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EMISSION OF LOW-ENERGY LUMINESCENCE FROM SURFACTANT MICELLES WITH AN AROMATIC CHROMOPHORE[1)]

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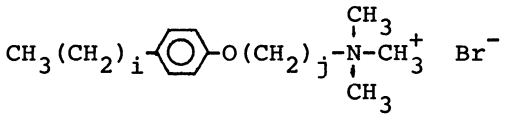
Fluorescence spectra of cationic surfactants, with a phenoxy group as a part of the molecular structure, were studied. On the formation of the micelles, luminescences with energy lower than that of the monomer were observed, and it was taken to indicate the presence of interactions involving photoexcited phenoxy group aligned in the micellar interior.

In relation to the study of light-harvesting pigments in chloroplast, it would be important to understand the mode of interactions between a photoexcited chromophore and its neighbor which are incorporated into biomembrane analogues. Some of the imformations may be obtained by the investigation of excimer (or exciplex) luminescence in micellar system. In ordinary micellar systems, however , the location of light-absorbing solubilizate is not easily fixed. In the present study, on the other hand, a series of surfactant molecules are designed so that an aromatic chromophore becomes a part of the main chain of cationic surfactant as shown by the following formula:



$i + j = 10$; C_1NB, $i = 0$; C_5NB, $i = 4$; C_8NB, $i = 7$

The surfactant molecule is denoted by C_iNB, where i stands for the number of methylene groups between the benzene ring and terminal methyl group. The sythesis of C_iNB was carried out by the procedure reported in a literature.[2)] The luminescence emitted from the aromatic moiety was measured by the use of a Shimadzu model RF-500 spectro-fluorometer.

The fluorescence spectra of C_iNB in the aqueous solution are independent of the concentration in the region below CMC. The wavelength of maximum intensity and the CMC-value for each surfactant are summarized in Table 1. In the case of C_1NB, a new luminescence maximum shows up as the surfactant concentration exceeds the CMC. The energy of the new luminescence maximum is considerably lower than the original peak observed in non-micellar system, and the intensity of the low-energy luminescence increases at the expence of the high energy luminescence as the temperature decreases (Fig. 1 (A)). The absorption spectra of C_iNB (λ_{max} = 280 nm), on the other hand, is only slightly affected either by the concentration or by the temperature.

Table 1. The CMC-values for C_iNB and the fluorescence maximum in the concentration region below CMC

Surfactant	CMC (10^{-3} M)	Fluorescence maximum (nm)
C_1NB	8.5	306
C_5NB	5.1	312
C_8NB	2.1	307

On the basis of these observations, it is strongly suggested that the new luminescence maximum at the low energy side is an excimer emission. The luminescence at the high energy side, of course, must be emitted from a free C_1NB molecule (called monomer luminescence hereafter).

The behavoir of C_5NB is fairly different from that of C_1NB. When the aqueous solution containing C_5NB (λ_{max} = 275 nm) is irradiated with light at 290 nm, the fluorescence spectra shows a single peak (Peak A) located at the wavelength (312 nm) close to that of C_1NB monomer luminescence. If the excitation is carried out at 305 nm and the fluorescence spectra is recorded under high amplification, two additional peaks are clearly observed: one at 345 nm (Peak B) and the other at 440 nm (Peak C). Neither Peak B nor Peak C shows appreciable intensity variation in the investigated temperature range (Fig. 1 (B)). The fluorescence spectra of C_5NB varies with the wavelength of the excitation light as shown in Fig. 2 (A). Then, it is strongly suggested that the excited states corresponding to Peak B and C are different from that which affords Peak A.

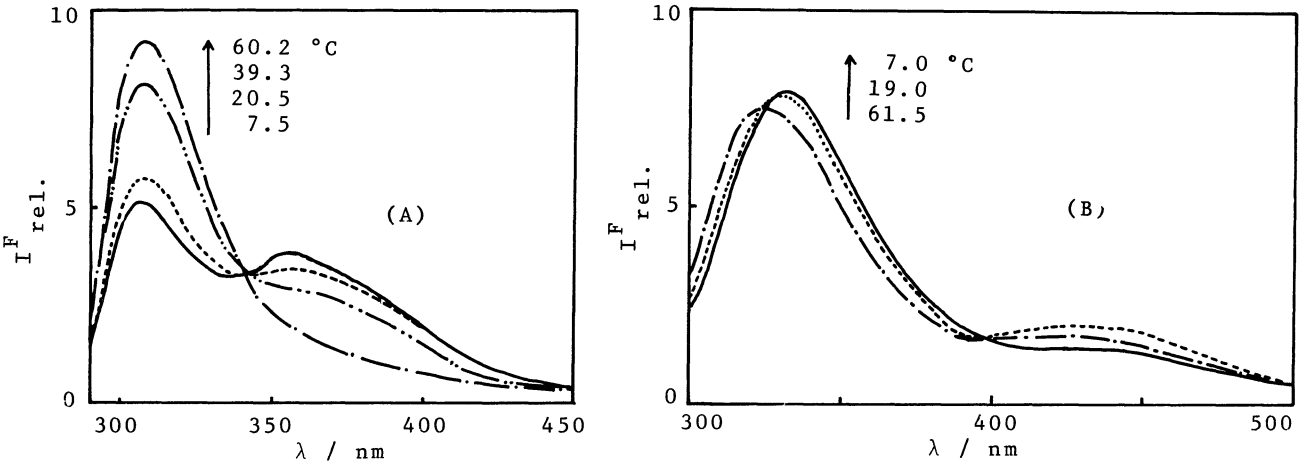


Fig. 1. Temperature dependence of the fluorescence spectra of C_iNB in the aqueous micellar solutions. (A), C_1NB (1.2×10^{-2} M) excited at 293 nm. (B), C_5NB (6.8×10^{-3} M) excited at 298 nm.

Taking into consideration of the above facts, the fluorescence spectra of C_1NB micelles were also investigated by the use of excitation light with various wavelength (Fig. 2 (B)). Here again, the intensity of the low-energy luminescence

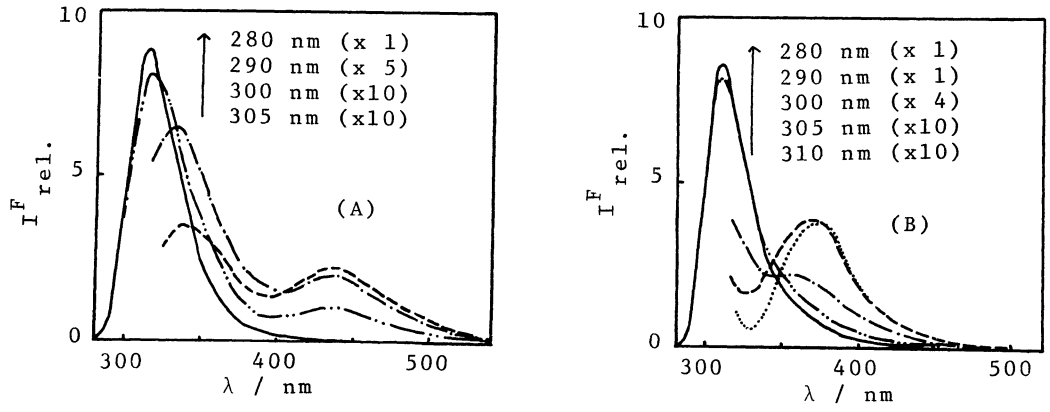


Fig. 2. The variation of the fluorescene spectra of C_iNB with the change in the wavelength of the excitation light at 25 °C. (A), C_5NB (7×10^{-3} M). (B), C_1NB (1.2×10^{-2} M). The numerals in the figures indicate the wavelength of the excitation light (nm) and the relative values for the amplifier gain (in parentheses).

relative to that of the monomer luminescence becomes large when the wavelength of the excitation light is located at the absorption edge, rather than the peak, of the elctronic spectra. In addition, careful examination of the electronic spectra of C_1NB also shows that the extinction coefficients in the energy region a little below the absorption maximum increases at lower temperatures. Then, it is quite conceivable that some of C_1NB molecules at the ground state are weakly associated each other in the micellar system.

As in the case of C_1NB and C_5NB, C_8NB micelles also afforded a low energy luminescence peak (a broad band around 420 nm) in addition to the monomer luminescence (307 nm). The intensity of the low energy peak, however, is so small in comparison with the monomer luminescence that it is rather difficult to be detected under ordinary experimental conditions.

The above experimental observations may be summarized as the following.

(1) In addition to the monomer luminescence, emission of low-energy luminescence are observed of C_iNB micelles.

(2) The relative intensity of the low energy peak and the temperature dependence vary considerably with the structure of the surfactant.

(3) The excited state responsible to the low-energy luminescence is different from that of the monomer luminescence.

(4) Relatively minor changes are observed of the electronic spectra of C_iNB micelles.

Taking into consideration of the above facts, one gets physical images of the micellar system under investigation. The luminescence of the solution below CMC is emitted from the photoexcited state of an isolated aromatic moiety (called phenoxy group, hereafter) of free surfactant molecules. On the formation of micelles, the surfactant molecules will be lined up so that average distances between the phenoxy groups become much shorter than the case of non-micellar solutions (Fig. 3). As a consequence, weak interactions between the phenoxy groups of the neighboring molecules will be expected to take place so that the electronic absorption spectra

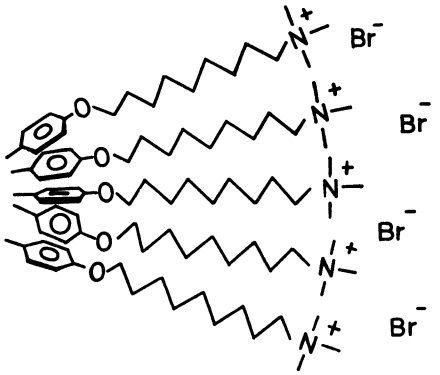


Fig. 3. Schematic presentation of the mode of alignment of phenoxy groups in the micellar interior.

becomes somewhat different from that without interactions. If one of the phenoxy groups is photoexcited, the intermolecular interaction becomes much more strong, and the low-energy luminescence is resulted. The average number of phenoxy groups in a given volume element decreases with an inverse of the second power of the distance between the center of the micelle and the location of the phenoxy group. This reasoning is in good agreement with the fact that the intensity of the low energy luminescence from C_8NB micelles is extremely small. The relatively large temperature dependence of the fluorescence intensities in C_1NB micelles may be explained by the fact that the phenoxy group in C_1NB has larger mobility than that in C_1NB as indicated by T_1-values of the ^{13}C NMR.[3] In the case of C_5NB micelles, it is quite likely that there are at least two types of associated species since two low-energy luminescence peaks are observed.

In a summary, fluorescence spectra of C_iNB micellar systems indicate the presence of relatively strong intermolecular interactions involving the photoexcited phenoxy group. The alignment of the phenoxy group in the micelles appears to be responsible to the specific interactions. The same type of intermolecular interactions will be expected of many chromophores incorporated into biomembranes or the analogues, which eventually serve as model systems of light-harvesting units in chloroplasts.

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REFERENCES AND NOTES

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3) Presented in part at the 14th Discussion Meeting on NMR Spectroscopy of Japan, October, 1975 (Fukuoka); The details will be reported in other paper.

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