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Emission and Quenching of the Pyrenesulfonate Excimer on a Dodecyltrimethylammonium Micellar Surface

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The excimer formation and decay dynamics of pyrenesulfonate on a cationic micellar surface have been studied by measuring the decay of monomer fluorescence as well as the rise and decay of the excimer emission. The excimer formation rate constant, lifetime, and quenching rate constant by the monomer were found to be $2.1 \times 10^7\,\mathrm{s}^{-1}$, 46.2 ns, and $2.6 \times 10^6\,\mathrm{s}^{-1}$, respectively.

Photoinduced reactions such as fluorescence quenching reactions in micro-heterogeneous systems are of interest not only in fundamental aspects but also in applied aspects such as solar energy conversion.[1] Pyrene (Py)[2–9] and its derivatives[10–23] have been widely used as fluorescence probes in micelles and vesicles to study microenvironments. The Py excimer formation reactions in micelles are applied to the determinations of the aggregation numbers of micelles.[4–9] Pyrenesulfonate ($\mathrm{PyS^-}$) has been used as an aqueous fluorescence probe in bulk heterogeneous systems such as liquid–liquid[10] and liquid–air interfaces[11,12] as well as in micro-heterogeneous solutions containing polymers,[13–15] micelles,[16] inverse micelles,[17,18] and bilayers.[19] Some of them[11,13,17,20] use $\mathrm{PyS^-}$ excimers as probes, but no kinetics have been studied. Reaction kinetics have been studied for the $\mathrm{PyS^-}$ monomer in micelles[16,21] and inverse micelles[22,23] but not for the $\mathrm{PyS^-}$ excimer. The kinetics of the $\mathrm{PyS^-}$ excimer has been studied only in a inverse micelle system.[17] As far as we know, there is no report on kinetics of the $\mathrm{PyS^-}$ excimer in aqueous micellar solutions. We would like to report here the formation and decay kinetics of the $\mathrm{PyS^-}$ excimer on the aqueous micellar surfaces.

Pyrenesulfonic acid sodium salt (NaPyS, Molecular Probes) was used without further purification. Dodecyltrimethylammonium chloride (DTACl, Tokyo Kasei, analytical reagent) was recrystallized four times by dissolving in hot methanol, adding acetone, and cooling the solution. Water used in this study was obtained by distilling deionized water twice.

Emission spectra for $\mathrm{PyS^-}$ excited at 346 nm were measured by a fluorescence spectrophotometer (Hitachi, F-7000). Fluorescence decay curves were measured by a nanosecond time-correlated single-photon counting apparatus (Horiba, NAES-550). The $\mathrm{PyS^-}$ ions were excited by UV light of a $\mathrm{H_2}$ arc lamp using a UV pass filter (Hoya, U-340). The monomer fluorescence and excimer emission were isolated from the excitation light using a UV cut filter (Hoya, L-37). The monomer fluorescence was detected at 378 nm. The excimer emission was detected at 520 nm to separate from the strong monomer fluorescence. The $\mathrm{PyS^-}$ concentration was 50 μM ($1\,\mathrm{M} = 1\,\mathrm{mol\,dm^{-3}}$). The DTACl concentrations were varied from 23 to 100 mM (23, 24, 25, 27, 29, 30, 40, 50, 60, 80, and 100 mM). The sample solutions were degassed via four freeze–pump–thaw cycles. The all measurements were performed at 25 °C.

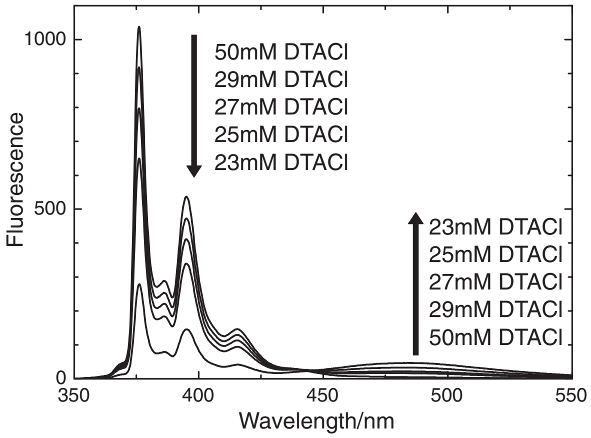

Figure 1. $\mathrm{PyS^-}$ monomer fluorescence and excimer emission spectra for 23, 25, 27, 29, and 50 mM DTACl systems.

The emission spectra for $\mathrm{PyS^-}$ in DTACl micellar solutions are shown in Figure 1. With decreasing DTACl concentration, the emission intensities at the wavelength from 370 to 430 nm decrease and, in contrast, the intensities at the wavelength from 450 to 550 nm increase. The 50 mM DTACl system shows only the emissions at the wavelength from 370 to 430 nm that are due to the $\mathrm{PyS^-}$ monomer fluorescence. The 23 mM DTACl system shows the monomer fluorescence and the other peak at 485 nm, which is due to the $\mathrm{PyS^-}$ excimer emission.[11,13,17,20] With decreasing DTACl concentration, the monomer fluorescence intensities decrease and the excimer emission intensities increase. This is due to the fluorescence quenching reaction by the $\mathrm{PyS^-}$ monomer (the excimer formation reaction) on the micellar surfaces because the number of $\mathrm{PyS^-}$ per micelle increases with decreasing DTACl concentration.

The monomer fluorescence decay curves for $\mathrm{PyS^-}$ adsorbed on the DTACl micellar surfaces are shown in Figure 2. The decay curve for the 100 mM DTACl system can be represented by a single exponential decay function,

$$I(t) = I_0 \exp(-t/\tau_0) \qquad (1)$$

where τ_0 is the monomer fluorescence time constant. The τ_0 value is 121 ns, which is close to the reported value, 126.4 ns on the surfaces of the hexadecyltrimethylammonium chloride micelles.[15] For the 80, 60, and 50 mM DTACl systems, the decay curves can be also represented using eq 1 and the τ_0 values are 122, 120, and 119 ns, respectively, which are in good agreement within experimental uncertainly. For the DTACl systems below 50 mM, the fluorescence intensities decay more rapidly with decreasing DTACl concentration. These decays cannot be fitted to eq 1 but are represented by the Tachiya–Infelta equation,[24,25]

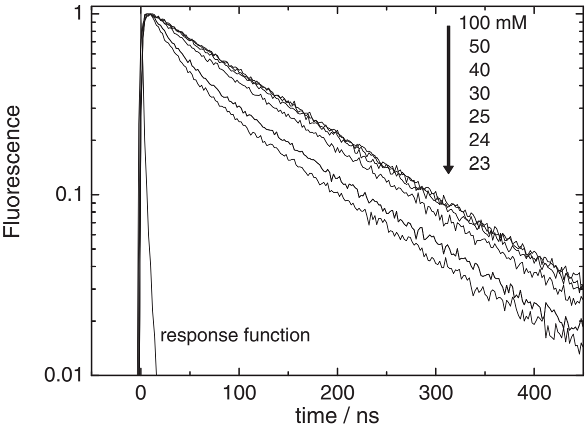

Figure 2. PyS^- monomer fluorescence decay curves detected at 378 nm for 23, 24, 25, 30, 40, 50, 60, 80, and 100 mM DTACl systems and response function.

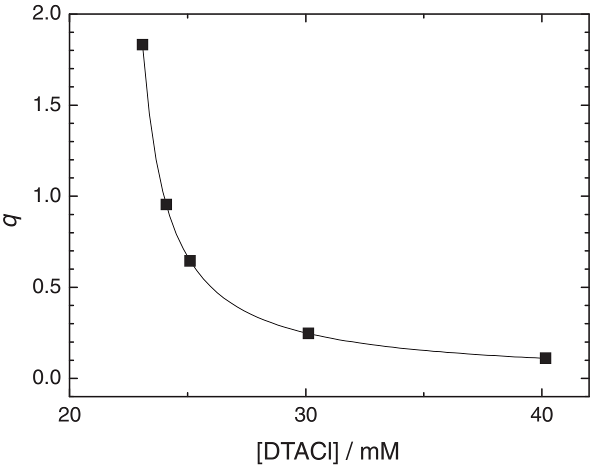

Figure 3. DTACl concentration dependence of q values. The solid line is a fitted curve using eq 5.

$$I(t) = I_0 \exp[q\{\exp(-kt) - 1\} - t/\tau_0] \tag{2}$$

$$q = [PyS^-]/[\text{micelle}] \tag{3}$$

$$[\text{micelle}] = ([\text{DTACl}] - \text{cmc})/N \tag{4}$$

where q is the average number of PyS^- molecules per micelle, k is the micellar fluorescence quenching rate constant (corresponding to the micellar excimer formation rate constant), cmc is the critical micelle concentration, and N is the aggregation number of a micelle. The decays were simultaneously fitted to eq 2 in the condition of k and τ_0 as linked (global) parameters and q as a nonlinked (local) parameter using the global analysis method. The obtained values of linked parameters, k and τ_0, are $0.021 \pm 0.001\,\text{ns}^{-1}$ and $120 \pm 2\,\text{ns}$, respectively. The q values are shown in Figure 3. The cmc and N values are 22 ± 1 mM and 40 ± 1, respectively, which were obtained by nonlinear least-squares fitting of eq 5 to the q values (Figure 3).

$$q = [PyS^-]N/([\text{DTACl}] - \text{cmc}) \tag{5}$$

These values are in good agreement with the reported cmc and N values which are 22 mM[8] and 43.6,[26] respectively. This suggests that the adsorbed reactants do not affect the values of cmc and N. Our obtained k value ($21 \times 10^{-3}\,\text{ns}^{-1}$) is as large as the excimer formation rate constant ($23.9 \times 10^{-3}\,\text{ns}^{-1}$)[4] for Py, which can freely diffuse within micelles, and larger than the diffusion-controlled reaction rate constants on the micellar surfaces (0.31–$5.7 \times 10^{-3}\,\text{ns}^{-1}$).[16,27,28] The large k value may suggest that the PyS^- ion is diffusing not only on the micellar surfaces but also partially in the bulk water because, generally, the diffusion on the micellar surfaces is slower than in the bulk liquid.[16,27,28]

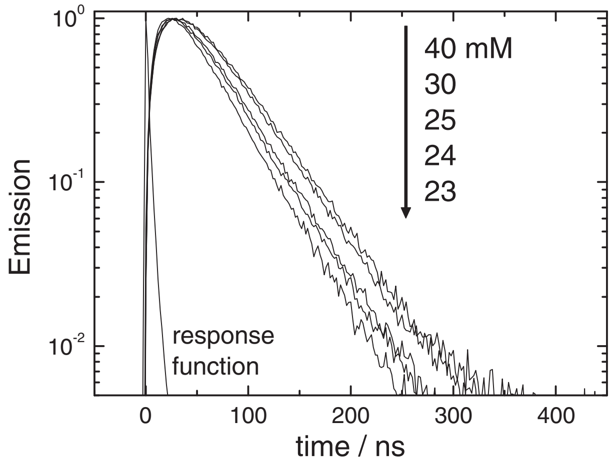

Figure 4. Emission decay curves for PyS^- excimer detected at 520 nm for 23, 24, 25, 30, and 40 mM DTACl systems and response function.

The emission rise and decay curves for the PyS^- excimers adsorbed on the DATCl micellar surfaces are shown in Figure 4. The emission intensities also rise and decay more rapidly with decreasing DTACl concentration. The rapid rises for the excimer emissions correspond to the rapid decays of the monomer fluorescence with decreasing DTACl concentration. These curves can be fitted to a double exponential function,

$$I(t) = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2) \tag{6}$$

where τ_1 and τ_2 are the excimer emission rise and decay time constants, and I_1 (<0) and I_2 (>0) are the preexponential factors for the rise and decay components, respectively. Figure 5 shows the dependence of the reciprocals of the time constants, ${\tau_i}^{-1}$, on the number of PyS^- per micelle, $[PyS^-]/[\text{micelle}]$. The reciprocals of the rise time constants, ${\tau_1}^{-1}$, increase with increasing number of PyS^- per micelle and shows a fairly good linear relationship to the number of PyS^- per micelle. The slope of the ${\tau_1}^{-1}$ values is $0.019\,\text{ns}^{-1}$. This value is thought to correspond to the PyS^- excimer formation rate constant and really is close to the PyS^- monomer fluorescence quenching rate constant, k ($0.021\,\text{ns}^{-1}$).

For the 50 mM DTACl system, the excimer emission was not observed (Figures 1 and 2). In the 40 mM system, the PyS^- excimers formed (Figures 1 and 2). Thus, the decay time constant (τ_2) for the 40 mM DTACl system, 46.2 ns can be taken as the lifetime of the PyS^- excimers. The reciprocals of the decay time constants, ${\tau_2}^{-1}$, also increase with increasing number of PyS^- per micelle (Figure 5). This increase in the ${\tau_2}^{-1}$ values is due to the quenching of the PyS^- excimer emission by PyS^- monomer. Because the plot of ${\tau_2}^{-1}$ values shows also a fairly

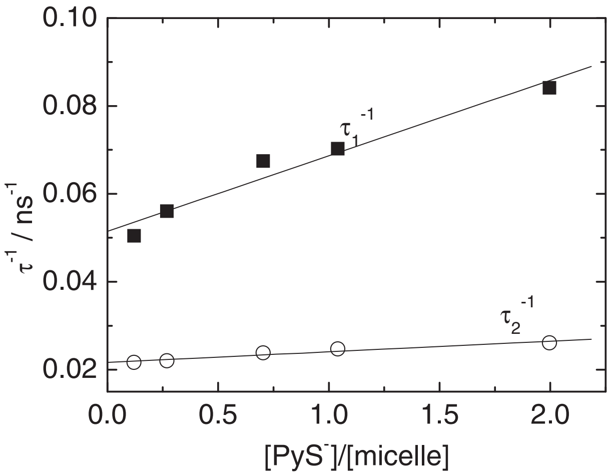

Figure 5. Dependence of τ_i^{-1} on PyS$^-$ numbers per micelle.

good linear relationship to the number of PyS$^-$ per micelle, the quenching rate constant for the PyS$^-$ excimer by the monomer is estimated to be 0.0026 ns^{-1} from the slope of the τ_2^{-1} values.

In summary, we have determined the PyS$^-$ excimer formation and decay rate constants on the DTACl micellar surfaces at very low PyS$^-$ concentration, 50 µM. The PyS$^-$ excimer formation reaction on the DTACl micellar surface is faster by a factor of more than 5 compared with other reactions on the micellar surfaces and as fast as the Py excimer formation in micelles. Furthermore, the PyS$^-$ excimers were found to be quenched by the PyS$^-$ monomers on the micellar surfaces.

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