Fluorescence and Laser Photolysis Studies on the Intramolecular Exciplex Systems in Micellar Solutions

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The behavior of intramolecular exciplex systems consisting of pyrene and *N*,*N*-dimethylaniline was studied in cationic, anionic and neutral micellar solutions. These systems are favorable for the study of photoinduced CT interaction in micellar systems, since (i) a pair of donor-acceptor is always solubilized in the micelle and (ii) the complicated effect of the intermolecular interaction can be prevented. No exciplex emission was detected and relative quantum yields as well as lifetimes were measured on the monomer fluorescence. The results are interpreted by assuming two solubilized forms in the micelle-water interface. Efficient quenching occurs in the dodecyltrimethylammonium chloride solution irrespective of the length of the methylene chain, suggesting a different solubilization from the cases of other detergents. The efficient quenching is ascribed to the rapid ion-pair formation in the micelle-water interface, which was directly demonstrated by the ns laser photolysis method.

Studies on the photoprimary processes of the excited electron donor-acceptor (EDA) systems are indispensable for the interpretation of photooxidation-reduction reactions. They are closely related to mechanistic organic photochemistry.[1-4] We have investigated the electronic structure and dynamic behavior of these systems, and shown that the dependence upon the molecular interaction between donor-acceptor pairs and upon the environment is essential.[1-3] Studies on the excited EDA systems in micellar solution are of interest from the view that (i) basic aspects of the EDA interaction in inhomogeneous systems of biological importance will be clarified, and (ii) new information might be obtained on the structure and function of the micelle, not obtained by means of fluorescence polarization and photoionization (electron ejection). So far the following two exciplex-micelle systems have been reported. The quaternary ammonium groups of the *N*-dodecyl-*N*,*N*-dimethylbetaine quenches the excited pyrene and forms an exciplex showing a fluorescence band with maximum at 480 nm and the lifetime of 70 ns.[5] A similar exciplex emission was also obtained in the case of pyrene solubilized in the mixed micelle of sodium dodecyl sulphate and dodecylamine.[6] However, since the distance and relative orientation between pyrene and the amines, and the environmental conditions of the solubilized probe molecule were not made clear, the quenching mechanism including an exciplex formation is unknown. Thus we have studied the typical intramolecular exciplex compounds (pyrene)–$(CH_2)_n$–(*N*,*N*-dimethylaniline) (abbreviated as P_n).

Experimental

Sodium dodecyl sulphate (SDS) and α-dodecyl-ω-hydroxypoly(oxyethylene) (Brij) (special grade, Nakarai), and dodecyltrimethylammonium chloride (DTAC), (pure grade, Tokyo Kasei), were used. Brij and SDS were recrystallized twice from ethanol; DTAC was recrystallized from benzene. They were dried under reduced pressure for a few days. The concentration of Brij was adjusted to 0.065 M, while, 0.1 M solutions were prepared in the case of ionic surfactants. The concentrations lead to $\approx 1.6 \times 10^{-3}$ M micelle concentration.[7] Deionized water was distilled, refluxed over potassium permanganate and redistilled. A 50 μl acetone solution of 10^{-3} M P_n was poured into a 5 ml measuring flask and dried. The prepared micellar solution was then added and treated with the ultrasonic cleaner for ten minutes. This gave the same solution as that prepared by stirring the solution for 3 h at 50 °C. The concentration of 10^{-5} M solubilizate was checked by optical density measurements. These solutions were flushed with nitrogen gas for 25 min.

Absorption spectra were measured with a Shimadzu MPS-50 L UV spectrophotometer. The fluorescence and excitation spectra were obtained with an Aminco-Bowman spectrophotofluorometer. The fluorescence rise and decay curves were observed with a pulsed nitrogen laser and Tektronix 585A oscilloscope.[8] Transient absorption spectra were obtained by the usual nanosecond laser photolysis method.[3]

Results and Discussion

1. Fluorescence Studies and the Solubilized Site of the P_n *Compounds in Micellar Solutions.* The effects of surrounding environments upon the exciplex have been revealed by the analysis of spectra, quantum yields and lifetimes of monomer as well as exciplex fluorescence. In the case of organic solvents,[1,2] the red shift of the fluorescence maxima and the decrease in the yield as well as lifetime is observed with the increase of solvent polarity. Exciplex emission is no longer detected, ionic dissociation being observed in polar solvents such as acetonitrile. On the other hand, exciplex formation is retarded with increase in the viscosity of the solvent. In the rigid solvents the molecular motion is completely suppressed and only the monomer fluorescence can be measured. The present P_n compounds in micellar solution have been investigated in view of the above tendencies.

The experimental conditions of the present probe molecules are suitable for studying the interaction between the donor-acceptor groups in micellar solutions for the following reasons. (i) A donor-acceptor pair is always solubilized in the micelle; (ii) the appropriate concentration of P_n for the laser photolysis, given that the absorbance at 337 and 347 nm is larger than 0.3, is *ca.* 10^{-5} M, one-hundredth of the micelle concentration, which indicates that the intermolecular interaction between the P_n molecules in the same micelle is completely neglected; (iii) without detergents the concentration of the aromatics in question is so low that the contribution of the molecules dissolved in water phase is neglected. The problem is to find a standard compound which is not quenched by the *N,N*-dimethylaniline moiety. Ethylpyrene (EP) is appropriate since (i) the absorption bands in the 300—360 nm region are almost identical with those of P_n compounds within 2 nm, although detailed information on the 380 nm band could not be obtained because of low concentration, and (ii) the absolute fluorescence yield of EP in cyclohexane (0.5) is almost equal to the value of P_1 in hexane (0.6), where no exciplex emission is observed.[9]

Table 1. Relative quantum yields of pyrene monomer fluorescence of P_n compounds in N_2-bubbled micellar solutions

	EP	P_1	P_2	P_3
Brij	1.0[a]	0.5_0	0.4_7	0.4_2
SDS	1.0[a]	0.4_8	0.3_0	0.2_0
DTAC	1.0[a]	0.0_1	0.0_3	0.0_3

a) Normalized to unity.

Table 2. Lifetimes of pyrene monomer fluorescence of P_n compounds in N_2-bubbled micellar solutions (nanoseconds)[a]

	EP	P_1	P_2	P_3
Brij	150	150	140	110
SDS	225	270	260	240
DTAC	170	short,[b] 130[c]	short,[b] 130[c]	short,[b] 180[c]

a) All values averaged, fluctuations being within 10 ns. b) Rise and decay curves determined with our time constant, *ca.* 5 ns with a Tektronix 475 oscilloscope. c) Errors large due to low intensity.

As regards the experimental results in micellar solutions, relative quantum yields and lifetimes of pyrene monomer fluorescence of EP and P_n are given in Tables 1 and 2, respectively. Although fluorescence quenching occurs in the case of P_n as compared to the results of EP, no new exciplex emission was detected. The monomer fluorescence intensity decreases with increase in the number of methylene (abbreviated as *n*) observed in the Brij and SDS solutions. The lifetime of P_1 is larger than that of EP in SDS solution, which may be due to the different solubilized sites of their molecules. Efficient quenching was observed independent upon *n* in the case of DTAC surfactant. As shown in Fig. 1, the decay in DTAC solution shows rapid and slow components. The latter seems to be single exponential, while the former is too short to be analysed. In the cases of Brij and SDS, no rapid component was observed, the values of the slow component decreasing with the increase of *n*. This might suggest dynamic quenching by the DMA group. In the case of DTAC solution the experimental error of the lifetimes is rather large because of their low intensity. No detailed discussion on the slow component can be given.

The micellar effect on the exciplex systems will be discussed on the basis of the present results. One problem of the micellar systems is the location of the probe molecule. Large aromatic molecules such as pyrene are often considered to be in the interior of the micelle. In fact a recent NMR study of pyrene in hexadecyltrimethylammonium bromide supports this view.[10] If the present P_n compound is also dissolved in the interior of the micelle, an exciplex emission can be expected because of the analogy between the aliphatic part of micelle and the viscous aliphatic solvents. We have observed no exciplex emission in the present system, although it is observed in viscous decaline.[9] If the large viscosity of the interior prohibits a molecular motion for exciplex formation, the fluorescence yield and lifetimes should remain unchanged when *n* is changed. Thus, the simple solubilization model is inconsistent with the present results.

We see from Tables 1 and 2, that yield and lifetime show different dependence upon *n*. The yield decreases with *n*, while the change of lifetime with *n* is rather small. This can be interpreted by assuming two solubilized forms of P_n in micellar systems. In one form the fluorescence quenching occurs quite rapidly, while in the other the molecular motion for the interaction between the two moieties is prohibited. The probability of taking the latter form decreases with the increase of *n*. The interpretation is also in line with the two-component decay of pyrene monomer fluorescence in DTAC solution. The solubilized forms are considered

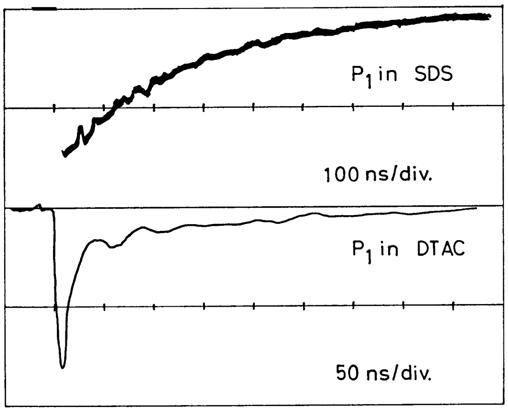

Fig. 1. Oscillograms observed at 400 nm, showing the pyrene monomer fluorescence decay of P_1 in SDS and DTAC solutions.

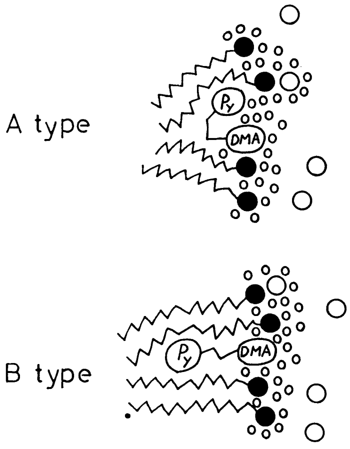

Fig. 2. Schematic representation of the solubilized form of intramolecular exciplex systems in micellar solution. ●: Head groups; ○: counter ion; o: H_2O molecule.

to be as follows. (i) Pyrene seems to be dissolved in the interior of the micelle, while DMA in hexadecyltrimethylammonium bromide indicates the predominating solubilization mechanism to be absorption close to the α-CH_2 groups.[11] The other data show the existence of DMA in the water-micelle interface.[6] The results suggest that both the solubilized sites are in the vicinity of the water phase. (ii) The fluorescence quantum yields of EP and P_1 in hexane are almost equal to each other, no exciplex emission of the latter being observed. This implies that the quenching by the DMA group of the P_1 system is impossible in nonpolar aliphatic environments such as the interior of the micelle. The yield of P_1 is about a half of that of EP even in Brij and SDS solutions, while no exciplex emission was observed. This is also ascribed to the more polar character of environments, in which the probe molecule is dissolved.

The above considerations are schematically given in Fig. 2. In the solubilization form of A, pyrene and DMA groups are in contact with water molecules and the excited states are easily quenched immediately after excitation. On the other hand, in the case of B the interaction between the pyrene and DMA groups hardly arises during the lifetime of the excited pyrene. The P_n compound may thrust the DMA moiety into the head groups of the surfactant, leaving the pyrene moiety in the interior. This form might be too rigid to undergo quenching interaction. The probability of form A being taken may increase from P_1 to P_3 as the freedom of the molecular motion increases. In the DTAC solution particularly, almost all the probe molecules take the A configuration, which might be ascribed to a different solubilization mechanism of DTAC from that of anionic and neutral detergents.

2. *Quenching Mechanism of P_n in the DTAC Solution.* Quenching is very efficient in the DTAC solution, irrespective of n. An oscillogram showing the short-lived transient is given in Fig. 3. The transient absorption spectra of P_1 obtained immediately after the excitation is shown in Fig. 4(a). These spectra are reproduced by a superposition of the bands of the pyrene anion and the DMA cation and easily assigned to the ion-pair of the acceptor anion and the donor cation. This is supported by the fact that the present spectra are similar to those of P_3 in acetonitrile,[12] shown in Fig. 4(b). Similar spectra were observed also in the cases of P_2 and P_3, while no such ionic species with short lifetime was detected in the Brij solution of P_2. Thus it is concluded that the rapid ion-pair formation leading to the quenching occurs easily in the DTAC solution. In general the formation of ionic species is possible when the molecular pair are set in the polar environment, as confirmed by the systems in organic solvents. The P_n compounds in the DTAC systems seem to be dissolved near the water-micelle interface and influenced by the polar water molecules, which is consistent with the result of the fluorescence studies. The ionic species of the exciplex systems are also formed in the micellar solution, as in the polar organic solvents. Confirmation by nanosecond photolysis indicates that the ionic dissociation processes play an important role in the photoprimary processes of aromatic molecules in water and micellar solutions.

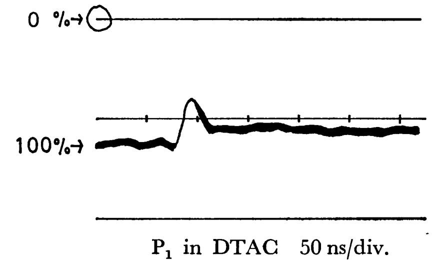

Fig. 3. Oscillogram observed at 500 nm, showing the transient absorption of P_1 in DTAC solution.

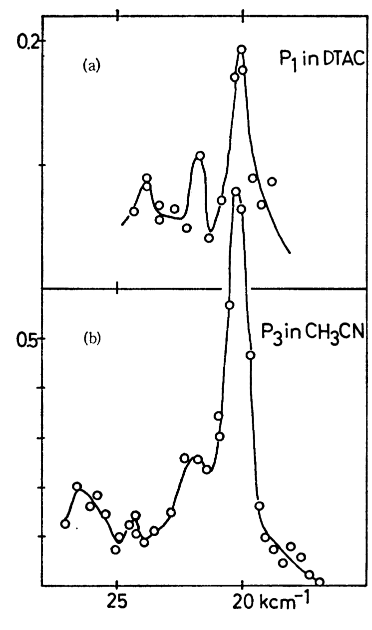

Fig. 4. (a) Transient absorption spectra of P_1 in DTAC solution obtained immediately after laser excitation. (b) Reference spectra of P_3 in acetonitrile.[12]

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