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Variations in the Vibrational Structures of Fluorescence Spectra of Naphthalene and Pyrene in Water and in Aqueous Surfactant Solutions

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Synopsis. Variations in the vibrational structures of the fluorescence spectra of naphthalene and pyrene in water and in aqueous solutions of sodium dodecyl sulfate (SDS) have been studied by comparison with those in various organic solvents. The results were applied to the determination of the critical micelle concentration of SDS.

In studies on the effect of solvent polarity on vibrational structures in the absorption and fluorescence spectra of condensed aromatic hydrocarbons,[1–5] remarkable intensity enhancement of the forbidden vibronic bands in various organic polar solvents was observed for some aromatic hydrocarbons.

The electronic spectra of condensed aromatic hydrocarbons in aqueous solutions might be important in view of solvent effects.[6,7] However, they have not been studied much. It is of interest to examine whether a similar band enhancement is observed in water, a highly polar solvent.

On the other hand, in view of recent interest in the spectroscopic studies in micellar systems,[8–10] the effects can be applied to micellar solutions to provide useful information on the micellar interior and permit determination of the critical micelle concentration (CMC).

In this work, the fluorescence spectra of naphthalene and pyrene have been investigated in water and in aqueous solutions of sodium dodecyl sulfate (SDS), a typical anionic surfactant.

Experimental

Naphthalene and pyrene were purified by recrystallization, sublimation, and zone-refining. SDS was repeatedly recrystallized from methanol. Water was distilled three times. All the organic solvents were of spectroscopic grade. The aqueous solutions of the aromatic hydrocarbons were prepared in the following way. Small amounts of the hydrocarbons were immersed in given quantities of water and the mixtures were treated with an ultrasonic cleaner to accelerate dissolution. In order to eliminate the undissolved microcrystals, the saturated solutions were carefully filtered with finest Whatman glass fiber papers, diluted with water, treated with an ultrasonic apparatus, and allowed to stand for a day before spectroscopic measurements. The solutions contained various amounts of SDS, the concentrations of hydrocarbons being constant. This was confirmed by measuring the absorbances at strong UV bands which were found to be *ca.* 2×10^{-5} and 3×10^{-7} M for naphthalene and pyrene, respectively. The fluorescence spectra were recorded on a Hitachi MPF-2A spectrofluorometer and the absorption spectra on a Hitachi EPS-3 spectrophotometer.

Results and Discussion

The fluorescence spectra of naphthalene and pyrene have been observed in organic solvents of varying polarities (Figs. 1 and 2). In the vibrational structures of these spectra, the intensities of the forbidden vibronic bands A, B, and C increase remarkably with the solvent polarity relative to the intensity of the allowed vibronic

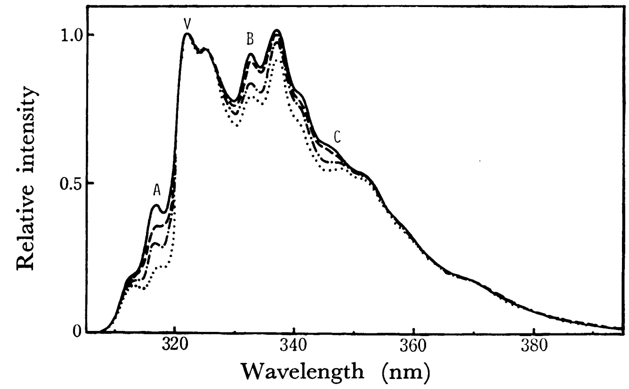

Fig. 1. Fluorescence spectra of naphthalene in several organic solvents. Solvent: cyclohexane (······), diethyl ether (·----·), 1,2-dichloroethane (----), and acetonitrile (——).

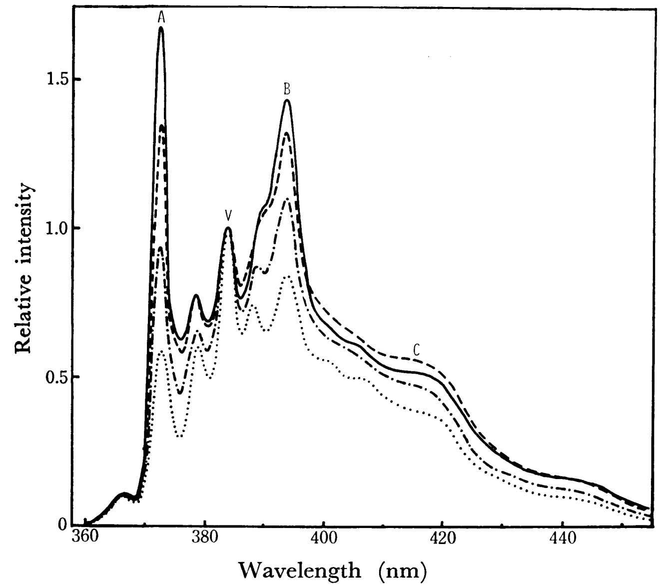

Fig. 2. Fluorescence spectra of pyrene in several organic solvents. Solvent: cyclohexane (······), diethyl ether (·----·), 1,2-dichloroethane (----), and acetonitrile (——).

band V, which is almost insensitive to the solvents.[1,2,4] Thus, these aromatic hydrocarbons can be employed as fluorescent probes for the characterization of their environments.

The fluorescence spectra of naphthalene (Fig. 3) and pyrene (Fig. 4) have been studied in aqueous solutions of various concentrations. The vibronic bands are considerably broadened in water as compared with those in organic solvents, the red shifts being small. Relatively large broadenings indicate the specific solvent effects of water. The relative intensities of bands A, B, and C are markedly enhanced in water, which is reasonable considering its high polarity. In aqueous surfactant solutions, the spectra at lower SDS concentrations are practically the same as those in pure water, whereas at higher SDS concentrations the band intensities are reduced to those as observed in a much less polar solvent. The CMC can thus be determined by means of the present medium effects.

The intensity enhancement can be expressed in terms of the intensity ratio of band A to band V, I_A/I_V. In Fig. 5, the ratios are plotted against the concentration of SDS. Changes in ratio occur in the relatively narrow concentration range, on either side of which the ratios remain constant. The concentration at which the breaks are observed may be taken as the CMC of SDS. Its values are estimated as 0.0065 and 0.007 M for naphthalene and pyrene, respectively (Fig. 5). These values are in rough agreement with those reported,[11,12] being slightly smaller. In the presence of aromatic hydrocarbons, the micellar formation may be more or less influenced; thus, the CMC values are somewhat reduced by the induction effects of probes.

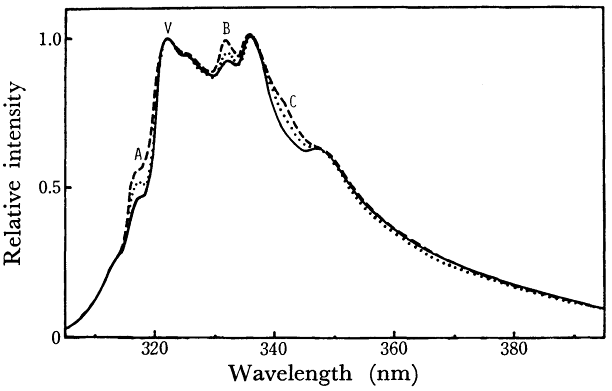

Fig. 3. Fluorescence spectra of naphthalene in water and in aqueous SDS solutions. SDS concentration: 0 and 5.22×10^{-3} M (----), 1.22×10^{-2} M (······), and 1.86×10^{-2} M (——).

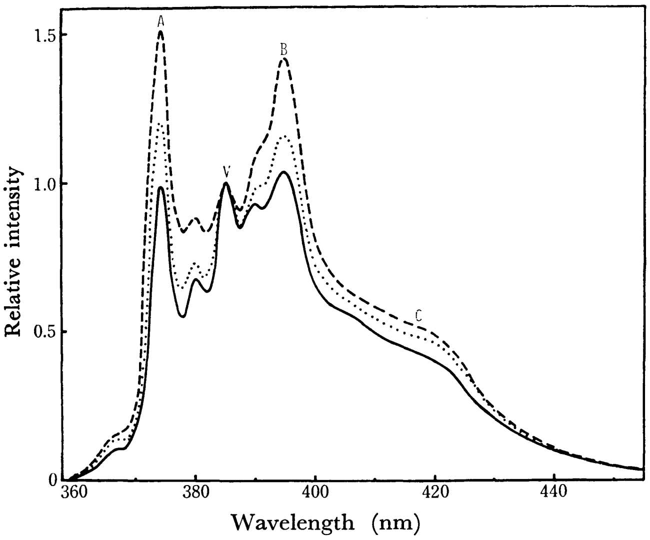

Fig. 4. Fluorescence spectra of pyrene in water and in aqueous SDS solutions. SDS concentration: 0 and 1.30×10^{-3} M (----), 8.16×10^{-3} M (······), and 4.99×10^{-2} M (——).

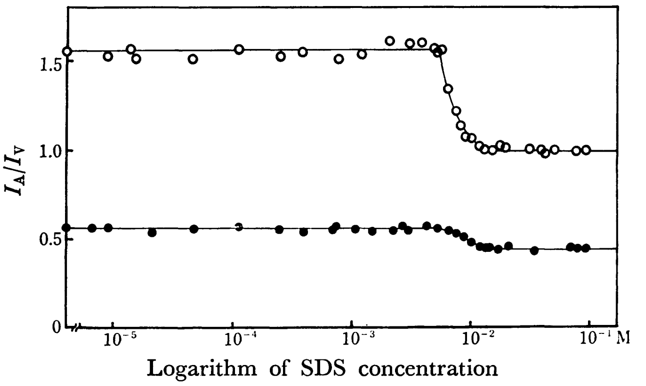

Fig. 5. Plots of relative intensities, I_A/I_V, *vs.* SDS concentration for naphthalene (●) and pyrene (○) probes.

In view of the band intensities in pyrene, the environment in the interior of micelle is considerably less polar than in ethanol but a little more polar than in diethyl ether. Such a weak polar environment might be caused by the influence of the ionic atmosphere around the micelles as well as the polarization of the surrounding water. In the case of naphthalene, however, a comparison of spectra indicates that the environment in micellar solution is much more polar than in organic polar solvents, implying that the probe molecules are preferably located near the micellar surface.[13]

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