

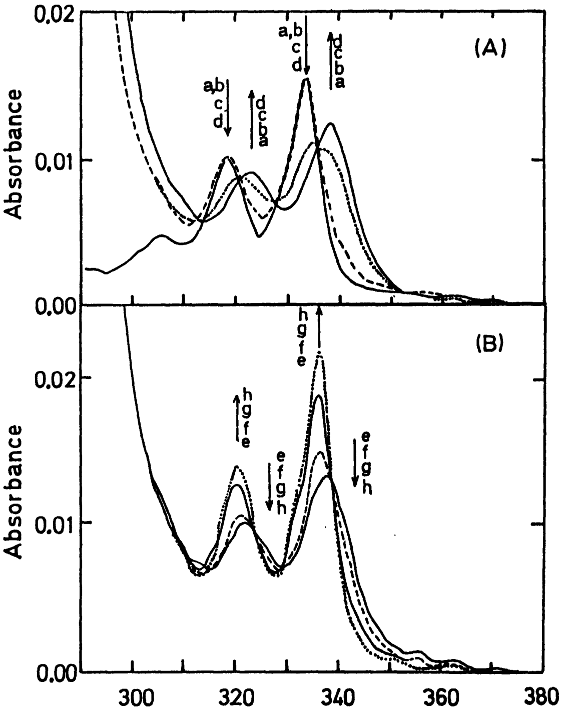

Fig. 2. Absorption spectra of pyrene-MV^{2+} system (x_β = 0). [SDS]: a) 0, b) 2, c) 4, d) 6, e) 7, f) 8, g) 10, h) 15 mmol dm^{-3}; path length: 1 cm. Curve a is the spectrum in the absence of MV^{2+}.

ties of pyrene in the absence and presence of MV^{2+} at a given x_β, respectively. The results are shown in Fig. 1 for the systems with x_β = 0, 0.2, and 0.4. Arrows indicate the CMC values reported previously.12) A remarkable feature of Fig. 1 is the appearance of the maxima in E_Q at [SDS]'s close to CMC. Note that efficient quenching is still observed even at [SDS]'s below CMC. Neither spectral evidence for complexation between pyrene and MV^{2+}, nor quenching was found both in pure water and in β-CDx solution (x_β = 1) under our experimental conditions. SDS is therefore an indispensable component in the present systems where the enhanced quenching takes place. Judged from these findings together with the fact that MV^{2+} is bound strongly to anionic SDS micelles,13) the enhanced quenching by SDS below CMC will reasonably be ascribed to the formation of the MV^{2+}-induced premicellar aggregates. This is consistent not only with the absorption and fluorescence spectral data (vide infra), but with previous suggestions1-3) for the presence of MV^{2+}-induced premicelles, though Atherton et al.5) reported that MV^{2+} is unable to form micelle-like clusters with SDS in the premicellar region.

Evidence for strong association between pyrene and such a premicelle is provided by the appearance of a longer-wavelength absorption of pyrene, as shown in Fig. 2 for the system with x_β = 0 in the presence of MV^{2+}. We can see in Fig. 2A that an increase in [SDS] below CMC (ca. 8.1 mmol dm^{-3}) leads to the new strongest band centered at 338 nm at the expense of the band at 334 nm, the typical strongest band in pure water. On the other hand, in the absence of MV^{2+}, any peak or shoulder was undetected around 338 nm. This fact indicates that the new band at 338 nm shown in Fig.2A is induced by the presence of MV^{2+}. This in turn suggests that MV^{2+} interacts strongly with SDS to give rise to the premicellar aggregates which solubilize or interact further with pyrene molecules. In other words, pyrene molecules are considered to locate in close neighborhood of MV^{2+}, because of a "solubilization" phenomenon of such premicellar aggregates. The enhanced quenching in the premicellar region can be thus explained. The 338-nm band disappears by the formation of micelles and a band centered at 336 nm appears at the expense of the former (Fig. 2B).

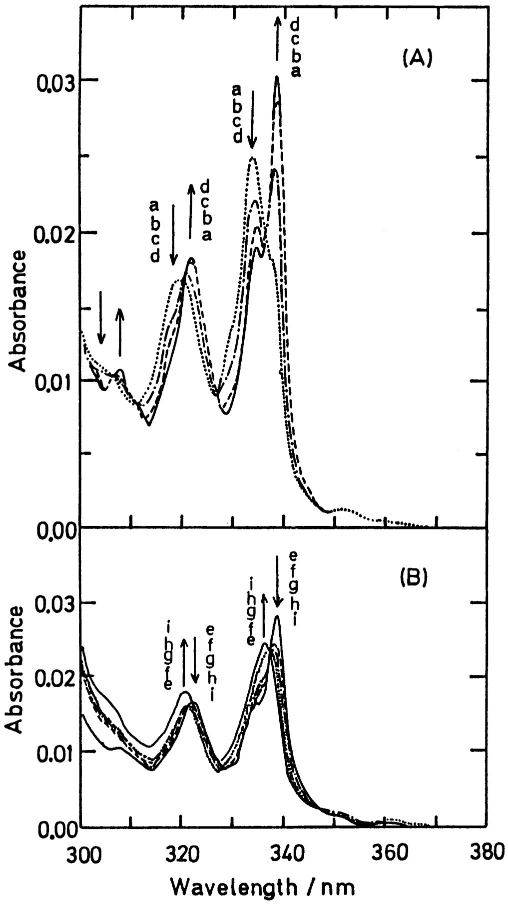

Fig. 3. Absorption spectra of pyrene-MV^{2+} system (x_{β} = 0.4). [SDS]([β-CDx]): a) 2(1.3), b) 4(2.7), c) 6(4.0), d) 8(5.3), e) 11(7.3), f) 17(11.3), g) 19 (12.7), h) 25(16.7), i) 50(33.3) in mmol $\mathrm{dm^{-3}}$; path length: 1 cm.

Similar behavior of absorption spectra was also observed in the presence of β-CDx, as illustrated in Fig. 3 for the system with x_{β} = 0.4. In the system with x_{β} = 1.0 (i.e., pyrene in aqueous β-CDx solution), in which a 1:1 pyrene-β-CDx inclusion compound is formed,[10-12,14] the absorption peak is located at 334 nm regardless of the presence of MV^{2+}. In addition, previous studies[10-12] have shown the presence of ternary inclusion complexes (with an absorption peak at 338 nm) composed of pyrene, β-CDx, and SDS below CMC in the absence of MV^{2+}; the amount of ternary complexes increases at the expense of that of the pyrene-β-CDx complex with an increase in x_{β}.[12] Therefore, the species giving rise to the 338-nm band in Fig. 3A is considered to consist probably of the MV^{2+}-induced premicelles and the ternary complexes described above. It has been shown that pyrene included in a ternary comlex undergoes less quenching, because of the geometric inhibitions resulting from the comlexation process.[11] It is also known that MV^{2+} forms no inclusion complex with β-CDx.[15] Therefore, if excited pyrene solubilized in a MV^{2+}-induced premicelle undergoes complete quenching, the maximum value of E_Q is expected to decrease considerably in the presence of β-CDx on account of the formation of ternary complexes. As is shown in Fig. 1, this is consistent with the finding that the maximum value of E_Q decreases with an increase in x_{β}.

We can see in Fig. 3B that a further increase in [SDS] through CMC (ca. 14.7 mmol $\mathrm{dm^{-3}}$) is accompanied by the regular decrease in the absorbance of 338-nm band and the appearance of a new peak at 336 nm. The 336-nm band is characteristic of the pyrene molecule solubilized into the mixed micelles containing β-CDx, as has been demonstrated in the systems without MV^{2+}.[12] The formation of such a mixed micelle has been suggested to be responsible for the increase in CMC upon the addition of α- and β-CDx.[12,16]

The fluorescence spectrum of pyrene in water exhibits five predominant peaks. It has been shown[17] that the ratio of intensity of the first (I at 373 nm) and third peaks (III at 384 nm) is a sensitive parameter characterizing the polarity of the pyrene environments, i.e., the I/III ratio increases drastically with an increase in medium polarity. The [SDS] dependences of I/III ratios in the absence and presence of MV^{2+} for the system with $x_\beta = 0$ revealed that in the premicellar region, the pyrene environment is more hydrophobic in the presence of MV^{2+} than in the absence of MV^{2+}. Similar differences in the pyrene environment with and without MV^{2+} were also found below CMC for the systems with $x_\beta = 0.2$ and 0.4. These findings give further indication that MV^{2+} induces the premicellar aggregates in the premicellar region. In addition, it is noteworthy that the pyrene environment has been found to be less hydrophobic in premicelles than in micelles above CMC.

Photoreduction of MV^{2+} has been shown to occur as a result of electron transfer from excited pyrene in homogeneous solution.18) No steady-state photochemical reaction, however, was observed upon photoirradiation in the absorption region of pyrene for all of the deaerated solutions studied. A dynamic study is now in progress.

We wish to thank Mr. S. Ihara for assistance with some of the experiments.

References

1) For a list of recent references, see: H. Sato, M. Kawasaki, M. Haga, K. Kasatani, T. Ban, H. Suenaga, and N. Kitamura, Nippon Kagaku Kaishi, 1984, 51.
2) H. Sato, M. Kawasaki, K. Kasatani, and T. Ban, Chem. Lett., 1982, 1139.
3) M. A. J. Rodgers and J. C. Becker, J. Phys. Chem., 84, 2762 (1980).
4) M. A. J. Rodgers, D. C. Foyt, and Z. A. Zimek, Radiat. Res., 75, 296 (1978).
5) S. J. Atherton, J. H. Baxendale, and B. M. Hoey, J. Chem. Soc., Faraday Trans. 1, 78, 2167 (1982).
6) J. Holzwarth, W. Knoche, and B. H. Robinson, Ber. Bunsenges. Phys. Chem., 82, 1001 (1978).
7) M. L. Bender and M. Komiyama, "Cyclodextrin Chemistry," Springer-Verlag, New York (1978).
8) I. Tabushi, Acc. Chem. Res., 15, 66 (1982).
9) See references cited in K. Kano, H. Matsumoto, S. Hashimoto, M. Sisido, and Y. Imanishi, J. Am. Chem. Soc., 107, 6117 (1985).
10) H. E. Edwards and J. K. Thomas, Carbohydr. Res., 65, 173 (1978).
11) S. Hashimoto and J. K. Thomas, J. Am. Chem. Soc., 107, 4655 (1985).
12) Y. Kusumoto, M. Shizuka, and I. Satake, Chem. Phys. Lett., in press.
13) J. K. Foreman, W. M. Sobol, and D. G. Whitten, J. Am. Chem. Soc., 103, 5333 (1981);T. Miyashita, T. Murakata, and M. Matsuda, J. Phys. Chem., 87, 4529 (1983).
14) A. Nakajima, Spectrochim. Acta, 39A, 913 (1983); A. Nakajima, Bull. Chem. Soc. Jpn., 57, 1143 (1984).
15) Y. Okuno, Y. Chiba, and O. Yonemitsu, J. Chem. Soc., Chem. Commun., 1984, 1638.
16) I. Satake, T. Ikenoue, T. Takenoshita, K. Hayakawa, and T. Maeda, Bull. Chem. Soc. Jpn., 58, 2746 (1985).
17) A. Nakajima, Bull. Chem. Soc. Jpn., 44, 3272 (1971); K. Kalyanasundaram and J. K. Thomas, J. Am. Chem. Soc., 99, 2039 (1977), and references cited therein.
18) R. S. Davidson, R. Bonneau, P. F. de Violet, and J. Toussot-dubien, Chem. Phys. Lett.,78, 475 (1981);P. K. Das, J. Chem. Soc.,Faraday Trans.1, 79, 1135 (1983).

(Received January 20, 1986)