The Solubilization of Oil-soluble Dyes by a Polysoap and a Monosoap

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In the preceding paper[1] the solubilization of oil-soluble dyes by polysoap was discussed by comparing the dye spectra in polysoap solutions with those in monosoap solutions and in hydrocarbons. In order better to understand the difference in solubilization between polysoap and monosoap, as well as the effect of solubilizate structure on the amounts solubilized, studies have now been made of the solubilizing power, viscosity and electrical conductivity of both polysoap and monosoap solutions.

The results of such studies are presented in this paper. As solubilizates, 1-benzeneazo-2-naphthol and three different 1-nitrobenzeneazo-2-naphthols were used, the same dyes as were employed in the preceding paper. The polysoap was obtained by the quaternization of poly-2-vinylpyridine with *n*-dodecyl bromide; the monosoap was *n*-dodecyl-α-picolinium bromide.

Experimental

Materials. — The materials used were polysoap (a *n*-dodecyl bromide addition compound of poly-2-vinylpyridine), monosoap (*n*-dodecyl-α-picolinium bromide) and four oil-soluble dyes; 1-benzeneazo-2-naphthol and three forms of 1-nitrobenzeneazo-2-naphthols (*ortho*, *meta* and *para*), which are abbreviated to BAN, *o*-nitro-BAN, *m*-nitro-BAN and *p*-nitro-BAN respectively. These materials were also used in the preceding investigation.[1]

A polyelectrolyte, poly-2-vinyl-*N*-ethylpyridinium bromide, was prepared from ethyl bromide and the poly-2-vinylpyridine described in the preceding paper. The method of Strauss et al.[2,3] was employed for preparing poly-4-vinyl-*N*-ethylpyridinium bromide. Analysis gave nitrogen 7.57%, bromine 32.3%.

Procedures.—Solubilizations were run in a water bath for 55 hr. to attain equilibrium, the method described in a previous paper[4] being employed. The amounts of solubilized dyes were determined by optical density measurements using a spectrophotometer, Hitachi Model EPU-2A.

Electrical conductivities were measured with a conductance bridge, Yanagimoto Model MY-7; the platinium electrodes were slightly platinized, and the cell constant was 0.482. The water used in preparing the solutions had a specific conductance of $1.0\sim1.5\times10^{-6}$ ohm^{-1} cm^{-1}.

The viscosities were measured with Ostwald-type viscometers, the flow times for pure water at 30°C being 67.7 and 140.5 sec.

Results and Discussion

The relationship between the solubilizing power of polysoap and the structure of oil-soluble dyes is shown in Fig. 1, where the extent of the solubilization of dyes is plotted against the concentration of polysoap. Figure 2 illustrates this relationship for monosoap. BAN, which contains no nitro group, is, in both soap solutions, more solubilized than the other dyes at any given soap concentration. This indicates that the introduction of a nitro group on the BAN molecule causes a lowering of the solubilization, probably because of the increase in its molecular volume[5] and the change in its polarity. The polysoap has greater solubilizing power, especially for dyes with a nitro group, than the monosoap. As for the dyes with a nitro group, it can be seen from Figs. 1 and 2 that in polysoap solutions the order of the amount solubilized is *m*-nitro-BAN>*p*-nitro-BAN>*o*-nitro-BAN, while in

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[1] F. Tokiwa, This Bulletin, 36, 1585 (1963).

[2] U. P. Strauss, S. J. Assony, E. G. Jackson and L. H. Layton, *J. Polymer Sci.*, 9, 509 (1952).

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

[4] F. Tokiwa, This Bulletin, 36, 222 (1963).

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

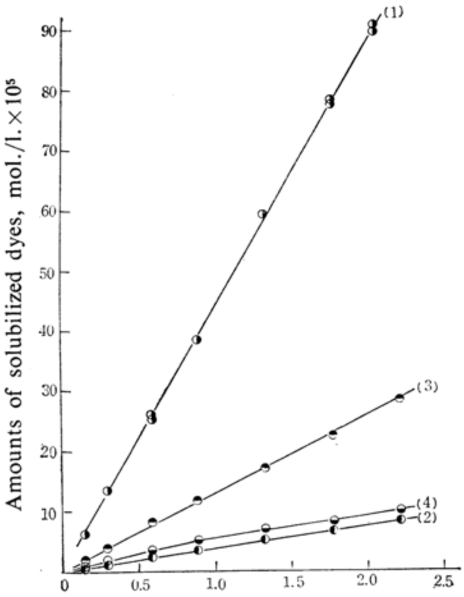

Fig. 1. The extent of solubilization of oil-soluble dyes plotted against the concentration of polysoap at 30°C.

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

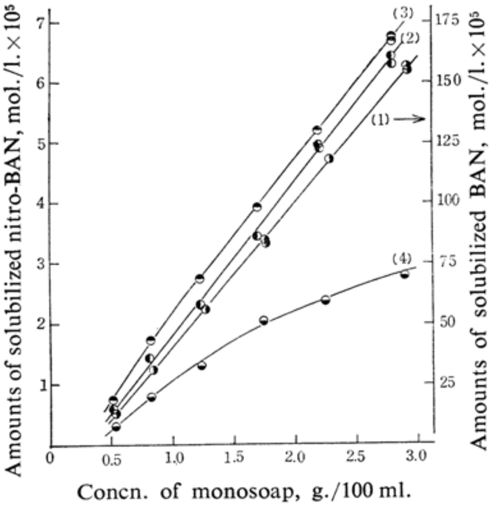

Fig. 2. The extent of solubilization of oil-soluble dyes plotted against the concentration of monosoap at 30°C.

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

monosoap solutions it is *m*-nitro-BAN>*o*-nitro-BAN>*p*-nitro-BAN. These results suggest that the solubilization depends not only on the volumes of the dye molecule, which may not considerably differ from one another in this case, but also on its structure.

The solubilizing powers of polysoap and monosoap at concentrations of 10.0 and 20.0 g./l. for each of the four dyes are compared in Table I, where the symbols C and S denote the concentration of soaps (g./l.) and the amount of solubilized dyes (mol./l.) respectively. The value of S/C represents the number of dye molecules solubilized by a gram of solubilizer. Comparing the values of S/C for polysoap and for monosoap, we find that the polysoap is a better solubilizer of the dyes with a nitro group than the monosoap. It is also of interest to calculate the value of T, the number of dye molecules which are solubilized per dodecyl group, since the presence of the dodecyl groups plays an important role in the solubilization.³⁾ These values are also given in Table I. From Table I, furthermore, we can calculate the ratio of the S/C-value of polysoap to that of monosoap (A) and the ratio of the T-value of polysoap to that of monosoap (B) at a given soap concentration. These values, which are listed in Table II, show more clearly the characteristics of the solubilization by polysoap and monosoap.

The significant feature of these results is the relatively high solubilization of the dyes with a nitro group in polysoap solutions. These results are most likely due to the greater number of soap molecules contained in a polysoap molecule; probably, also, the soap molecules form larger and hence more efficient micelles when they are attached to a polymer chain than when they are free. The hydrocarbon chain of the polymer, too, may contribute to the solubilization. The fact that the structure of polysoap molecules is less compact and more disordered than that of monosoap micelles⁷,⁸⁾ may also play a role. However, the way in which the solubilizing efficiency depends on the position of the nitro group in the dye molecule is not clear.

In order to learn more about the polysoap and monosoap molecules when they are saturated with the dyes, the viscosities of the solutions were measured. The effects of saturation with dyes on the viscosities of polysoap and monosoap solutions, in which the dyes reached their respective solubilization limits, are shown in Figs. 3 and 4, where the reduced viscosity, η_{sp}/C, is given as a function of the concentration of soaps. For comparison, the viscometric behavior of polyelectrolyte without a dodecyl side-chain is also illustrated in Fig. 3.

The curve of the polyelectrolyte is a familiar pattern: the reduced viscosity, which is very

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6) U. P. Strauss and L. H. Layton, *J. Phys. Chem.*, **57**, 352 (1953).

7) H. B. Klevens, *J. chim. phys.*, **49**, 615 (1952).

8) H. B. Klevens, *Kolloid-Z.*, **128**, 61 (1952).

TABLE I. SOLUBILIZATION LIMITS

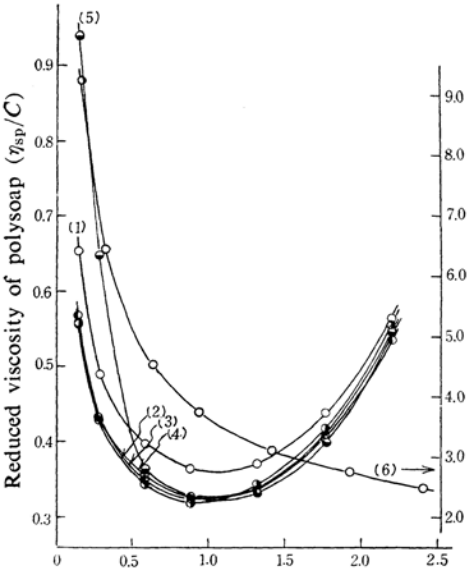
		BAN			*o*-Nitro-BAN		
Soap	*C* g./l.	*S* mol./l. $\times 10^5$	*S/C* mol./g. $\times 10^6$	*T* mol./mol. C_{12} $\times 10^3$	*S* mol./g. $\times 10^5$	*S/C* mol./g. $\times 10^6$	*T* mol./mol. C_{12} $\times 10^3$
Monosoap	10.0	40.0	40.0	13.7	1.82	1.82	0.622
	20.0	100	50.0	17.1	4.36	2.18	0.746
Polysoap	10.0	43.7	43.7	24.6	3.80	3.80	2.14
	20.0	87.2	43.6	24.5	7.40	3.70	2.08

		m-Nitro-BAN			*p*-Nitro-BAN		
Soap	*C* g./l.	*S* mol./l. $\times 10^5$	*S/C* mol./g. $\times 10^6$	*T* mol./mol. C_{12} $\times 10^3$	*S* mol./g. $\times 10^5$	*S/C* mol./g. $\times 10^6$	*T* mol./mol. C_{12} $\times 10^3$
Monosoap	10.0	2.18	2.18	0.746	1.06	1.06	0.363
	20.0	4.72	2.36	0.807	2.21	1.11	0.380
Polysoap	10.0	13.0	13.0	7.32	5.40	5.40	3.04
	20.0	25.8	12.9	7.26	9.20	4.60	2.59

TABLE II. THE COMPARISON OF THE SOLUBILIZING POWER OF POLYSOAP AND THAT OF MONOSOAP

Concn. of soap	BAN		*o*-Nitro-BAN		*m*-Nitro-BAN		*p*-Nitro-BAN	
g./l.	A	B	A	B	A	B	A	B
10.0	1.09	1.80	2.09	3.44	5.96	9.81	5.09	8.37
20.0	0.872	1.43	1.70	2.79	5.47	9.00	4.14	6.82

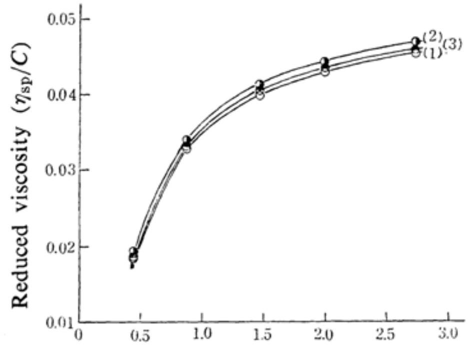
A: (*S/C*-value of polysoap)/(*S/C*-value of monosoap)
B: (*T*-value of polysoap)/(*T*-value of monosoap)



Concn. of polysoap, g./100 ml.

Fig. 3. The effect of saturation with dyes on the viscosity of polysoap at 30°C.

(1) None (2) BAN
(3) *o*-Nitro-BAN (4) *m*-Nitro-BAN
(5) *p*-Nitro-BAN
(6) Viscometric behavior of poly-2-vinyl-*N*-ethylpyridinium bromide at 30°C.



Concn. of monosoap, g./100 ml.

Fig. 4. The effect of saturation with dyes on the viscosity of monosoap at 30°C.

(1) None (2) BAN
(3) *m*-Nitro-BAN: *o*-nitro-BAN and *p*-nitro-BAN are similar to curve 3.

large at a high dilution because of the highly extended configuration of the flexible polyions, decreases with an increasing polymer concentration as the electrostatic repulsion between ionized groups is diminished. Since reduced viscosity can be interpreted as a measure of the effective specific volume of a polymer molecule,[3,9] the structure of the polysoap

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[9] U. P. Strauss, N. L. Gershfeld and E. H. Crook, *J. Phys. Chem.*, **60**, 577 (1956).

molecule in water is considerably more compact than that of the polyelectrolyte molecule. The effect of attaching dodecyl chains to a flexible polymer chain is to pull the polymer molecule together.

Now, let us consider the state of monosoap micelles and polysoap molecules after the solubilization of the dyes. In the case of the monosoap, the very small change in viscosity may be explained as being due to the swelling of the micelles as a result of the dye solubilization.¹⁰⁾ On the other hand, the addition of the dyes to a polysoap solution decreases the viscosity, except for that of *p*-nitro-BAN at low concentrations of polysoap. The observed decrease in viscosity can be ascribed to the contraction of polysoap molecules as a result of the dye solubilization. However, the difference in the effect of the structure of dyes on the viscometric behavior of polysoap is small, with the one exception described below.

Among the dyes studied, *p*-nitro-BAN produced an extra-ordinary increase in the viscosity of the polysoap solution upon its solubilization. The reason for this experimental finding is not clear. However, the steep rise of curve 5 in Fig. 3 in the low concentration region of polysoap may be an indication of either an anomalous extension of polysoap molecules or of an anomalous interaction among different polysoap molecules. According to Strauss et al.³⁾ the following mechanism also seems possible. The dye molecules are predominantly solubilized, with their polar nitro groups located in the polar region near the polymer backbone and with their hydrophobic portions extending into the hydrocarbon region of the polysoap molecule. This will contract the polar region, which, therefore, will be less able to shield the hydrocarbon region from the aqueous medium. The hydrocarbon which is thus exposed at the surface of the polysoap molecule will be attracted by the van der Waals force to similarly-exposed hydrocarbon of other polysoap molecules, with the resul that the polysoap molecules will tend to stick to one another. However, the reason why such an anomalous increase in viscosity occurs exclusively in the case of the solubilization of *p*-nitro-BAN and why it appears in the low concentration region of polysoap is not explainable by the above mechanism.

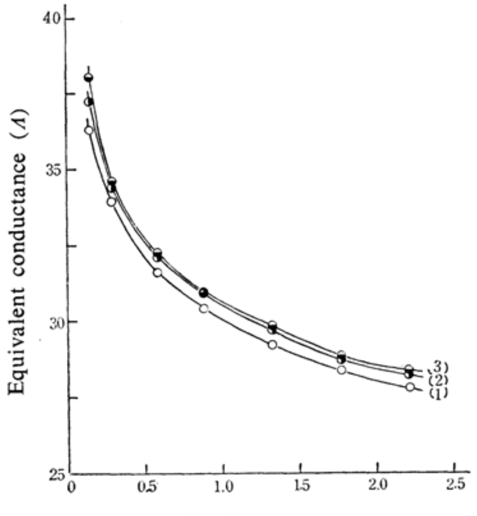

Fig. 5. The effect of saturation with dyes on the equivalent conductance of polysoap at 30°C.

(1) None (2) BAN
(3) *p*-Nitro-BAN: *o*-nitro-BAN and *m*-nitro-BAN are similar to curve 2.

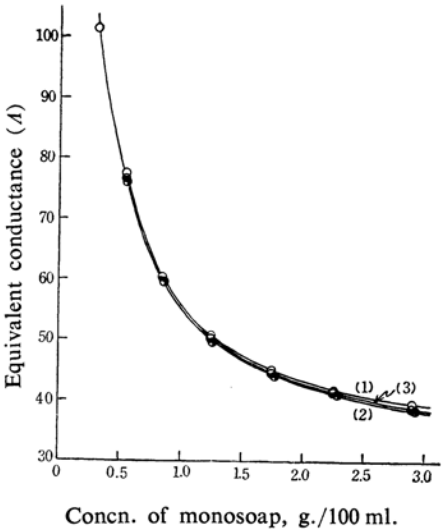

Fig. 6. The effect of saturation with dyes on the equivalent conductance of polysoap at 30°C.

(1) None (2) BAN
(3) *p*-Nitro-BAN: *o*-nitro-BAN and *m*-nitro-BAN are similar to curve 3.

To find out more about the nature of these effects, a study was also made of the electrical conductance of polysoap solutions containing solubilized dyes. Figure 5 illustrates the effect of saturation with dyes on the equivalent conductance, Λ, as a function of the polysoap concentration, where the values of Λ are based on the bromide-ion content of the polysoap. A similar figure for the monosoap is given in Fig. 6.

With the monosoap, the conductance is affected very little by solubilized dyes. With

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10) A. F. H. Ward and A. G. Chitale, *Proc. 2nd Int. Cong. Surface Activity*, Vol. 1, 319 (1956).

the polysoap, contrary to expectation, each solubilized dye produces a small increase in conductance, but no significant difference among them could be found. This suggests that the locus of the solubilization of the dyes inside the polysoap molecule does not strongly affect the conductance. The finding also eliminates the possibility that the anomalous increase in viscosity with *p*-nitro-BAN is caused directly by the electrical charge effect.

Summary

The solubilization of several oil-soluble dyes, 1-benzeneazo-2-naphthol (BAN) and three 1-nitrobenzeneazo-2-naphthols (nitro-BAN), by a polysoap and a monosoap has been studied by measuring the solubilizing power, the viscosity and the electrical conductance of the solutions of both soaps.

The polysoap is a better solubilizer than the monosoap. BAN was more solubilized than nitro-BAN at any given concentration of soap. The amount of nitro-BAN solubilized by the polysoap was increased in the order *m*-nitro-BAN$>$*p*-nitro-BAN$>$*o*-nitro-BAN, while the solubilization by the monosoap was in the order *m*-nitro-BAN $>$ *o*-nitro-BAN $>$ *p*-nitro-BAN. However, there appears to be no simple interpretation of the effect of the structure of dyes upon the solubilization. The addition of the dyes to the polysoap solutions decreased the viscosity, except for that of *p*-nitro-BAN at low concentrations of polysoap. *p*-Nitro-BAN produced an anomalous increase in the viscosity, the reason for this being not certain. In the case of polysoap, every solubilized dye produced a small increase in electrical conductance, but no significant difference among them could be found.

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