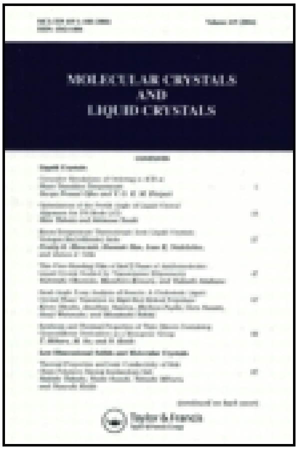

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# Intramolecular Excimer Formation Dynamics of 1,3-Bis(1-pyrenyl)propane Incorporated into the Surfactant Assembly Formed at the Silica-Water Interface

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Fluidity of nonionic surfactant assembly formed at the silica-water interface was investigated on the basis of intramolecular excimer formation dynamics of 1,3-bis(1-pyrenyl)propane. It was found that the rate constant of intramolecular excimer formation is almost independent of the adsorption density of surfactant molecules. These results imply that local structure of hydrocarbon region in surfactant assembly is almost unchanged in a wide range of adsorption density, although whole structure of the assembly varies with the adsorption density at the interface.

Keywords: nonionic surfactant; silica-water interface; 1,3-bis(1-pyrenyl)propane; intramolecular excimer ; molecular assembly; Triton X-100

## INTRODUCTION

Nonionic surfactants form micelle-like or bilayer-like molecular assemblies at a hydrophilic silica-water interface. Microscopic structures and static feature of these assemblies have been studied by a variety of experimental and theoretical techniques[1-5]. However, little is known about the dynamical behaviors of these assemblies. Excimer formation rate of pyrene derivatives reflects fluidity of the molecular assemblies. Especially, intramolecular excimer formation is favorable for probing the microscopic viscosity of various media including molecular assemblies, because it is a monomolecular process which is independent of the probe concentration. In the present study, we attempt to investigate the fluidity of the nonionic surfactant assemblies formed at the silica-water interface on the basis of intramolecular excimer formation dynamics of 1,3-bis(1-pyrenyl)propane ( Py(3)Py ) .

## EXPERIMENTAL

Polyoxyethylene(10) octylphenyl ether (Triton X-100) was used as a nonionic surfactant molecule. The silica used was macroporous silica gel (Silicagel 1000, Merck), with a mean pore diameter of 1000 Å, BET surface area of 30 $m^2 g^{-1}$, and a particle size between 5 and 40 μm. Intramolecular excimer forming probe Py(3)Py (Dojindo Lab., Co.) was dissolved in aqueous Triton X-100 solution containing 0.1 mol $dm^{-3}$ sodium perchlorate and 2%(v/v) methanol. The solution was shaken with silica for 6 h at 25 °C, and the silica/water suspensions were placed in quartz cell, then degassed by repeating freeze-pump-thaw cycles.

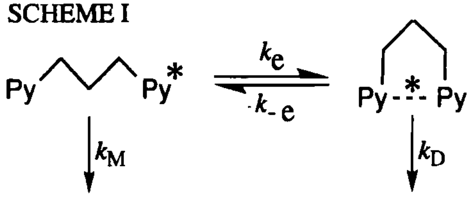
Steady state fluorescence spectra were measured by a JASCO FP-550 spectrofluorometer. The excitation wavelength was 333 nm. Time-resolved fluorescence were examined using a third harmonic (wavelength 257 nm, pulse width ~200 fs) of a mode-locked Ti:sapphire laser (Spectra-Physics, Tsunami 3960) as an excitation source, and the fluorescence was detected by a synchroscan streak scope system (Hamamatsu C4334) equipped with a polychromator. Decay profiles of monomeric and excimer-like fluorescence were obtained by accumulating the fluorescence in the wavelength range from 370 to 420 nm, and 470 to 570 nm, respectively.

## RESULTS AND DISCUSSION

The fluorescence spectra of Py(3)Py incorporated into the Triton X-100 assemblies show structured band at ca. 380 nm and broad structureless band at ca. 480 nm. The former fluorescence is ascribed to the monomeric pyrenyl units, and the latter is ascribed to intramolecular excimer between two pyrenyl units or pre-association of pyrenyl units at ground state[8, 10].

When aggregation of pyrenyl units at ground state is absent, intramolecular excimer formation is expressed as SCHEME I in the simplest model[6-8]. In the scheme, $k_e$ and $k_{-e}$ are excimer formation and dissociation rate constants, respectively. $k_M$ and $k_D$ are reciprocal lifetime of locally excited pyrenyl units and that of intramolecular excimers, respectively. At high viscous environment, dissociation of excimer can be neglected[1, 6], and the time profiles of monomer fluorescence and excimer fluorescence are given by equation(1) and equation(2).

SCHEME I



$$I_M(t) \sim \exp(-\lambda_1 t) \tag{1}$$

$$I_D(t) \sim \exp(-\lambda_1 t) - \exp(-k_D t) \tag{2}$$

$$\lambda_1 = k_M + k_e \tag{3}$$

The value of $k_M$ can be approximated by reciprocal lifetime of 1-alkylpyrene[7], and the reciprocal lifetime of 1-methylpyrene was experimentally determined in the present study. Excimer formation rate constant $k_e$, which reflects the fluidity of assembly phase, is the most important parameter for the present investigation. This value can be determined by a difference between $\lambda_1$ and $k_M$. Although more complex models have been proposed for intramolecular excimer formation of Py(3)Py in homogeneous organic solvents[7, 9], the above simplified model may be effective as a first approximation for discussion on intramolecular excimer formation dynamics in the present system.

FIGURE 1 shows fluorescence decay profiles measured at the maximum adsorption density ( $2.5\times10^{-6}$ mol $m^{-2}$ ) of Triton X-100. The short lifetime component ( $\tau \sim 10$ ns ) detected just after pulsed excitation is blank fluorescence originating from silica or Triton X-100 judging from the fact that it is observed also in the absence of Py(3)Py. Thus analysis of the decay profile was performed excluding the above time region. For excimer-like fluorescence, characteristic rise and decay profile was obtained except for the existence of the above short-

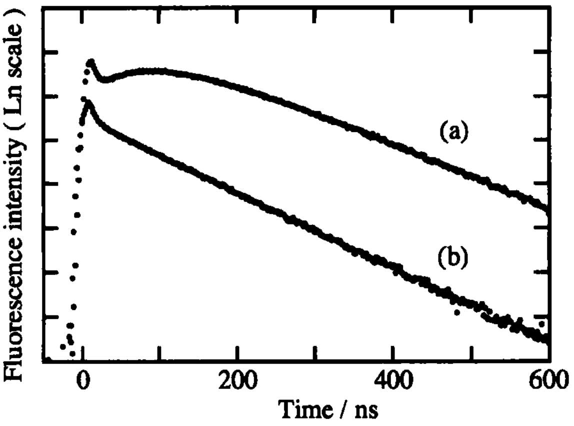


FIGURE 1 Fluorescence decay profiles of Py(3)Py observed at adsorption density of $2.5\times10^{-6}$ mol $m^{-2}$
(a) excimer-like fluorescence ( 470 - 570 nm )
(b) monomer fluorescence ( 370 - 420 nm )

lived component. This profile is fitted well by equation(2). Furthermore as shown in FIGURE 1(b), monomeric fluorescence decayed according to a single-exponential function. These results indicate that the above model is valid for this condition. Decay parameters obtained were summarized in TABLE I. The $k_e$ value of $2.7\times10^6$ $s^{-1}$ is much lower than the value of $1.5\times10^8$ $s^{-1}$ reported for a methylcyclohexane solution[6]. Restriction in mobility is a common characteristic of the molecules existing in variety of molecular assemblies[8].

At a low adsorption density, fluorescence decay profile is quite different from that observed at the maximum adsorption density. FIGURE 2 shows the

TABLE I Flourescence decay parameters of Py(3)Py

| $\Gamma$/ $10^{-6}$ mol $m^{-2}$ | $\lambda_1{}^a$ / $10^6$ $s^{-1}$ | $k_M{}^b$ / $10^6$ $s^{-1}$ | $k_e$ / $10^6$ $s^{-1}$ |
|---|---|---|---|
| 2.5 | 8.6 | 5.9 | 2.7 |
| 0.1 | 8.7 | 6.2 | 2.5 |

a ; determined from decay profile of monomer fluorescence of Py(3)Py
b ; determined from fluorescence decay profile of 1-methylpyrene

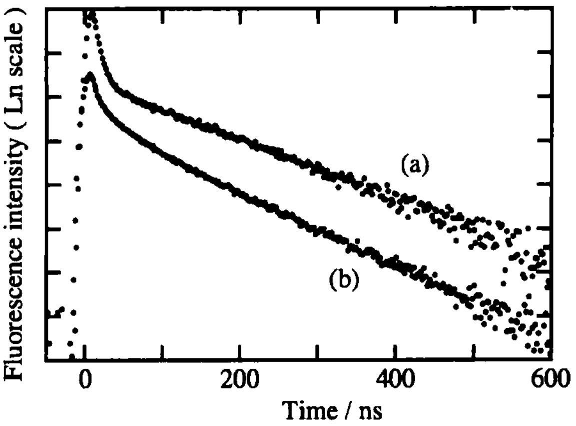


FIGURE 2 Fluorescence decay profiles of Py(3)Py observed at adsorption density of $1\times10^{-7}$ mol $m^{-2}$
(a) excimer-like fluorescence ( 470 - 570 nm )
(b) monomer fluorescence ( 370 - 420 nm )

decay profiles observed at $\Gamma = 1\times10^{-7}$ mol $m^{-2}$. The short lifetime component just after pulsed excitation also is a blank fluorescence. In the profile of excimer-like fluorescence, characteristic rising part observed in FIGURE 1(a) is almost absent, and such a decay profile corresponds to the existence of ground state aggregation of pyrenyl units[8, 10]. When aggregation at ground state cannot be neglected, excimer-like fluorescence shows multiexponential decay[8]. On the other hand, a decay of monomer fluorescence shown in FIGURE 2(b) was found to be approximated by a single-exponential function, and the lifetime was smaller than that of 1-methylpyrene. The difference between the fluorescence lifetime of Py(3)Py and that of 1-methylpyrene can be ascribed to the intramolecular excimer formation. Consequently, excimer-like fluorescence observed in this condition can be interpreted as a mixture of two kinds of fluorescence originating from ground state aggregation and dynamical excimer formation. Assuming that dissociation of aggregated species at excited state can be neglected, rate parameters were determined from a decay profile of monomer fluorescence and that of 1-methylpyrene. (TABLE I) The $k_e$ value of $2.5\times10^{6}$ $s^{-1}$ is close to the value determined at the maximum adsorption density.

Aggregation number of Triton X-100 assemblies formed at the silica-water interface drastically varies with $\Gamma$[1, 11], and has been determined to be about 50 at $1\times10^{-7}$ mol m$^{-2}$ and more than 200 at $2.5\times10^{-6}$ mol m$^{-2}$ [11]. Furthermore a lot of experimental parameters, such as contact angle[2], differential enthalpy of adsorption[3], and partition coefficient of probe molecules into assembly phase[11] are clearly dependent on adsorption density. Based on these investigations, it has been recognized that whole structure of the surfactant assembly is varied with the adsorption density. This characteristic is in contrast with the fact that intramolecular excimer formation rate constants are almost same regardless of the adsorption density. The $k_e$ value reflects the mobility of pyrenyl units in the assembly phase, and may be closely related to the local structure of hydrophobic region which consists of hydrocarbon parts in surfactant molecules where Py(3)Py molecules exist. Therefore, the results described above indicate that microscopic structure and local properties of hydrocarbon region are almost unchanged although whole structure of the assembly phase is varied with the adsorption density.

In conclusion, the present study clarified different aspects of nonionic surfactant assemblies formed at the silica-water interface, namely they are whole structure of the assembly dependent on adsorption density and local structure of hydrocarbon region independent of adsorption density.

## References

[1.] P. Levitz, H. V. Damme, D. Keravis, *J. Phys. Chem.*, **88**, 2228 (1984)

[2.] G. Gonzalez, A. M. Travalloni-Louvisse, *Langmuir*, **5**, 26 (1989)

[3.] S. Partyka, M. Lindheimer, B. Faucompre, *Colloid Surf. A*, **76**, 267 (1993)

[4.] D. C. McDermott, J. R. Lu, R. K. Thomas, A. R. Rennie, *Langmuir*, **8**, 1204 (1992).

[5.] C. M. Wijmans, P. Linse, *J. Phys. Chem.*, **100**, 12583 (1996).

[6.] K. A. Zachariasse, W. Kühnle, A. Weller, *Chem. Phys. Lett.*, **59**, 375 (1978).

[7.] M. J. Snare, P. J. Thistlethwaite, K. P. Ghiggino, *J. Am. Chem. Soc.*, **105**, 3328 (1983).

[8.] K. Kano, T. Ishibashi, T. Ogawa, *J. Phys. Chem.*, **87**, 3010 (1983).

[9.] K.A. Zachariasse, G. Duveneck, R. Busse, *J. Am. Chem. Soc.*, **106**, 1045 (1984).

[10.] J. K. Rice, J. Christopher, U. Narang, W. R. Peifer, F. V. Bright, *Analyst*, **119**, 505 (1994).

[11.] K. Bessho, Y. Kanda, Y. Harada, T. Uchida, N. Teramae, in preparation