The Absorption Spectra of Oil-soluble Dyes Solubilized by a Polysoap and a Monosoap

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Polysoaps constitute a very special class of soap. In a certain sense the micelles are already formed, because each molecule of polysoap may be regarded as the equivalent of a micelle, each molecule acting as a prefabricated soap micelle.[1] The phenomena associated with the critical concentration and the micelle equilibrium should, accordingly, be absent from polysoap solutions. From this point of view the polysoap is entirely different from ordinary soaps. Strauss and his co-workers[1-5] have extensively studied the solubilization effects of cationic polysoap, formed by adding dodecyl bromide to polyvinylpyridine, and have found that polysoap molecules undergo a considerable change in their structure upon solubilization. They have also pointed out that the solubilization mechanism depends on the nature of the solubilizates.[3,5]

However, no systematic study has as yet been reported either of the solubilization of oil-soluble dyes by polysoap or of the differences between polysoap and monosoap in the solubilization mechanisms of the dyes. The results of such a study, dealing with 1-benzeneazo-2-naphthol and three 1-nitrobenzeneazo-2-naphthols, are presented in this paper and in a subsequent paper. These three 1-nitrobenzeneazo-2-naphthols are equivalent in molecular weight, differing only in the position of the nitro group in the benzene ring.

Spectral measurement furnishes a simple means of obtaining information on the states of solubilized dyes in polysoap and monosoap solutions, although such a measurement is qualitative. In this experiment the absorption spectra of the dyes were measured in polysoap and monosoap solutions, and also in some hydrocarbons for purposes of comparison. The polysoap used was an *n*-dodecyl bromide addition compound of poly-2-vinylpyridine, while the monosoap was *n*-dodecyl-α-picolinium bromide, which seems to be closely related in its chemical structure to the polymeric unit of the above polysoap.

The present paper is a study of absorption spectra, leading to an understanding of the states of solubilized dyes in polysoap and monosoap solutions and of the way in which they are solubilized.

Experimental

Polysoap (*n*-Dodecyl Bromide Addition Compound of Poly-2-vinylpyridine).—Poly-2-vinylpyridine was prepared by polymerizing freshly-distilled 2-vinylpyridine (b. p. 57°C at 17 mmHg) in ligroin (purified by sulfuric acid) in the presence of benzoyl peroxide at 40°C for 3 days, followed by the purification procedure described by Strauss et al.[6] The nitrogen content of the purified polymer was 13.29%; calcd. 13.33%. (All the nitrogen analyses reported in this paper were performed by the Elementary Analysis Center, Kyoto University.) The intrinsic viscosity, $[\eta]$, in 92 weight per cent ethanol was 0.636 at 25°C; this value corresponds to a molecular weight of 1.27×10^5 and a degree of polymerization of 1.2×10^3, assuming that the values of K and α in a viscosity equation, $[\eta]=KM^\alpha$, are equal to those of poly-4-vinylpyridine.[7]

The polymer was then quaternized with *n*-dodecyl

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[1] L. H. Layton and U. P. Strauss, *J. Colloid Sci.*, **9**, 149 (1954).

[2] M. E. L. McBain and E. Hutchinson, "Solubilization," Academic Press, New York (1955), p. 236.

[3] U. P. Strauss and N. L. Gershfeld, *J. Phys. Chem.*, **58**, 747 (1954).

[4] U. P. Strauss and S. S. Slowata, ibid., **61**, 411 (1957).

[5] U. P. Strauss and L. H. Layton, ibid., **57**, 352 (1953).

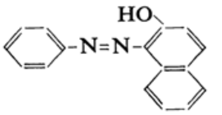
[6] U. P. Strauss and E. G. Jackson, *J. Polymer Sci.*, **6**, 649 (1951).

[7] A. G Boyes and U. P. Strauss, ibid., **22**, 463 (1956).

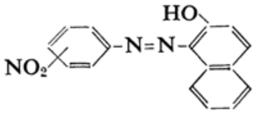
bromide (b. p. 112°C at 3.0 mmHg, prepared from dodecyl alcohol of a high purity) in nitroethane at 80°C for 13 days. Purification was accomplished as reported by Strauss et al.,⁶⁾ using petroleum ether instead of isoöctane and ligroin. The polysoap finally purified contained 6.72% nitrogen and 16.70% bromine. The polysoap gave a slightly acidic pH in water (the 0.10% solution had a pH of 3.48). Titration with sodium hydroxide gave an average value of 4.82×10^{-3} equivalent of hydrogen ions per gram of polysoap. From these analytical data, it follows that 33.5% of the nitrogen is quaternized with *n*-dodecyl bromide, while 10.0% carries hydrogen bromide. Only one-third of the nitrogen reacted with *n*-dodecyl bromide in spite of the high temperature and the long time of reaction.

Monosoap (*n*-Dodecyl-*α*-picolinium Bromide).—Monosoap was prepared by the quaternization of *α*-picoline with *n*-dodecyl bromide according to the ordinary method. The soap was then purified by repeated recrystallization from acetone. The nitrogen was 4.08% (calcd. 4.09%); Br, 23.16% (calcd. 23.35%).

Oil-soluble Dyes.—The four dyes, 1-benzeneazo-2-naphthol (abbreviated to BAN) and 1-(*ortho-*, *meta-* and *para-*)nitrobenzeneazo-2-naphthol (abbreviated to *o*-nitro-BAN, *m*-nitro-BAN and *p*-nitro-BAN respectively), were synthesized by coupling diazotized aniline or nitroaniline with *β*-naphthol in alkaline solutions. The starting materials—aniline, (*ortho-*, *meta-* and *para-*)nitroaniline, and *β*-naphthol—were purchased from the Wako Pure Chemicals Co. The crude dyes were thoroughly washed with water and dried in vacuo. The purification of the dyes was carried out by repeated recrystallization from benzene or a benzene-methanol mixture. The dyes were finally obtained as fine crystalline powders.



BAN



(*o*-, *m*-, *p*-)Nitro-BAN

The wavelengths of the absorption maxima ($\lambda_{\max}$) of these dyes in ethanol and the molar extinction coefficients ($\varepsilon_{\max}$) at the maxima are listed in Table I.

TABLE I. THE $\lambda_{\max}$ AND $\varepsilon_{\max}$ OF OIL-SOLUBLE DYES

Dyes	$\lambda_{\max}$, mμ	$\varepsilon_{\max}$, $\times10^{-4}$
BAN	485	1.46
o-Nitro-BAN	495	2.11
m-Nitro-BAN	478	1.65
p-Nitro-BAN	491	2.52

The Preparation of Polysoap Solutions.—Polysoap solutions were prepared according to the method of Strauss et al.⁴,⁸⁾ The residual HBr was removed from the polysoap by ion-exchange as follows: an anion-exchange resin, Amberlite IRA-410, in the hydroxide form, contained in a bag made of Visking's dialysis casing, was immersed briefiy in an aqueous solution of the polysoap to raise the pH to around 6.

Solubilization.—The solubilization was run in a water bath at 30±0.1°C for 55 hr. to attain equilibrium. The method used was the same as that used in a previous investigation.⁹⁾ In the present experiment, appropriate concentrations of polysoap and monosoap were chosen for the solubilization of dyes on the basis of the results of a preliminary experiment, for the reason described under "Results and Discussion."

Absorption Spectra.—Spectral measurements were performed with a Shimadzu Model RS-27 automatic spectrophotometer at room temperature (about 30°C) immediately after the solubilization.

Results and Discussion

Figures 1 and 2 show the absorption spectra of solubilized dyes in polysoap and in monosoap solutions respectively. Since the solubilizing power of polysoap and monosoap is highly dependent on the structure of the dyes (this will be reported on in more detail in a subsequent paper), it is difficult to compare the spectra of the dyes solubilized by equal concentrations of polysoap and monosoap. It is, therefore, necessary to choose appropriate concentrations of soaps in order to obtain the maximum absorbance of solubilized dyes ranging from 0.6 to 0.8, a convenient range for the comparison of the spectra Unfortunately, the polysoap solution itself exhibits a slight yellow color depending on the

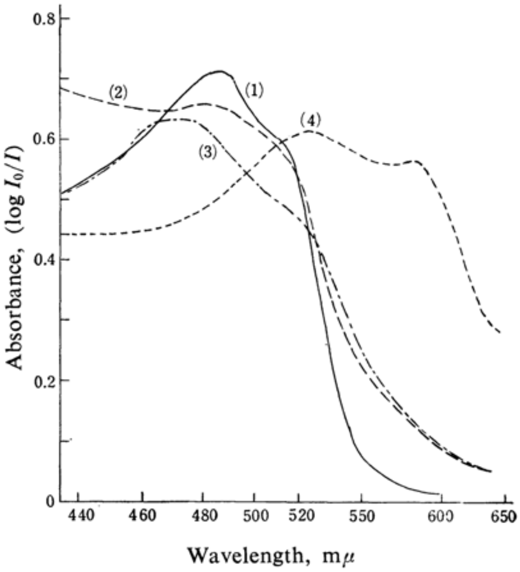


Fig. 1. Absorption spectra of oil-soluble dyes solubilized by polysoap.

(1) BAN (2) *o*-Nitro-BAN
(3) *m*-Nitro-BAN (4) *p*-Nitro-BAN

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8) L. H. Layton, E. G. Jackson and U. P. Strauss, ibid., 9, 295 (1952).

9) F. Tokiwa, This Bulletin, 36, 222 (1963).

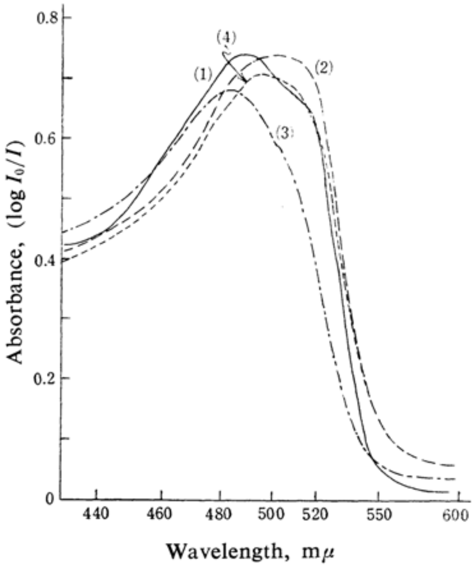

Fig. 2. Absorption spectra of oil-soluble dyes solubilized by monosoap.

(1) BAN (2) *o*-Nitro-BAN
(3) *m*-Nitro-BAN (4) *p*-Nitro-BAN

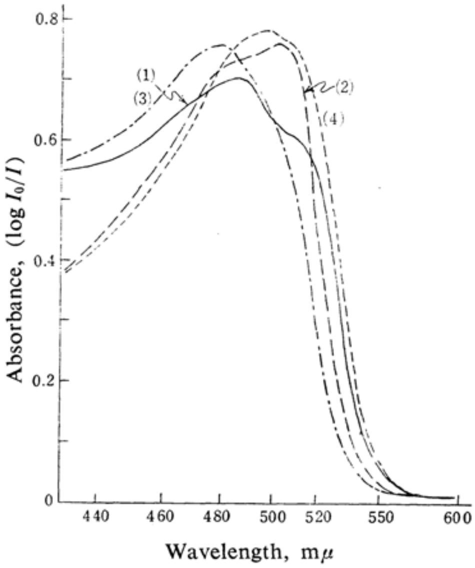

Fig. 3. Absorption spectra of oil-soluble dyes in benzene.

(1) BAN (2) *o*-Nitro-BAN
(3) *m*-Nitro-BAN (4) *p*-Nitro-BAN

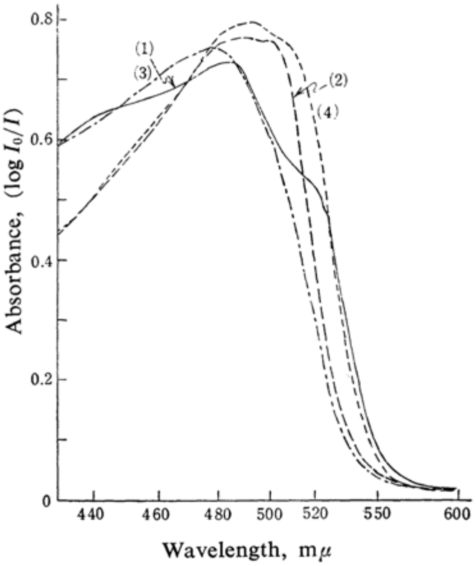

Fig. 4. Absorption spectra of oil-soluble dyes in hexane.

(1) BAN (2) *o*-Nitro-BAN
(3) *m*-Nitro-BAN (4) *p*-Nitro-BAN

TABLE II. THE $\lambda_{\max}$ OF THE DYES IN SOAP SOLUTIONS AND HYDROCARBONS

Dyes	$\lambda_{\max}$, mμ			
	Polysoap	Mono-soap	Ben-zene	Hexane
BAN	487	488	486	485
o-Nitro-BAN	480	502	502	(490)～500
m-Nitro-BAN	465～475	483	481	479
p-Nitro-BAN	523, 582	495	495	493

concentration, although its spectrum has no absorption maximum, as Fig. 5 shows. This makes the spectrum of the dye somewhat obscure because of the overlap of dye and polysoap spectra. Therefore, to show the spectrum of the dye alone, without the contribution from polysoap, each spectrum shown in Fig. 1 has been obtained by substracting the absorbance of polysoap from the observed absorbance.

It is generally accepted that, in most aqueous solutions of ordinary soaps, the solubilization of oil-soluble dyes occurs in the interior of the micelles.[10] Therefore, if the dyes studied are solubilized in the interior of the soap micelle, which consists of a dense hydrocarbon region, then some similarities are to be expected between the spectra of the dyes solubilized in soap solutions and those of the dyes dissolved in hydrocarbons.[11] Figures 3 and 4 illustrate the spectra of four dyes in benzene and in hexane respectively. Aside from the shapes of the spectra, one notes that the wavelength of the absorption maximum of each dye in a monosoap solution corresponds closely to that in hydrocarbons (Table II). The wavelength difference is between 0 and 4 mμ; in benzene the difference is much less.

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[10] M. E. L. McBain and E. Hutchinson, "Solubilization," Academic Press, New York (1955), pp. 45, 147.

[11] L. Michaelis and S. Granick, *J. Am. Chem. Soc.*, **67**, 1212 (1945).

This may indicate that the dyes studied are solubilized in the hydrocarbon region of monosoap micelles. In the case of BAN, furthermore, its spectra in both polysoap and monosoap solutions show a good similarity, as may be seen in Figs. 1 and 2. The similarity suggests that the way of the solubilization of BAN by both soaps is nearly the same. This suggestion is supported by the fact that the amounts of BAN solubilized by the two soaps are nearly equal, as will be shown in a following paper.

When one compares Fig. 1 with Figs. 2, 3 and 4, on the other hand, one notes that the spectra of nitro-BAN in polysoap solutions are not similar either to those in monosoap solutions or to those in hydrocarbons. These differences in spectra may be considered to arise from the fact that the state of nitro-BAN solubilized by the polysoap is not similar to that of nitro-BAN solubilized by the monosoap; they also suggest that nitro-BAN molecules are solubilized in different ways by the two soaps. It has been proposed that benzene and heptanol are solubilized between the polar heads of the side-chains of polysoap, in a manner similar to the micelle penetration which occurs with such polar materials as alcohols in ordinary soap solutions.[3,5] By analogy, whatever the detailed mechanism may be, the difference in spectra could be explained as follows: The loci of the solubilization of dyes in the polysoap molecule are not only the dense hydrocarbon region of the interior but also the polar region near the polymer backbone. In this case, the nitro group of the dye molecule seems to play an important role in the solubilization. Among the three nitro-BAN's, *p*-nitro-BAN exhibits a behavior totally different from that observed for the other dyes; that is, its two absorption maxima appear in the longer wavelength region. In view of the fact that the structures of these nitro-BAN molecules differ only in the position of the nitro group on the benzene ring, the solubilization of nitro-BAN molecules may depend upon their molecular volumes as well as on their polarities.

When the polysoap solution containing solubilized *p*-nitro-BAN was diluted with a large amount of ethanol (about 5 times by volume), the two peaks of its spectrum, at 523 and 582 mμ, disappeared and, simultaneously, a new absorption maximum arose, the wavelength of which is approximately equal to that of the maximum observed in hydrocarbons or in a monosoap solution. Any change in the spectrum of the dye molecule may be attributed to the redistribution of the electrons in the molecule.[11,12] Therefore, this means that dilution by ethanol changes the electron distribution in the *p*-nitro-BAN molecule; it also suggests that the electron distribution in this molecule is strongly affected by the polar region of the polysoap molecule as a result of the solubilization. In the case of the solubilization of *p*-nitro-BAN, especially, the polar region of the polysoap appears to act as a strong solubilizing locus.

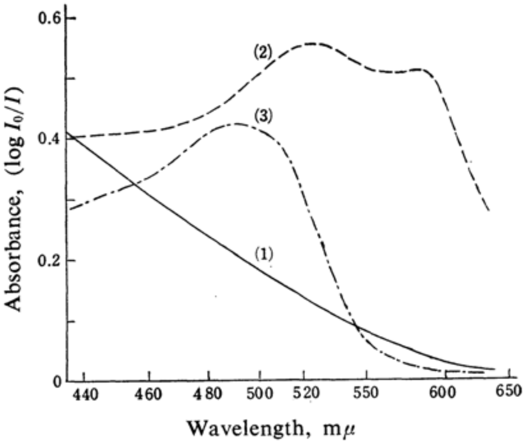

Fig. 5.

(1) Absorption spectrum of polysoap (1.0% aqueous solution): and the effect of dilution with ethanol on the spectrum of *p*-nitro-BAN
(2) Before dilution
(3) After dilution

Summary

The absorption spectra of several oil-soluble dyes, 1-benzeneazo-2-naphthol and three 1-nitrobenzeneazo-2-naphthols, have been measured in aqueous solutions of polysoap and monosoap and in hydrocarbons. The spectra of the above dyes in monosoap solutions are similar to those in hydrocarbons, while the spectra of dyes with a nitro group in polysoap solutions, especially the spectrum of *p*-nitro-BAN, are different. The differences in the solubilization behavior of the dyes in polysoap and in monosoap solutions and the ways in which the dyes are solubilized have been discussed. It has also been proposed that the loci of the solubilization in the polysoap molecule are not only the dense hydrocarbon region in the interior but also the polar region near the polymer backbone. In this case, the nitro group of the dye molecule seems to play an important role in the solubilization.

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[12] I. Maruta and F. Tokiwa, *J. Chem. Soc. Jacan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 1657 (1961); I. Maruta, ibid., **83**, 788 (1962).

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