BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 179—185 (1966)

The Interaction between a Polysoap and a Monosoap

By Fumikatsu TOKIWA

Kao-Atlas Laboratory, Kao Soap Co., Ltd., Minato-Yakushubata, Wakayama

(Received June 10, 1965)

The way in which a cationic polysoap, prepared by quaternizing the nitrogen of poly-2-vinylpyridine with *n*-dodecyl bromide, interacts with additives, such as a cationic monosoap (*n*-dodecyl-α-picolinium bromide), a non-ionic surfactant (polyoxyethylene dodecyl ether) and potassium bromide, has been studied in aqueous solutions in terms of the viscosity and solubilizing power for oil-soluble dyes of the mixed solutions of the polysoap and the additives. An experiment on the effects of these additives on the behavior of a polyelectrolyte (poly-2-vinyl-*N*-ethylpyridinium bromide), prepared from the same parent polymer as the polysoap, has also been included for the purpose of comparison. The hydrophobic hydrocarbon chains in the polysoap and additive molecules play an important role in the interaction of the polysoap with the additives. Co-micellization or mixed micellization occurs between the polysoap and the monosoap or the non-ionic surfactant in aqueous solutions.

In previous papers[1,2] the solubilization behavior of cationic polysoap and monosoap was compared in terms of the spectra of some oil-soluble dyes solubilized by both soaps,[1] as well as in terms of the solubilizing power, the viscosity and the electrical conductivity of the soap solutions.[2] In general, a polysoap molecule has been regarded as a model of a micelle of ordinary soaps in the sense that the molecule acts as a prefabricated soap micelle.[3] However, this is not necessarily true. It has, for instance, been pointed out by the present author that the polysoap, *n*-dodecyl bromide addition compound of poly-2-vinylpyridine, differs considerably in its behavior, such as in the solubilization of oil-soluble dyes, from the monosoap, *n*-dodecyl-α-picolinium bromide, which is considered to be very similar in its chemical structure to the polymeric unit of the polysoap.[1,2] It will also be of interest to study the properties of mixed solutions of the polysoap, which is a long flexible chain of a macroion with a great number of hydrocarbon side chains, with the monosoap.

With respect to the properties of aqueous solutions of the mixtures of a cationic polysoap and a monosoap, Narasaki and Ito[4,5] have reported that whether the addition of the monosoap to the polysoap solutions leads to a synergistic or to an antigistic effect on some physicochemical property varies from case to case.

The present paper is a study of mixed solutions of a polysoap and a monosoap in terms of viscosity and solubilization; this study leads to an understanding of the way in which the polysoap and the monosoap interact in aqueous solutions. The effects of a simple electrolyte and a non-ionic surfactant upon the behavior of the polysoap are also included. An experiment in which the polysoap was replaced by the polyelectrolyte prepared from the same parent polymer as the polysoap is also included for purposes of comparison.

Experimental

Materials.—The polysoap, *n*-dodecyl bromide addition compound of poly-2-vinylpyridine, was prepared and purified by a method previously described.[1] The molecular weight of the parent polymer, poly-2-vinylpyridine, was 1.16×10^5, as estimated from its intrinsic viscosity in 92% ethanol by weight[6]; this value corresponds to a degree of polymerization of 1.10×10^3. The analysis of the polysoap revealed that 32.5% of the nitrogen was quaternized with *n*-dodecyl bromide, while 9.6% carried hydrogen bromide.

The monosoap, *n*-dodecyl-α-picolinium bromide, was prepared by the quaternization of α-picoline with *n*-dodecyl bromide according to the ordinary method. The soap was then purified by repeated recrystallizations from acetone.

The polyelectrolyte, poly-2-vinyl-*N*-ethylpyridinium bromide, was prepared from ethyl bromide and the poly-2-vinylpyridine described above. The method of Strauss et al.[7] was employed from preparing poly-4-vinyl-*N*-ethylpyridinium bromide. Analysis gave nitrogen 7.57% bromine 32.3%.

The non-ionic surfactant, polyoxyethylene dodecyl ether (abbreviated hereafter as PODE), was the same sample as that used in a previous investigation[8]. The

---

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

[2] F. Tokiwa, ibid., **36**, 1589 (1963).

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

[4] H. Narasaki and N. Ito, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **64**, 1790 (1961).

[5] H. Narasaki, ibid., **64**, 1955 (1961).

[6] A. G. Boyes and U. P. Strauss, *J. Polymer Sci.*, **22**, 463 (1956).

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

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

average degrees of the polymerization of polyoxyethylene chain, p, of the two samples used were 7.6 and 15.8, the number written after PODE representing the value of p.

The potassium bromide was a special-grade product obtained from the Wako Pure Chemicals Co. Solubilizates, the 1-benzeneazo-2-naphthol and 1-p-nitrobenzeneazo-2-naphthol (abbreviated hereafter as BAN and p-nitro-BAN respectively) were the same samples as those described in a previous paper.1) The details of these samples were reported in that paper

Procedure.—The solubilizations were run in a water bath at 30±0.1°C for 40 hr. in order to attain equilibrium, the method described in a previous paper8) being employed. The amount of solubilized dyes was determined by optical density measurements using a spectrophotometer, Shimadzu Model B60.

The viscosities were measured in a water bath at 30±0.01°C with Ostwald-type viscometers, the flow times for pure water at 30°C being 102.8 and 128.3 sec.

Results

The viscometric behavior of the polysoap in pure water and in aqueous solutions of additives, i. e., monosoap, potassium bromide and PODE, is shown in Figs. 1 and 2, where the reduced viscosity, η_{sp}/c of the polysoap is plotted against the concentration, c. In this paper the aqueous solution with the same concentration of one of the above additives was taken to be the solvent for the polysoap.

Figure 1 shows the η_{sp}/c - c curves of the polysoap at a constant concentration of the additives. The η_{sp}/c of the polysoap in the monosoap solution is lower than that in water, and the η_{sp}/c - c curve runs linearly with c, giving an intrinsic viscosity, $[\eta]$, of 0.17. The curve in the potassium bromide solution is also linear and $[\eta]=0.17$. On the other hand, the η_{sp}/c in the PODE solution becomes abnormally higher as the concentration of the polysoap decreases. Figure 2 illustrates the effect of the concentration of the additives on the η_{sp}/c of the polysoap. Each additive influences the polysoap viscosity in a different way. The viscosity in the PODE solution increases abruptly with the increase in the PODE concentration. The viscosity rise of the polysoap in the PODE solution became more striking with the increase in the polyoxyethylene chain-length of PODE.

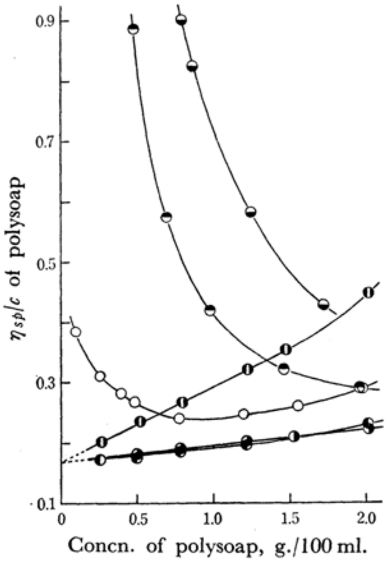

Fig. 1. The reduced viscosity vs. concentration of polysoap curves at a constant concentration of 0.77×10^{-2} M monosoap (◐), 2.26×10^{-2} M monosoap (◑), 2.05×10^{-2} M PODE-7.6 (◓), 2.11×10^{-2} M PODE-15.8 (◒) or 2.03×10^{-2} M KBr (◍); polysoap alone (○) at 30°C.

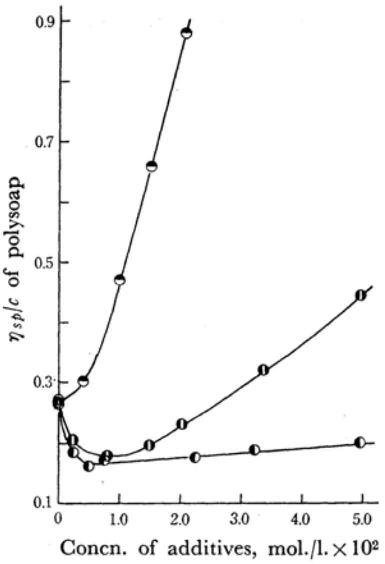

Fig. 2. The effect of additive concentrations on the reduced viscosity of polysoap of a constant concentration at 30°C: ◐, monosoap (polysoap concn. 0.407 g./100 ml.); ◓, PODE-7.6 (polysoap concn. 0.498 g./100 ml.); ◍, KBr (polysoap concn. 0.497 g./100 ml.).

The results of the solubilzation of BAN by the mixed solutions of the polysoap with the monosoap, potassium bromide or PODE are shown in Figs. 3 and 4. Figure 3 shows the amounts of BAN solubilized by that mixed solution in which the concentration of the polysoap is varied while that of the additive remains constant. Since the monosoap and PODE have a solubilizing power above their critical micelle concentration (CMC), the amount of BAN solubilized by the mixed solutions is greater than that solubilized by the polysoap solution alone. However, the effect of the monosoap on the solubilization differs from that of PODE. Figure 4 illustrates the effect of the additive concentrations on the solubilizing power of that mixed solution in which the concentration of the polysoap remains constant while that of the additive is varied. For comparison, the solubilizing power of the solution of the monosoap or PODE without the polysoap is also given in Fig. 4. The presence of potassium bromide slightly lowers the solubilizing power of the polysoap.

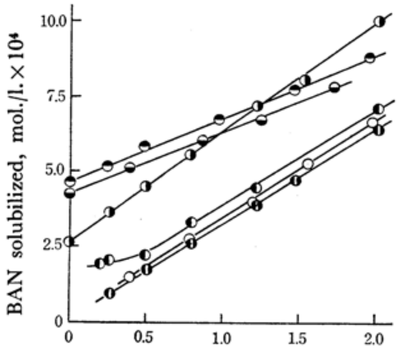

Fig. 3. The solubilization of BAN vs. concentration of polysoap curves at a constant concentration of 0.77×10^{-2} M monosoap (◐), 2.26×10^{-2} M monosoap (◑), 2.05×10^{-2} M PODE-7.6 (◓), 2.11×10^{-2} M PODE-15.8 (⊖) or 2.03×10^{-2} M KBr (◍); polysoap alone (○) at 30°C.

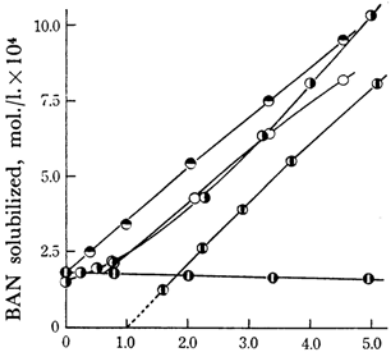

Fig. 4. The effect of additive concentrations on the solubilization of BAN by the mixed solutions of polysoap and additive at 30°C: ◑, monosoap (polysoap concn. 0.407 g./100 ml.); ◓, PODE-7.6 (polysoap concn. 0.498 g./100 ml.); ◍, KBr (polysoap concn. 0.497 g./100 ml.); ⦶, monosoap alone; ○, PODE-7.6 alone.

The results of the solubilization of *p*-nitro-BAN by the same solutions are shown in Fig. 5. *p*-Nitro-BAN showed a more characteristic solubilization behavior than the two other nitro substituents studied in a previous experiment.2) The amount of *p*-nitro-BAN solubilized by the mixed solution of the polysoap with the monosoap or PODE is considerably smaller than that solubilized by the polyaoap solution alone, in spite of the presence of the monosoap or PODE with solubilizing power.

For comparison, the viscosities of the polyelectrolyte with no dodecyl side chain, in the absence of and in the presence of the additives, are shown in Fig. 6. The η_{sp}/c - c curve of the polyelectrolyte

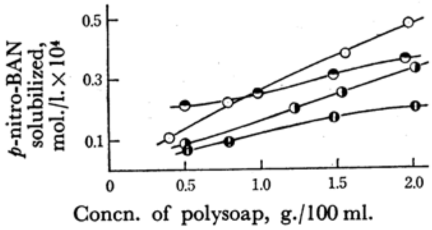

Fig. 5. The solubilization of *p*-nitro-BAN vs. concentration of polysoap curves at a constant concentration of 2.26×10^{-2} M monosoap (◑), 2.05×10^{-2} M PODE-7.6 (◓) or 2.03×10^{-2} M KBr (◍); polysoap alone (○) at 30°C.

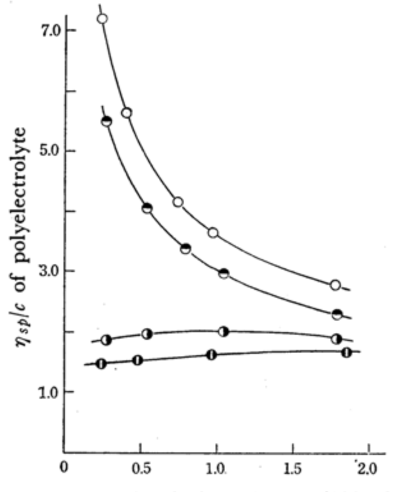

Fig. 6. The reduced viscosity vs. concentration of polyelectrolyte curves at a contant concentration of 2.03×10^{-2} M monosoap (◑), 2.06×10^{-2} M PODE-7.6 (◓) or 2.00×10^{-2} M KBr (◍); polyelectrolyte alone (○) at 30°C.

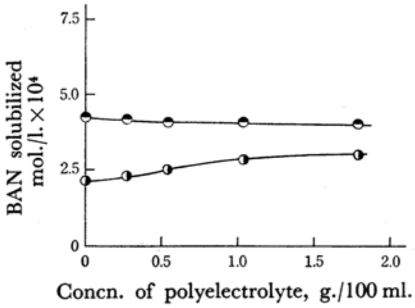

Fig. 7. The effect of poly electrolyte concentration on the solubilization of BAN by 2.03×10^{-2} M monosoap (◑) or 2.06×10^{-2} M PODE-7.6 (◓) at 30°C; the polyelectrolyte alone has no solubilizing power.

in water shows a familiar pattern. In the monosoap or potassium bromide solution, the reduced viscosity depression at the lower concentrations is remarkable. However, the polyelectrolyte molecule in a PODE solution behaves similarly to that in water.

Figure 7 shows the effect of polyelectrolyte concentrations on the solubilizing power of the monosoap and PODE for BAN. The polyelectrolyte makes the solubilizing power of the monosoap slightly higher, while it leaves that of PODE almost unchanged.

Discussion

Interaction between the Polysoap and the Monosoap.—The effect of potassium bromide on the viscosity of the polysoap has already been investigated by Strauss et al.[9] While at first the reduced viscosity of the polysoap decreases with an increase in the potassium bromide concentration, in time it reaches a minimum and then rises sharply, as may be seen in Fig. 2. They ascribed the initial viscosity decrease to the contraction of the polysoap molecule, and the viscosity rise with the added potassium bromide to interaction between the molecules. It the monosoap, which is a kind of electrolyte although it has a long hydrocarbon chain, would act on the polysoap only like potassium bromide, it might be expected to show a viscosity behavior similar to that in a potassium bromide solution. However, the results obtained in the monosoap solution are different from those obtained in the potassium bromide solution, as is shown in Figs. 1 and 2. This difference in viscosity behavior can be considered to arise from the long hydrocarbon chain in the monosoap molecule.

It is known that such polar materials with long hydrocarbon chain as higher alcohols are solubilized, with their polar groups located in the polar region near the polymer backbone and with their hydrocarbon chains penetrating into the hydrocarbon region of the polysoap molecule, in a way similar to their penetration into micelle. The solubilized hydrocarbon which supplies additional van der Waals' force to the hydrocarbon atomsphere inside the polysoap molecule causes the molecule to contract further.[3,7]

If the hydrocarbon chains of the monosoap cations penetrate into the interior of the polysoap molecule in the similar manner described above, this penetration will cause a contraction of the polysoap molecule. At the same time the surface of the polysoap molecule will be covered for the most part with hydrophilic ionized groups of the monosoap cations. An increase in the electrical charge on the surface leads to an enhancement of the electrostatic repulsion between different polysoap molecules, which will simultanously diminish the interaction between them. Although this will cause a swelling of the polysoap molecule, the van der Waals' attraction between hydrocarbon chains compensates for the ionic repulsion, so the resulting polysoap molecule is more compact than the initial molecule. This interaction between the polysoap and the monosoap may be regarded as a type of "co-micellization" or" mixed micellization." If the above argument is reasonable, the interaction may not be involved in the micelle formation of the monosoap. In fact, an insignificant change in viscosity could be found below and above the CMC of the monosoap (1.02×10^{-2} mol./l.), as may be seen in Fig. 1. After the penetration of the monosoap reaches the saturation point, the free monosoaps, which do not contribute directly to the co-micellization with the polysoap, will act on the polysoap in a way similar to potassium bromide.

On the other hand, in the case of the polyelectrolyte, there is no significant difference between the monosoap and potassium bromide in their effects on the reduced viscosity, as Fig. 6 shows. The hydrocarbon chain of the monosoap cation, which plays an important role in the interaction with the polysoap, can not act effectively with regard to the interaction with the polyelectrolyte having no long hydrocarbon side chains. In this case the monosoap cation seems to act on the polyelectrolyte as an electrolyte. This indicates the importance of the hydrocarbon chains of the polysoap, and supports the mechanism described above. However, the action of the monosoap cations on the polyelectrolyte is not completely negligible. The monosoap cations seem to interact slightly with the polyelectrolyte between the hydrocarbon chain of the cation and the hydrophobic portion in the backbone of the polyelectrolyte. The slight increase in the solubilizing power of the monosoap in a polyelectrolyte solution to be seen in Fig. 7 may be attributed to this interaction.

It is instructive to consider the intrinsic viscosity of the polysoap in the monosoap solution in the light of the general principle developed by Flory et al.[10] The Θ-solvent intrinsic viscosity, $[\eta]_\theta$, of poly-4-vinylpyridine[7] is:

$$[\eta]_\theta = 8.1 \times 10^{-4} M^{1/2}$$

Assuming that the $[\eta]_\theta$ of poly-2-vinylpyridine is equal to that of poly-4-vinylpyridine, the $[\eta]_\theta$ of the parent polymer used in this experiment, whose molecular wieght is 1.16×10^5, equals 0.276. From this value, according to Strauss' assumption,[7] one can calculate the expected value for the $[\eta]_\theta$ of the quaternization product, i. e., the polysoap, by the relation:

---

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

[10] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y. (1953), Chap. 12—14.

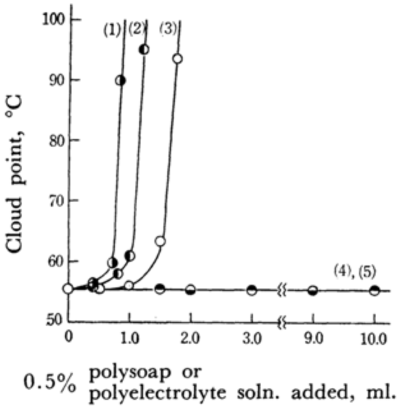

Fig. 8. The effect of polysoap and polyelectrolyte on the cloud point of PODE-7.6 solution of 10 ml.; PODE concn. (1) 0.82, (2) 1.13, (3) 1.63, (4) 0.80, (5) 1.60 g./100 ml. (1), (2) and (3) refer to the polysoap, and (4) and (5) refer to the polyelectrolyte.

$$[\eta]_{\theta,\mathrm{Q}} = [\eta]_{\theta,\mathrm{P}} \ (M_\mathrm{P}/M_\mathrm{Q})$$

where the subscripts P and Q refer to the parent polymer and the quaternization product respectively. The resulting estimate of $[\eta]_{\theta,\mathrm{Q}}$ is 0.15, slightly lower than the observed intrinsic viscosity of 0.17 shown in Fig. 1. It has been reported⁹⁾ that polysoaps can dissolve in aqueous media without phase separation, even when the intrinsic viscosity, $[\eta]$, is lower than the value of $[\eta]_\theta$. Further, the Einstein figure for a compact sphere is 0.025. Thus there is considerable room left inside the polysoap molecule for the solubilization for oil-soluble materials, even when the polysoap molecule is contracted by the penetration of monosoap cations.

The oil-soluble dye, BAN, would be mainly solubilized in an interior of a micelle, i. e., a dense hydrocarbon region of a micelle.²⁾ Therefore, it may be expected that an increase in the hydrocarbon region in the interior of the polysoap molecule, as a result of its co-micellization with monosoap molecules, will enhance the solubilizing power of the polysoap similarly to the effect of alcohols with a long hydrocarbon chain on the solubilizing power of ordinary soaps.¹¹⁾ As may be seen in Figs. 3 and 4, the amount of BAN solubilized by the mixed solution of the polysoap and the monosoap is greater than the total amount solubilized by the respective solution of the corresponding concentration. This is an indication of the synergistic effect of the mixed micelle of the polysoap and the monosoap. It is noteworthy that an increase in solubilizing power is appreciable in the mixed solution in which the concentration of the monosoap is lower than the CMC. On the other hand, the addition of potassium bromide slightly lowers the solubilizing power of the polysoap, because potassium bromide acts as only a simple electrolyte.

The results of the solubilization of *p*-nitro-BAN are very interesting in contrast with that of BAN. The amount of *p*-nitro-BAN solubilized by the mixed solution of the polysoap and the monosoap is considerably smaller than that solubilized by the polysoap solution alone. Essentially, *p*-nitro-BAN is not so solubilized by soaps as is BAN.²⁾ The present author has previously pointed out that the loci of the solubilization of oil-soluble dyes in the polysoap molecule are not only in the dense hydrocarbon region in the interior but also in the polar region near the polymer backbone. In the case of the solubilization of *p*-nitro-BAN especially, the polar region of the polysoap molecule acts as a strong solubilizing locus.¹,²⁾ With this picture in mind, the electrical charge on the surface of the polysoap molecule appears to be more correlated with the solubilization of *p*-nitro-BAN than the interior of the polysoap molecule. The addition of the monosoap or potassium bromide may change the electrical charge on the surface and at the same time change the atomosphere of the polar region. These changes, which may be disadvantageous for the solubilization of *p*-nitro-BAN, will lead to a lowering of the solubilizing power of the polysoap.

The Effect of a Non-ionic surfactant on the Behavior of the Polysoap.—Since PODE has no ionized group in its molecule, at first it may be expected to be able to show only the hydrocarbon effect on the polysoap. However, unexpected results for the viscosity were obtained. That is, the polysoap exhibited an extraordinary viscosity rise in the presence of PODE. In Figs. 1 and 2 we can see that the viscosity rise of the polysoap becomes higher with an increase in the ratio of PODE to the polysoap. A similar result was obtained by Narasaki when non-ionic surfactants, such as polyoxyethylene compounds, were added to the aqueous solution of the cationic polysoap prepared by quaternizing the nitrogen of poly-α-vinyl-β-ethylpyridine with *n*-dodecyl bromide and ethyl bromide.⁵⁾ The steep rise in the viscosity curves may be an indication of either an anomalous extension of the polysoap molecules or of an anomalous interaction between different polysoap molecules. The effect of the length of the polyoxyethylene tail on the viscosity of the polysoap —the longer the tail, the higher the viscosity— suggests that the polyoxyehtylene tail is responsible for the viscosity rise. Furthermore, the fact that the viscosity of the polyelectrolyte with no long hydrocarbon chain is almost not affected at all by PODE, as may be seen in Fig. 6, suggests the importance of the interaction by van der Waals'

---

11) M. E. L. McBain and E. Hutchinson, " Solubilization and Related Phenomena," Academic Press, New York (1955), pp. 45, 147.

force between the hydrocarbon chain of the polysoap and that of PODE. The two following mechanisms seem possible ways by which the polysoap interacts with PODE:

1) The PODE molecules penetrate into the hydrocarbon-water interface of the polysoap molecule in such a way that the polyoxyethylene tails are in the water, while the hydrocarbon chains are anchored in the hydrocharbon region of the polysoap molecule. The polyoxyethylene tails thus exposed on the surface of the polysoap molecule will interact with similarly-exposed polyoxyethylene tails belonging to other polysoap molecules, with the result that the viscosity of the poysoap will tend to increase. This interaction between polyoxyethylene tails may occur through the hydrogen bonding between the tails, probably by the medium of the water.

2) It is well-known that ordinary soap micelles swell as a result of hydrocarbon solubilization,11) and that sometimes polysoap molecules also swell under certain conditions of solubilization.9) The swelling of the polysoap molecules may be another type of mechanism to explain the reduced viscosity increase. When the PODE molecules penetrate into the polysoap molecule, the bulky polyoxyethylene tails may reduce the van der Waals' force between different parts of the same polysoap molecule as a result of a steric effect. As a result, the polysoap molecules will swell and extend beyond their original size, resulting in the viscosity rise.

Of course, it is difficult, on the basis of only the present experiment, to say which type of the mechanism is the more probable. The clear resolution of this problem will have to await further study. At any rate, however, the importance of polyoxyethylene tails in this interaction may easily be understood from the effect of the tail length.

In contrast to the synergistic effect of the solubilization exhibited by the polysoap and the monosoap, the amount of BAN solubilized by the mixed solution consisting of the polysoap and PODE is smaller than the total amount solubilized by the respective solution of the corresponding concentration. Namely, the PODE exerts an antigistic effect with regard to the solubilization of BAN. A similar effect has been observed when ethyl alcohol is added to some soaps.11) Whether the presence of additives leads to a greater or a lesser solubilizing power varies from case to case; no valid generalization is possible at this stage.

Evidence for the existence of the interaction between the polysoap and PODE is also provided by the disappearance of the "clouding phenomenon" which is observed in the aqueous PODE-7.6 solution. As Fig. 8 shows, the addition of a very small amount of the polysoap to the PODE solution raises the "cloud point." A further addition makes the cloud point disappear. This may be an indication of the formation of the co-micelle or mixed micelle of the polysoap and PODE.12) The amount of the polysoap required to make the clouding disppear increases in proportional to the concentration of PODE, the value being 5.4×10^{-2} g. polysoap/1 g. PODE. The clouding phenomenon is generally considered to be a phase separation resulting from the breaking of the hydrogen-bonding between the polyoxyehtylene portion of PODE and the water at a high temperature.13) Therefore, the disappearance of the clouding means that the polysoap makes the PODE, which is insoluble in water at an elevated temperature, soluble in water in terms of interaction or co-micellization.12)

On the other hand, the polyelectrolyte has no influence upon the cloud point of the PODE-7.6 solution, even when a fairly large amount of the polyelectrolyte is added to the solution, as may be seen in Fig. 8. This indicates that no interaction occurs between the polyelectrolyte and PODE.14) The absence of interaction must be due to the lack of long hydrophobic side chains in the polyelectrolyte molecule, for it is only in this respect that the two types of polymers, i. e., the polysoap and the polyelectrolyte, are chemically distinct. The interaction between the polysoap and PODE is, therefore, characterized by the presence of the dodecyl side chains in the polysoap molecules.

Summary

The viscosity and solubilizing power of a polysoap (the *n*-dodecyl bromide addition compound of poly-2-vinylpyridine) in aqueous solutions of a monosoap (*n*-dodecyl-α-picolinium bromide), a non-ionic surfactant (polyoxyethylene dodecyl ether, PODE) or potassium bromide have been measured. A similar experiment with a polyelectrolyte (poly-2-vinyl-*N*-ethylpyridinium bromide) has also been carried out for purposes of comparison. The effect of the polysoap on the cloud point of PODE has also been included.

The presence of the monosoap in the polysoap solution lowers the reduced viscosity, η_{sp}/c, of the polysoap. Potassium bromide has a similar effect at lower concentrations, while it causes the η_{sp}/c of the polysoap to rise at higher concentrations. The η_{sp}/c in the PODE solution is markedly high, and it becomes even higher as the PODE/polysoap ratio increases. In the case of the polyelectrolyte, on the other hand, the monosoap and potassium bromide show a similar effect on the η_{sp}/c of the

---

12) W. N. Macley, *J. Colloid Sci.*, **11**, 272 (1956).

13) A. M. Schwartz, J. W. Perry and J. Berch, "Surface Active Agents and Detergents," Vol. II, Interscience Publishers, New York (1957), p. 120.

14) I. Murata, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **83**, 861 (1962).

polyelectrolyte, and the PODE deos not affect the η_{sp}/c significantly. The addition of the monosoap to the polysoap solution promotes the solubilization for 1-benzeneazo-2-naphthol, while that of PODE lowers the solubilization. 1-*p*-Nitrobenzeneazo-2-naphthol exhibits an interesting behavior with regard to solubilization, and it is less solubilized by the mixed solution of the polysoap with the monosoap or PODE than by the polysoap solution alone. The cloud point of the aqueous PODE solution disappears when a very small amount of the polysoap is added.

From these results, the way in which the polysoap interacts with the monosoap or the non-ionic surfactant has been discussed. The interaction can be explained by the co-micellization or the mixed micellization of the polysoap and the nonosoap or the non-ionic surfactant.

The author wishes to express his hearty thanks to Professor Toshizo Isemura of Osaka University for his helpful discussion. He also wishes to express his appreciation to Kao Soap Co., Ltd. for permission to publish this paper.