The Studies on Micelles of Surfactants. I. The Phase in the interior of Micelles of Surfactants

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(Received March 24, 1956)

Introduction

It is well known that organic compounds with conjugated bonds show light absorption in the visible and ultraviolet regions. These bands characteristic for the conjugated system are called K[1] or π[2] bands, because π electrons are responsible for them. The intensity of π bands has the order of $\varepsilon=10000-20000$ and their maximum shifts towards red when solvents are changed from nonpolar to polar or the conjugated system becomes larger[3].

It is known too that so-called R bands[1] appear when hetero atoms which have n electrons (nonbonding electrons, i.e., lone pair) are conjugated to the planar conjugated organic system[4]. Afterwards R bands have been usually called n bands. The intensity of n bands has the order of $\varepsilon=10-1000$ and the position of them is always at the region of the longer wave length than that of π bands when the two kinds of bands appear in one system. N bands shift towards blue when solvents are changed from nonpolar to polar liquids which act as proton donor[5], but shift towards red if solvents act as proton accetor[6].

The definitions of both bands were given by Kasha[7]. We can readily distinguish the n band from the π band by their relative positions, intensities and shifts when solvents are changed.

The band which is characteristic of the benzenoid system and can not be observed in the aliphatic conjugated system is called B band. Its position and intensity are the media between the π and the n band ($\varepsilon=250-3000$). This band is caused by the vibration of the ring and has many fine structures[8].

It has been believed that the interior of micelles of surfactants is constructed by hydrocarbon but this fact is not yet experimentally determined. When the substances, which are insoluble or hardly soluble in water, are solubilized in the aq. surfactant solutions and their spectra are compared with those of the same substances in nonpolar solvents, and if there is no spectral change, we may safely draw the conclusion that the interior phase of surfactant-micelles is perfectly nonpolar. But if the spectral change is observed, we can say that the solubilizate molecules are under the influence of water molecules. If the latter case is observed it is our purpose to show whether some of those water molecules are contained in the micelles or not.

In our present work we have used azobenzene, Yellow OB (which have the π and the

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[1] A. Burawoy, *Ber.*, **63**, 3155 (1930).

[2] H. L. McMurry, *J. Chem. Phys.*, **9**, 241 (1941). H.L. McMurry and R.S. Mulliken, *Proc. Nat Acad. Sci. US.* **26**, 312 (1940).

[3] J.R. Platt, *J. Chem. Phys.*, **19**, 101 (1951).

[4] R.S. Mulliken. *J. Chem. Phys.*, **3**, 564 (1935).

[5] (a) H. McConnel, ibid., **20**, 700 (1952): (b) G.J. Brealey and M. Kasha, *J. Am. Chem. Soc.*, **77**, 4462 (1955).

[6] S. Nagakura and H. Baba, *J. Am. Chem. Soc.*, **74**, 5693 (1952).

[7] M. Kasha, *Disc. Faraday Soc.*, No. **9**, 14 (1950).

[8] F.O. Rice and E. Teller, "The Structure of Matter", John Wiley and Sons, Inc., New York (1949), p. 273.

n bands), anthracene and phenanthrene (which have the B and the π bands) as the solubilizates or the absorbers to study the phase of the micelle. These four absorbers are insoluble in aq. phase but soluble in various organic solvents and also solubilized in aq. surfactant solutions.

Materials and Experimental Methods

1) **Samples.**—Sodium dodecyl sulfate (SDS), offered by The Daiichi Seiyaku Co., was purified with ether and recrystallized from alcohol. Trimethyl dedecylammonium chloride (TMD), offered by The Nihon Yushi Co., was purified by the extraction with isopropyl alcohol. Nonionic surfactant Emulgen 120 (E120), (lauryl-polyethylene ether) offered by The Kaō Sekken Co., has been used with no purification except to remove the water by desiccation. Yellow OB and azobenzene, which are of chemical pure grade and consist mainly of trans type, have been used after being extracted several times with hexane. Anthracene and phenanthrene which are also chemical pure grade have been used after several extractions with benzene. As we need only the relative positions and intensities of the bands of these absorbers and not the absolute ones, the influences of minute impurities contained in these absorbers are thought to be negligible.

2) **Methods.**—The measurements of the absorption spectra have been carried out by the Beckman DU Spectro-photometer at the room temperature.

Results

1) Experiments with Azobenzene as the Solubilizate.—a) The Concentration Dependence of the Absorption Spectra of Azobenzene in the Nonpolar Solvent.—In Fig. 1 the absorption spectra of azobenzene in CCl_4 are shown. The absorption maximum at 320 mμ (curve I) is the π band which depends remarkably on the concentrations. The reason why the π band depends on the concentration comes from the nature of benzene ring responsible for producing the π band which is able to act as π acid and as π base[9]. The maximum at 445 mμ is the n band and its dependence on the concentration is very little, because the azo-group which is responsible for producing the n band acts only base and its electronic state is hardly affected by the association.

b) The Dependence of the Spectra on the Concentration of Azobenzene in the Aqueous Surfactant Solutions.—As the azobenzene molecules are thought to be equally distributed in every micelle in surfactant solutions, the change of the π band can not occur so long as the number of absorbent molecules does not exceed that of micelles. From the curve I, III, and IV in Fig. 2 it is seen, when the 10% aq. SDS solution is used, the spectral changes of azobenzene are little until its concentration exceeds about 10^{-4}M.

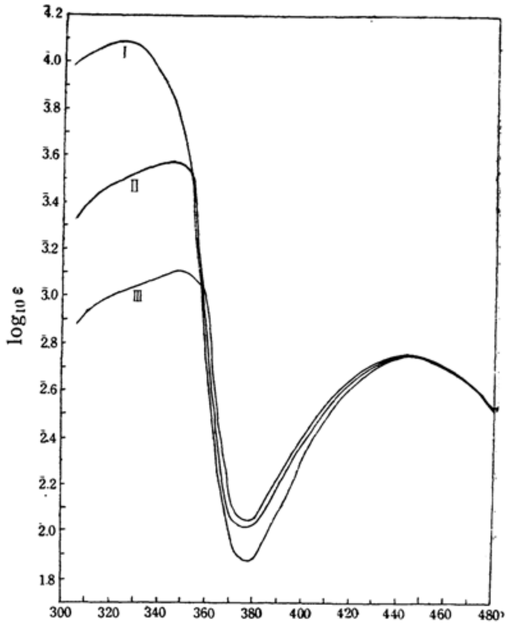

Fig. 1. Absorption spectra of azobenzene in CCl_4, measured three days after preparation. Concentration of azobenzene: I. 1.183×10^{-4}M. II. 1.183×10^{-3}M. III. 3.94×10^{-3}M/L.

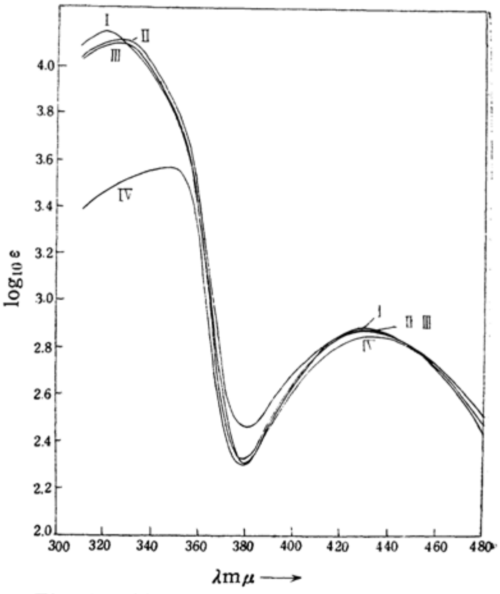

Fig. 2. Absorption spectra of azobenzene. Concentration of azobenzene: I. 2.283×10^{-5}, II and III. 2.283×10^{-4}, IV. 1.183×10^{-3}. Solvents: I. 10% SDS aq., II and III. 10% SDS+1.5% CCl_4 solubilized, IV. 10% SDS+2.5% CCl_4 solubilized. Reference: I. water, others. solvents. Measured 3 days (I and IV), 8 hours (II and III) after preparation.

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[9] R. S. Mulliken, *J. Am. Chem. Soc.*, 74, 811 (1952).

Using this fact, it is thought possible to determine the number of micelles, accordingly* the number of surfactant molecules which form every micelle at the definite concentration. The details on this subject will be reported in our next paper.

c) The Scattering and Absorbing Effects by the Micelles.—In Fig. 2 the curve II and III are almost the same except that the intensity of the latter is a little less than that of the former. When we use the solvent (including aq. surfactant solutions) as the reference liquid we need not be concerned about the scattering and absorbing effects by the micelles[10].

d) The Time-dependence of the Intensity of the Bands.—In Fig. 3a it is seen that the intensities of π bands decrease a little with time but the positions of their maxima do not alter. The intensities of the n bands (not the positions of maxima), however, depend markedly on time. This is, we suppose, because of the increasing amount of hydrogen-bonding between the azo-group and the water molecules. In Fig. 3a the solid curve (measured eight hours after preparation) I (5% SDS) has the higher intensity than that of the solid curve II (10%); this shows that in 5% SDS the n electrons of azo-group are much more perturbed at first by the water molecules than in 10% SDS. The broken curve (measured seven days after preparation) I (5% SDS) of Fig. 3a, on the contrary, has the lower intensity than that

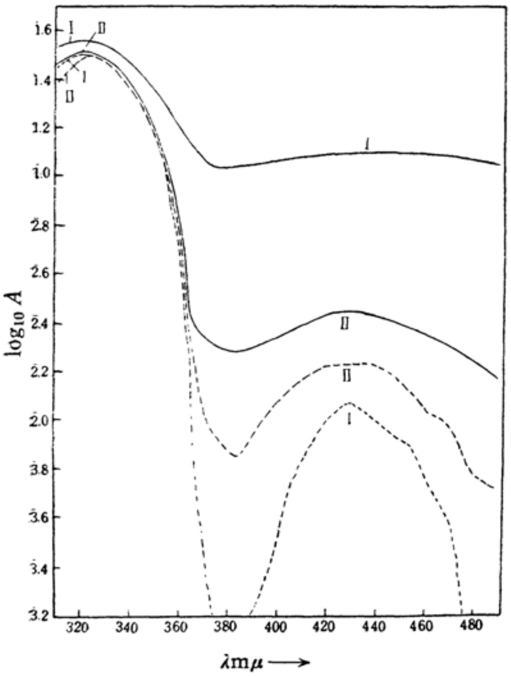

Fig. 3a. Absorption spectra of azobenzene. ——— Measured 8 hours, ---- measured 7 days after preparation. Concentration of azobenzene 2.278×10^{-5} M. b (the width of the cell) = 1 cm. Solvents: I. 5% SDS aq., II. 10% SDS $A=(\log_{10})I_0/I$.

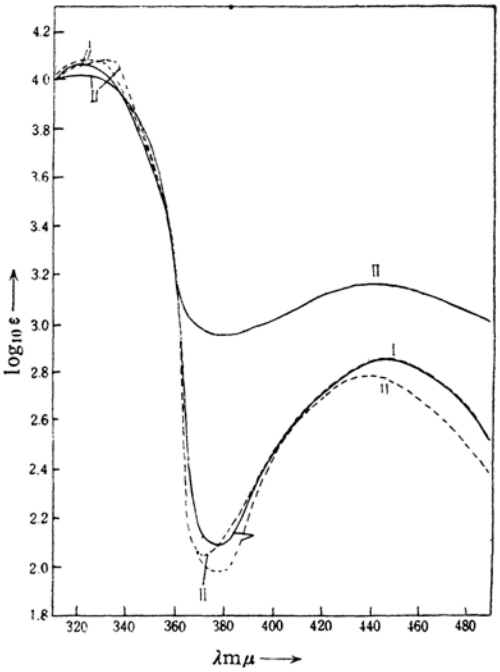

Fig. 3b. Absorption spectra of azobenzene 1.006×10^{-4} M/l. ——— Measured 8 hours, ---- measured 7 days after preparation. Solvents: I. CCl_4, II, C_2H_5OH.

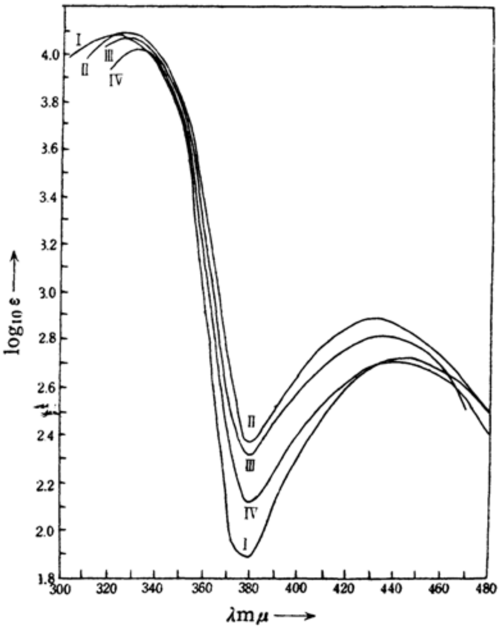

Fig. 4. Absorption spectra of azobenzene measured three days after preparation. Concentration of azobenzene 1.183×10^{-4} M. Solvents: I. CCl_4, II. 5% SDS, III. 5% TMD, IV. 2.5% E 120.

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[10] E. Freiver, W. Berndt and H. Toplak, *Angew. Chem.*, **67**, 69 (1955).

of the broken curve II (10%). This is because of the velocity of the hydrogen-bonding being greater in 5% SDS than in 10% SDS.

In alcohol the intensity of the n band also changes with time, and the effect of the association appears in the π band, but in a nonpolar liquid such as CCl_4 the n band is not affected and the lowering of the intensity of the π band is very little with time (Fig. 3b).

e) The Absorption Spectra of Azobenzene in Various Aqueous Surfactant Solutions.—In Fig. 4 it is seen, if we take the maxima in the CCl_4 solution as the standard, all the n bands shift towards blue and all the π bands shift towards red in aq. surfactant solutions, which show that the solubilizate molecules are in contact with water molecules as is the case of Fig. 3a.

f) The Dependence of Absorption Spectra of Azobenzene on the Concentration of Surfactants.—In Fig. 5a (measured eight hours after preparation) and 5b (seven days) it is seen that the spectra of azobenzene in aq. surfactant solutions deviate from that in CCl_4 in the order 5% SDS>10% SDS>5% SDS+1.2% CCl_4 solubilized.

2) Experiment with Yellow OB.—In the case of Yellow OB the degree of the shift of the π band is more marked. The maximum at 440 mμ in CCl_4 is the π band (Fig. 6a) which shifts towards red in the surfactant solutions. The n band is covered by this massive π band and can not be observed. The maximum at 350 mμ seems to correspond to the third maximum (about 260 mμ) of Benzeneazo-α-naphthalene (Fig. 6b), which makes the skeleton of Yellow **OB**, caused probably by

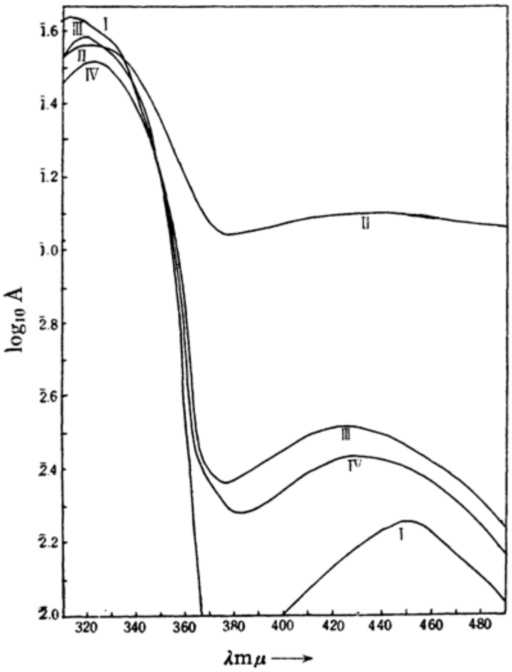

Fig. 5a. Absorption spectra of azobenzene measured 8 hours after preparation. Concentration of azobenzene is 2.278×10^{-5} M. b=1 cm. Solvents: I. CCl_4, II. 5% SDS, III. 5% SDS+1.2% CCl_4 solubilized, IV. 10% SDS.

$$A=\log_{10}\frac{I_0}{I}$$

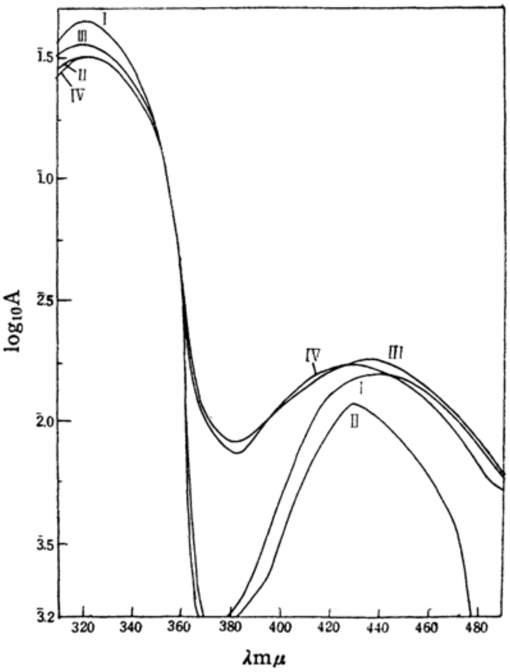

Fig. 5b. Absorption spectra of azobenzene measured 7 days after preparation. Concentration of azobenzene 2.278×10^{-5} M. b=1 cm. Solvents: I CCl_4, II. 5% SDS, III. 5% SDS+1.2% CCl_4 solubilized. IV. 10% SDS.

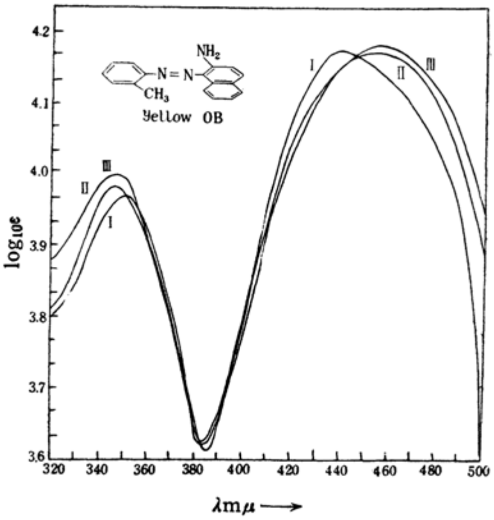

Fig. 6a. Absorption spectra of Yellow OB measured three days after preparation. Concentration of Yellow OB is 1.245×10^{-5} M. Solvents: I. CCl_4, II. 5% SDS, III. 5% TMD.

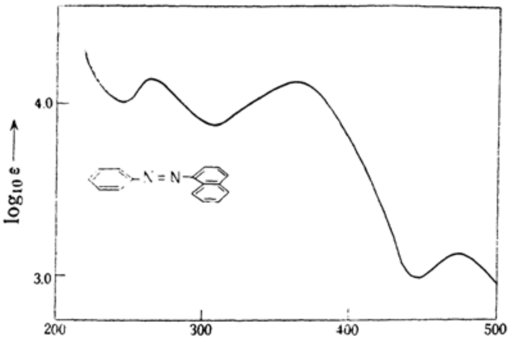

Fig. 6b. Absorption spectrum of benzene-azo-α-naphtharene from A. Burawoy, J. C. S., 1177 (1939).

the π-π*second excited transition, and diffuses and shifts a little towards blue in the aq. surfactant solution.

(3) The Changes of B Bands of Anthracene in the Aqueous Surfactant Solutions.—In Fig. 7 are shown the B bands of anthracene in hexane, alcohol and the aq. TMD solutions. The changes of the B bands in alcohol are not remarkable, but in the aq. TMD solutions they shift wholly towards red about 3 mμ and particularly in the 1% aq. TMD solution the marked intensity lowering occurs. The influence of the added hexane is also observed.

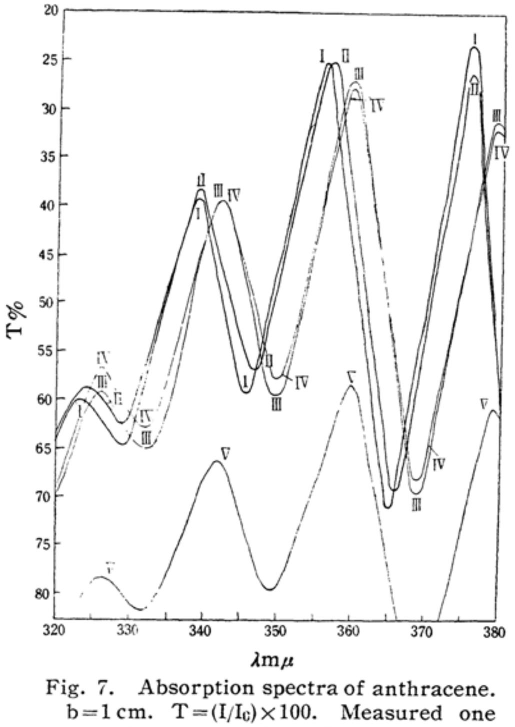

Fig. 7. Absorption spectra of anthracene. b=1 cm. T=(I/I₀)×100. Measured one day after preparation. Concentration of anthracene=10^{-4} M/l. Solvents: I. Hexane, II. C_2H_5OH, III. 10% TMD+2% Hexane, IV. 1% TMD, V. 10% TMD.

(4) The Changes of π Bands of Phenanthrene in the Aqueous Surfactant Solutions.—In Fig. 8 are shown the π bands of phenanthrene. In the aq. TMD solutions these π bands shift toward red 2–3 mμ; in 1% TMD the intensity lowering is also observed. As the result of the red shift of the π bands the maximum at 300 mμ, one of the B bands, disappears in the surfactant solutions.

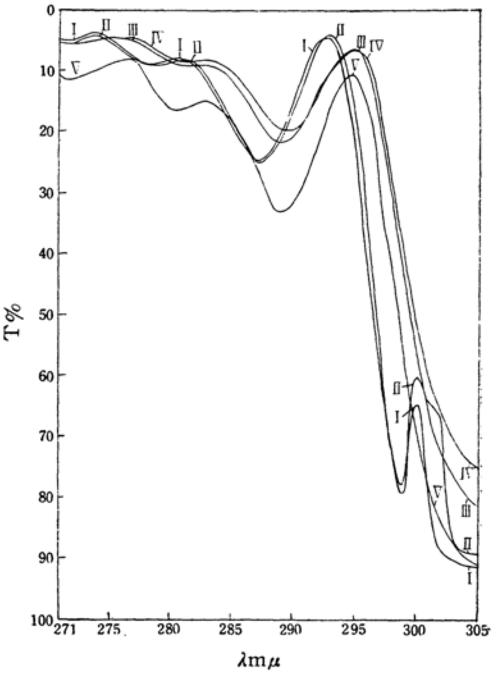

Fig. 8. Absorption spectra of phenanthrene. b=1 cm.. Measured one days after preparation. Concentration of phenanthrene=1.115×10^{-4} M/l. Solvent: I. Hexane, II. C_2H_5OH, III. 10% TMD+2% Hexane solubilized. IV, 10% TMD, V. 1% TMD.

Discussion

(1) From the changes of the absorption bands such as the time dependence and blue shift of the n band, the red shifts of the π and the B bands, it is apparent that the solubilizates are under the influences of some polar solvents.

(2) We suppose first that there is no water molecule in the micelle, and these spectral changes are caused by the longe-range electrostatic force in the water, and thus a solubilizate molecule and a water molecule are not in contact with each other.

This supposition is refuted by the consideration of the experiments of Foster[11]: he has shown that no spectral change occurs except when the functional group of the solute molecule and the solvent molecule,

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[11] L. S. Foster, *J. Am. Chem. Soc.*, **77**, 1417 (1955).

which has the ability to affect the electronic state of the former, are in contact with each other directly. Therefore it is sure that the solubilizate must be in contact with some polar molecules.

(3) We suppose next that there is no water molecule in the micelle but the polar groups of some surfactant molecules are contained in the micelle.

Such a random structure of the micelle is hardly acceptable.

(4) Next we suppose that there are no water molecules in the micelle but the solubilizate such as azobenzene and Yellow OB, which have azo or amino groups, are in the palisade and these groups of the solubilizate molecules are in contact with some water molecules.

But the changes of the π bands show that the benzene rings are also under the influence of water molecules. To explain this fact, the greater part of a solubilizate molecule is in the aq. phase and the lesser part of it is in the palisade. Such a situation is not conceivable. Especially in the case of anthracene and phenanthrene which have no hydrophilic group and are never solubilized in the palisade, there occur also similar spectral changes.

(5) When a small amount of the nonpolar organic liquid is added to the solubilized absorber systems, the spectral changes occur. The solubilized nonpolar liquid must be thought to drive the water molecules which are contained out of the micelle.

When the concentration of the surfactant is in creased, the spectral changes also becomes less. This is thought to show that the micelles become more compact with increasing concentration, and at the same time the number of the water molecules contained in the micelle decreases.

From the consideration discussed above we must conclude that some water molecules are contained in the micelle at least until 10% surfactant concentration.

(6) The reason why surfactant micelles contain some water molecules may easily be understood from the consideration of the fact that such a small volume as the interior of micelles are under the intense thermal agitation of the water molecules.

(7) Because of the fact that some water molecules are contained in the micelle, it is natural to think that in the initiation of the emulsion polymerization[12], the catalyser which is in the aq. phase diffuses into the inside of the micelle and activates the modifier or monomer molecule solubilized there.

Summary

From the spectral changes of the n, π, and B bands, it is concluded that the surfactant micelle, at least until 10% concentration, contains some water molecules.

The authors wish to express their sincere thanks to Prof. N. Sata for his advice and encouragement, and to The Kaō Sekken Co., The Daiichi Seiyaku Co. and The Nihon Yusi Co., for offering us the samples.

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[12] W.D. Harkins, "Physical Chemistry of Surface Films", Reinhold Publishing Co., New York (1952).