Fluorescence Spectra of 9-Anthracenecarboxylic Acid in Heterogeneous Environments

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The fluorescence spectra of 9-anthracenecarboxylic acid (9ACA) were studied in surfactant solutions of sodium dodecyl sulfate and Triton X-100 as a function of surfactant concentration. In addition to an anthracene-like sharp fluorescence, a broad fluorescence with a peak around 470 nm appeared at 330 nm excitation above critical micellar concentrations. Only a broad fluorescence was seen at 400-nm excitation. Based on the excitation and absorption spectra, the broad fluorescence is thought to be caused by hydrogen-bonded dimers dissolved in the micelles. Intercalation of 9ACA was done for two alkylammonium-montmorillonites. The fluorescence spectra of 9ACA showed a broad peak with increase in loading levels of 9ACA in the alkylammonium-montmorillonites. The fluorescence was not similar to the excimer in a head-to-head configuration with a maximum at 510 nm observed in the crystals, but rather to the broad one in the micelles. Therefore, the hydrogen-bonded dimers are also attributed to the origin of the broad fluorescence in the interlayer spaces.

The fluorescence of 9-anthracenecarboxylic acid (9ACA) in ethanol shows pronounced concentration dependence.[1−4] The fluorescence spectrum has an anthracene-like sharp structure below $\approx 10^{-5}$ M (1 M = mol dm^{-3}). In addition to the sharp fluorescence, broad structureless fluorescence appears at 470 nm with an increase in 9ACA concentrations, resulting in only broad and large Stokes' shifted fluorescence above $\approx 10^{-3}$ M. Bazilevskaya and Cherkasov[1] attributed the broad band to an excimer with the parallel planes of anthracene formed from the linear-type dimer of 9ACA bridged by COOH groups, whereas the sharp fluorescence was caused by ionic ($ACOO^-$) and monomer (ACOOH) forms.

The structured fluorescence is observed in basic aqueous solutions or ethanol, whereas the broad fluorescence is observed in acidic aqueous solutions or ethanol. Werner and Hercules[2] attributed these changes to the acid−base equilibrium between two conformers and explained the broad fluorescence as follows: an excited-state rotation of the carboxyl group in the plane of the anthracene ring causes Stokes' shifted broad fluorescence. This rotation is considered to occur only in the neutral form, because the ionic form in protonic solvents is inhibited by strong ground-state solvation.

Suzuki et al.[3] measured absorption spectra in ethanol as a function of 9ACA concentration and ascribed the spectral changes not to the acid−base equilibrium but to the monomer−dimer equilibrium based on pK_a. The broad fluorescence of 9ACA was classified as dimer fluorescence and excimer fluorescence formed from dimers (an excited tetramer). The sharp fluorescence was attributed to a monomer species hydrogen-bonded with ethanol clusters, preventing the excited-state rotation of the carboxyl group.

Diffusionally formed excimer and excited tetramer from two dimers were discarded as the source of the broad fluorescence because a diffusional encounter rate constant would require 2 or 3 orders of magnitude greater than the ones usually observed.[2,4] Ghoneim et al.[4] considered the roles of dimers in ethanol important for explaining the increase in the quantum yields of the broad and sharp fluorescence with an increase in 9ACA.

Agbaria et al.[5] found that the broad fluorescence increases in the presence of β-cyclodextrin in aqueous solutions and considered that acid−base equilibrium was a more plausible explanation for the dual fluorescence than the formation of dimers, because a host−guest inclusion complex of 9ACA with β-cyclodextrin should reduce the presence of dimers.

It seems to be a consensus that deprotonated 9ACA may have sharp fluorescence similar to anthracene. However, the origin of the broad and large Stokes' shifted fluorescence of 9ACA is still controversial. In this article, we study the fluorescence properties of 9ACA in surfactant solutions and 9ACA intercalated in alkylammonium-montmorillonites to clarify the nature of the broad fluorescence.

Experimental Section

9-Anthracenecarboxylic acid (9ACA, Aldrich Chemical, 99%) was purified by recrystallization from ethanol. Sodium dodecyl sulfate (SDS) from Wako Pure Chemical and Triton X-100 from Kishida Chemicals were used as received. Surfactant solutions with 9ACA were sonicated for several hours and allowed to stand overnight before measurements. Basic solutions were prepared by adding 20 μL of NH_4OH (6 M) to 10 mL of SDS solutions.

Dimethyldioctadecylammonium (DMDODA) and octadecyltrimethylammonium (ODTMA) chlorides and Na-montmorillonite (Kunipia-F) were obtained from of Tokyo Kasei and Kunimime Industries, respectively. Alkylammonium-exchanged montmorillonite was prepared by cation exchange of Na-montmorillonite as previously reported.[6] The intercalation of 9ACA was done by mixing DMDODA-montmorillonite or ODTMA-montmorillonite and 9ACA for 3 h with an agate mortar and pestle at room temperature.[6] The intercalated samples

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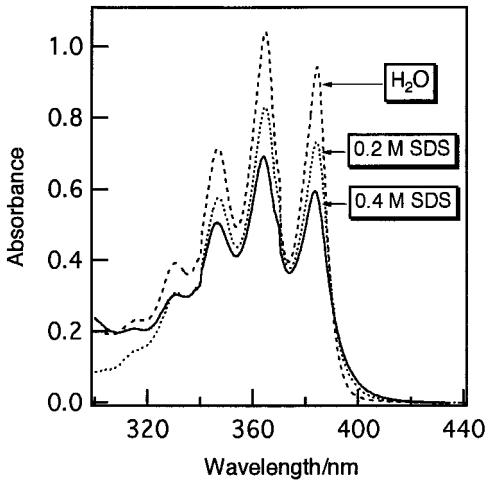

Figure 1. Absorption spectra of 1×10^{-4} M 9ACA in neutral aqueous solutions of SDS.

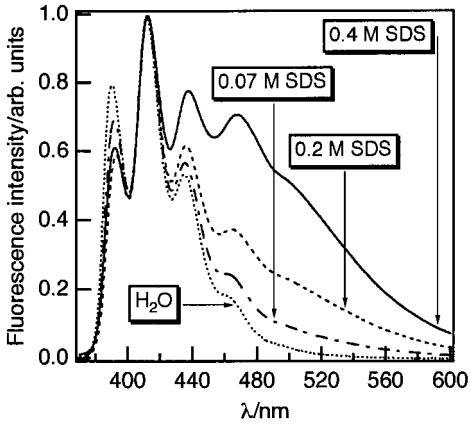

Figure 2. Fluorescence spectra of 1×10^{-4} M 9ACA in neutral aqueous solutions of SDS. Excitation wavelength, 330 nm.

were heated at 120 °C for 1 h under reduced pressure to remove surface-adsorbed 9ACA.

Absorption spectra were recorded with a JASCO V-570 spectrophotometer. Fluorescence and excitation spectra were taken with a JASCO FP-777 fluorescence spectrophotometer. An ordinary excitation wavelength was 330 nm. X-ray powder diffraction was measured with a Rigaku RINT 2200 diffractometer using Cu Kα radiation. All measurements were made at room temperature.

Results and Discussion

Surfactant Solutions. Figure 1 shows the absorption spectra of 1×10^{-4} M 9ACA in neutral aqueous solutions of SDS. The absorption spectrum in water shows the several peaks at 384, 365, 347, and 330 nm assigned to the ^{1}La band. The spectrum is ascribed to the anion of $9ACOO^-$, where A indicates anthracene, because pK_a in water 2.4 indicates that >90% of the acid exists in the ionized form ($9ACOO^-$).[2] The peaks became broader and weaker with increased concentration of SDS with isosbestic points at 390 and 370 nm in the spectra. A tail around 400 nm is seen at 0.4 M SDS. These spectral changes appear to be similar to those in acid−base equilibrium[2] or monomer−dimer equilibrium.[3] Therefore, the spectral changes of 9ACA induced by adding SDS would be attributed to the acid−base or monomer−dimer equilibrium.

Figure 2 shows the fluorescence spectra of 1×10^{-4} M 9ACA in SDS solutions. Fluorescence shows a sharp spectrum in water without SDS, which is assigned to the anion of $9ACOO^-$ as

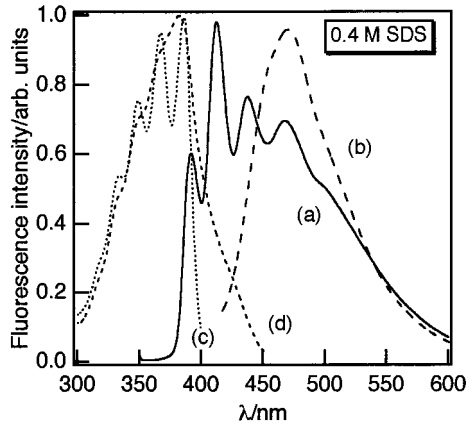

Figure 3. Fluorescence and excitation spectra of 1×10^{-4} M 9ACA in neutral solution of 0.4 M SDS: (a) fluorescence excited at 330 nm, (b) fluorescence excited at 400 nm, (c) excitation monitored at 412 nm, and (d) excitation monitored at 470 nm.

described above. Broad fluorescence around 470 nm gradually increases with increase in SDS concentration above the critical micellar concentration (8×10^{-3} M)[7] and changes little above 0.4 M. Therefore the appearance of the broad fluorescence is related to the formation of SDS micelles. According to the article by Suzuki et al.,[3] neutral 9ACA monomers are hardly soluble in hydrocarbons because of the hydrophilic carboxyl group, whereas hydrogen-bonded dimers of 9ACA can dissolve in hydrocarbons because the hydrophilic character of the carboxyl group is masked by dimer formation. 9ACA would thus be considered to dissolve initially as the anions in water and gradually as the hydrogen-bonded dimers in the hydrophobic micelles formed with increase in SDS. The excited state makes possible rotation of the two carboxyl groups into the plane of anthracene rings, so that broad fluorescence emerges.[3] Swayambunathan and Lim[8] also reported that 9ACA exists mainly in the hydrogen-bonded dimer form in supersonic free jets and that electronic excitation leads to rotation of the dimer bridge of the two carboxyl groups into the plane of the anthracene rings.

Figure 3 shows the fluorescence and fluorescence excitation spectra of 1×10^{-4} M 9ACA in 0.4 M SDS neutral solutions. Figure 3a shows the sharp and the broad fluorescence around 470 nm at 330-nm excitation. The excitation spectrum monitored at 412 nm (Figure 3c) shows peaks corresponding to those of the absorption spectrum in water. However, the excitation spectrum monitored at 470 nm reveals broader peaks with a tail toward 450 nm. The features of the excitation spectrum are the same as those of the absorption for 0.4 M SDS neutral solution. Only broad fluorescence around 470 nm is observed at 400-nm excitation as shown in Figure 3b. These results clearly indicate that the broad fluorescence is not due to the excited-state conformer of 9ACA monomer induced by carboxyl group rotation or excimer from 9ACA molecules, but to a different species in the ground state. The ground-state hydrogen-bonded dimers of 9ACA are the most probable species as discussed above.

Figure 4 shows the fluorescence spectra of 9ACA in 0.4 M neutral solutions of SDS. The sharp fluorescence with moderate contribution of the broad fluorescence is observed for 1×10^{-5} M. It is evident that the intensity at 470 nm due to the broad fluorescence increases with 9ACA concentration, exceeding that of the sharp fluorescence at 1×10^{-3} M. The effects of 9ACA concentration on fluorescence spectra in SDS solutions can be explained by the equilibrium between monomer anions of $9ACOO^-$ in the aqueous phase and dimers in the micelles.

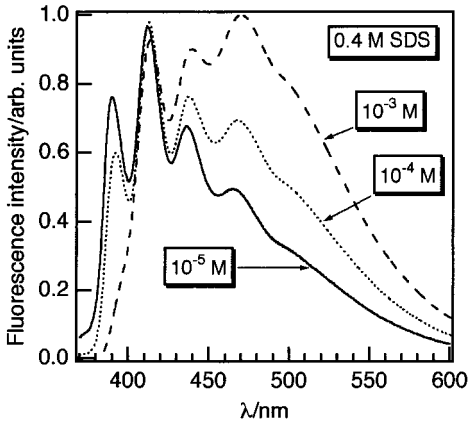

Figure 4. Fluorescence spectra at different concentrations of 9ACA in 0.4 M neutral aqueous solutions of SDS excited at 330 nm.

$$(2ACOO^- + 2H^+)_{aqua} = (2ACOOH)_{aqua} = (ACOOH{\cdot}HCOOA)_{micelle} \quad (1)$$

The micelle concentration for 0.4 M SDS is calculated as 6.5×10^{-3} M, from the critical micellar concentration (8×10^{-3} M) and micelle aggregation number (60) of SDS.[7] The average number of 9ACA per micelles is 0.015 for 10^{-4} M and 0.15 for 10^{-3} M 9ACA, based on the assumption of 100% monomeric 9ACA form. Considering that 9ACA mostly dissolves in aqueous phase as $ACOO^-$, the average number of 9ACA dimers per micelles would be considerably smaller than the values above. Concentration dependence of 9ACA fluorescence differs from that for pyrene in micelles, where excimer fluorescence increases with pyrene concentration because micelles dissolve more pyrene.[7] In this case, 9ACA is dissolved more as the dimer in SDS micelles with an increase in 9ACA.

Fluorescence changed to the structured spectra when NH_4-OH was added to SDS solutions as shown in Figure 5. The spectra are essentially the same except for the peaks around 390 nm and very similar to those in neutral or basic aqueous solutions. 9ACA would thus appear to dissolve mostly in the aqueous phase of basic SDS solutions as the anion form, because of the shift of equilibrium (1) toward the left. Consequently, no broad fluorescence due to the dimers is observed. The intensity decrease around 390 nm with an increase in 9ACA is most probably due to reabsorption caused by spectral overlap with the absorption.

Very similar results were obtained for Triton X-100 solutions. Figure 6 shows the fluorescence spectra of 1×10^{-4} M 9ACA in various Triton X-100 solutions. The broad band fluorescence around 470 nm grows with an increase in Triton X-100 concentration above the critical micellar concentration ($2.4-2.6 \times 10^{-4}$ M)[9] and changes little over 3×10^{-2} M. These results also confirm that Triton X-100 micelles dissolve the 9ACA dimers in a manner similar to SDS micelles.

From these results, we ascribe the broad fluorescence of 9ACA in micelles to 9ACA solubilized as the hydrogen-bonded dimers in hydrophobic micelles. Dimer formation is promoted in micelles because the hydrophilic nature of the carboxyl group is masked by the dimer structure.

Alkylammonium-exchanged Montmorillonite. Intercalation of 9ACA was confirmed by X-ray diffraction. Basal spacing of the DMDODA-montmorillonite gradually increased with loading levels of 9ACA (host:9ACA in w/w): 3.0 nm (100:0); 3.5 nm (100:5); 3.7 nm (100:10); 3.9 nm (100:20) as summarized in Table 1, indicating the intercalation of 9ACA in the interlayer space. Basal spacing did not change before and after heating at

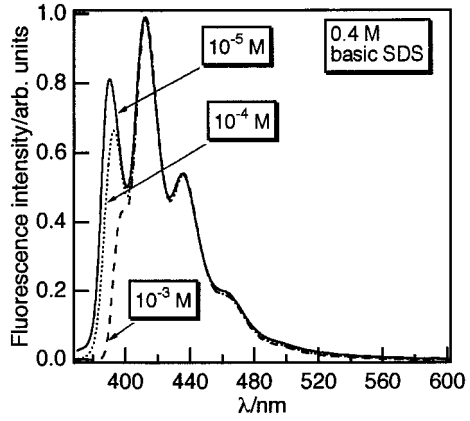

Figure 5. Fluorescence spectra at different concentrations of 9ACA in 0.4 M basic aqueous solutions of SDS excited at 330 nm.

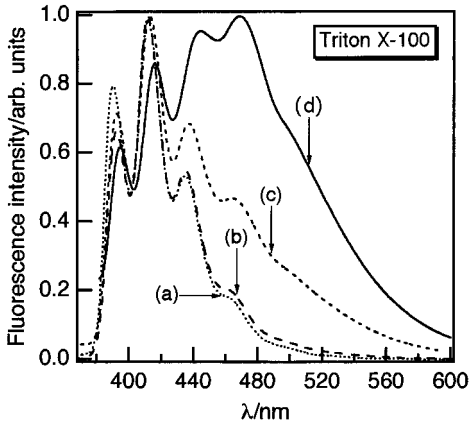

Figure 6. Fluorescence spectra of 1×10^{-4} M 9ACA in Triton X-100 neutral solutions excited at 330 nm: (a) 0 M, (b) 3×10^{-4} M, (c) 3×10^{-3} M, (d) 3×10^{-2} M.

TABLE 1: Basal Spacing for 9ACA Mixed with DMDODA- and ODTMA-Montmorillonite (mont)

host	host:guest ratio (w/w)	basal spacing (nm)
DMDODA-mont	100:0	3.0
	100:3	3.3
	100:4	3.4
	100:5	3.5
	100:10	3.7
	100:20	3.9
	100:32[a] (anthracene)	3.8[a]
ODTMA-mont	100:0	2.2
	100:15	2.2
	100:59[a] (anthracene)	3.7[a]

[a] Taken from Ref. 6.

120 °C for 1 h, but decreased after heating at 150 °C for 1 h, which suggests evaporation of intercalated 9ACA. The heating condition may be considered appropriate for removing only surface 9ACA. The maximum basal spacing of 3.9 nm agrees with those in DMDODA-montmorillonite:anthracene (3.8 nm) and DMDODA-montmorillonite:pyrene (3.9 nm).

Figure 7 shows the fluorescence spectra of 9ACA intercalated in DMDODA-montmorillonite at different loading levels and 9ACA crystals. The fluorescence spectrum (Figure 7a) shows vibronic bands such as at 421 and 445 nm with a blurred shoulder around 400 nm for 100:3 (w/w) of DMDODA-montmorillonite:9ACA. The excitation spectrum (Figure 7e) shows peaks at 394 and 375 nm. These features are similar to those monitored at the sharp fluorescence in ethanol, although

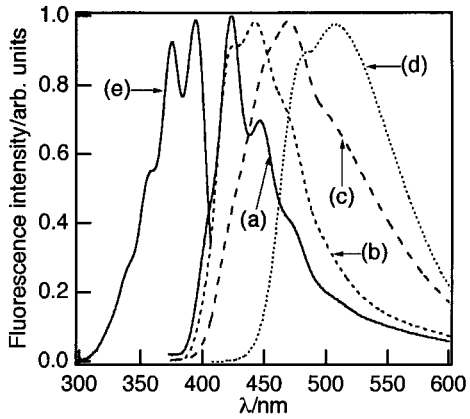

Figure 7. Fluorescence and excitation spectra of 9ACA intercalated in DMDODA-exchanged montmorillonite at various host:guest ratios in weight and 9ACA crystals: fluorescence excited at 330 nm, (a) 100:3, (b) 100:10, (c) 100:20, (d) crystals, and (e) excitation monitored at the fluorescence peak (421 nm) at a.

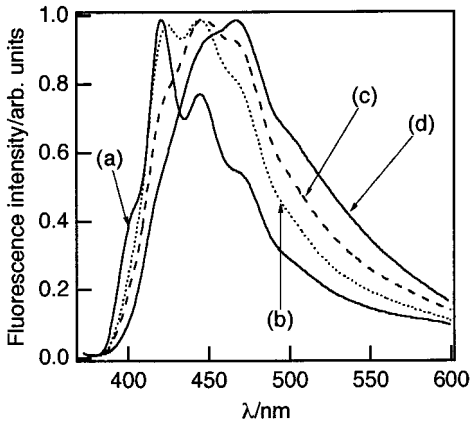

Figure 8. Fluorescence spectra of 9ACA intercalated in ODTMA-exchanged montmorillonite at various host:guest ratios in weight: fluorescence excited at 330 nm, (a) 100:3, (b) 100:5, (c) 100:10, and (d) 100:15.

the spectrum was red-shifted about 10 nm. The intensity at 470 nm became stronger and the spectra became broader as loading increased. At 100:20 (Figure 7c), the fluorescence spectrum changed to a red-shifted broad peak at around 470 nm with a shoulder around 510 nm.

This concentration dependence of fluorescence is the same as those in ethanol and SDS solutions. Explanation for the fluorescence of 9ACA intercalated is as follows: 9ACA is solubilized in the alkyl chains of DMDODA in neutral monomer form at low loading levels. As the loading of 9ACA increases, the hydrogen-bonded dimer is formed, showing a peak at 470 nm, because of poor solubility of monomer 9ACA in the alkyl chains due to the hydrophilic character of the carboxyl group. The fluorescence of the 9ACA crystals has a broad peak at 510 nm, as shown in Figure 7d, due to an excimer with a head-to-head configuration.[10] This is clear evidence that the species of the broad fluorescence around 470 nm is different from that of the excimer fluorescence. The fluorescence shoulder around 510 nm in Figure 7c may suggest the formation of such crystals at a loading of 100:20.

Figure 8 shows the fluorescence spectra of 9ACA intercalated in ODTMA-montmorillonite at different loading. The fluorescence at 100:3 shows a structured spectrum like that of DMDODA-montmorillonite. A red-shifted broad peak strongly appears at lower loading of 9ACA in comparison with DMDODA-montmorillonite. The intercalation did not change the basal spacing of 2.2 nm, but only broadened the diffraction peaks for loading conditions from 100:0 to 100:15 (Table 1). It was found that the basal spacing of ODTMA-montmorillonite critically increases from 2.2 to 3.7 nm above a certain loading level of arenes.[6] This is in great contrast to DMDODA-montmorillonite that shows gradual increase in the basal spacing. The difference is attributed to the particular arrangements of the alkylammonium ions in the interlayer, leading to distinctive intercalation behavior; DMDODA-montmorillonite is somewhat more capable of dispersing arenes in the interlayer space than ODTMA-montmorillonite.[6] Therefore, the dimer is formed in ODTMA-montmorillonite more than in DMDODA-montmorillonite, with consequently the stronger broad fluorescence in ODTMA-montmorillonite than in DMDODA-montmorillonite.

Conclusions

The fluorescence spectra of 9ACA showed broad fluorescence around 470 nm in surfactant solutions of SDS and Triton X-100 above the critical micellar concentrations. From the excitation and absorption spectra and effects of excitation wavelength on fluorescence spectra, it could be concluded that the broad fluorescence was due to hydrogen-bonded dimers dissolved in micelles. The dimer structure, which masks the hydrophillic character of the carboxyl group, facilitates the dissolution of 9ACA into the hydrophobic micelles. The fluorescence spectra of 9ACA intercalated in DMDODA- and ODTMA-montmorillonites show a broad peak with the increased loading of 9ACA. The fluorescence spectrum is similar to the broad one in micelles, indicating that the hydrogen-bonded dimers are also formed in the interlayer spaces of the alkylammonium-montmorillonites. These results indicate that bimolecular and unimolecular processes found in aqueous solutions with β-cyclodextrin can induce the dual fluorescence of 9ACA.

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