# Solubilization Behavior of the Surfactant–Polyethylene Glycol Complex in Relation to the Degree of Polymerization

Fumikatsu Tokiwa and Kaoru Tsujii
*Research Laboratories, Kao Soap Company, 2-1-3 Bunka, Sumida-ku, Tokyo 131*

(Received March 22, 1973)

The solubilization behavior of the complexes composed of a surfactant and polyethylene glycol (PEG) toward an oil-soluble dye, Yellow OB, has been studied in relation to the degree of polymerization, *n*, of PEG. The solubilizing powers of the anionic surfactants, sodium dodecyl sulfate and sodium *p*-octylbenzene sulfonate, become greater on the addition of PEG, the extent depending on *n*. They increase as *n* increases. It is proposed that there are at least two different types of complexes, *i.e.*, "oligomeric" and "polymeric" PEG–surfactant complexes. The boundary between the oligomeric and polymeric PEG's is estimated to be around an *n* value of 10—15. With an oligomeric PEG–surfactant complex, the solubilization of Yellow OB would occur mainly in the hydrocarbon part of the surfactant micelle. With a polymeric PEG–surfactant complex, on the other hand, the solubilization would take place in the region of a complex rich in PEG. Electrical-conductivity and absorption-spectral data on the complexes are also included in this paper.

When a surfactant is mixed with a polymer in an aqueous solution, a kind of complex is formed by the binding of the surfactant molecules onto the polymer molecule.[1-9] The physicochemical properties of the respective components are, in general, changed by the formation of this complex. For example, the solubilizing power of the surfactant becomes greater on the addition of the polymer.[1,2,8,9] However, the mechanism of the increase in the solubilizing power by the polymer–surfactnat complex formation has not yet been elucidated. The dependence of this complex formation on the degree of polymerization of the polymer is also not well understood.

In the present work, the solubilization behavior of polymer–surfactant complexes toward an oil-soluble dye, Yellow OB, has been studied in relation to the degree of polymerization of the polymer, using two anionic surfactants and polyethylene glycols with different degrees of polymerization. Discussion has also been made of the mechanism of the solubilization of Yellow OB by the complexes composed of the surfactant and polyethylene glycol.

## Experimental

*Materials.* The samples of sodium dodecyl sulfate (abbreviated to $NaC_{12}S$) and sodium *p*-octylbenzene sulfonate (abbreviated to $NaC_8\phi S$) were the same as those used in previous experiments.[10,11] The polyethylene glycols (abbreviated to PEG) were of a reagent grade and had been purified by ion-exchange with Amberite IR-120 and IRA-410.[12] The average degrees of polymerization, *n*, of these PEG samples were 2, 3, 5, 9, 14, 20, 35, 91, and 136; these figures were determined from their hydroxyl values. The Yellow OB used as a solubilizate was of a reagent grade; it had been obtained from Wako Pure Chemicals Co. and recrystallized twice from an ethanol–water mixture (80/20).

*Solubilization.* The stock solution of a surfactant containing 1.0% PEG was prepared. A sample solution of the desired concentration was made up volumetrically by the dilution of the stock solution with the 1.0% PEG solution. The solubilization of Yellow OB was carried out in a water bath at 30±0.1 °C for 65 hours to attain equilibrium, a method described elsewhere[10] being employed. The amount of the solubilized dye was determined by optical-density measurements at a wavelength of 445 mμ with a Shimadzu Model AQV-50 spectrophotometer.

*Electrical Conductivity.* A sample solution was prepared by the procedure described above. The conductivity measurements were made with a Toa Electronics Model CM-1DB conductometer at 25±0.01 °C. The observed values were checked by measuring the conductivities of standard solutions of potassium chloride.

*Absorption Spectra.* The spectral measurements were performed with the above spectrophotometer at room temperature (about 25 °C).

## Results and Discussion

In Fig. 1, the amounts of solubilized Yellow OB, *A*, in the presence of PEG with different *n* values are plotted against the concentration, *C*, of $NaC_8\phi S$, the concentration of PEG being kept constant at 1.0%. The *A vs. C* curves similar to those shown in Fig. 1 were obtained for the $NaC_{12}S$–PEG complex. As may be seen in this figure, there is a linear relation between *A* and *C*. The solubilizing power of the PEG–$NaC_8\phi S$ complex, which corresponds to the slope of each *A vs. C* curve, increases as the degree of polymerization of PEG, *n*, increases. Further, the concentration of $NaC_8\phi S$ at which the solubilization sets in shifts to a lower concentration with an increase in the *n*.

*Mechanism of the Solubilization of Yellow OB by the Polymer–Surfactant Complex.* When a polymer is mixed with a surfactant in an aqueous solution, a

---

[1] S. Saito, *Kolloid Z.*, **154**, 19 (1957).
[2] S. Saito, *ibid.*, **158**, 120 (1958).
[3] T. Isemura and A. Imanishi, *J. Polymer Sci.*, **33**, 337 (1958).
[4] C. Botre, F. DeMartiis, and M. Solinas, *J. Phys. Chem.*, **68**, 3624 (1964).
[5] M. N. Jones, *J. Colloid Interface Sci.*, **23**, 36 (1967).
[6] K. E. Lewis and C. P. Robinson, *ibid.*, **32**, 539 (1970).
[7] M. L. Fishman and F. R. Eirich, *J. Phys. Chem.*, **75**, 3135 (1971).
[8] H. Lange, *Kolloid-Z. Z. Polymere*, **243**, 101 (1971).
[9] H. Arai, M. Murata, and K. Shinoda, *J. Colloid Interface Sci.*, **37**, 223 (1971).
[10] F. Tokiwa, *J. Phys. Chem.*, **72**, 1214 (1968).
[11] F. Tokiwa and K. Tsujii, *ibid.*, **75**, 3560 (1971).
[12] I. Maruta ,*Nippon Kagaku Zasshi*, **83**, 782 (1962).

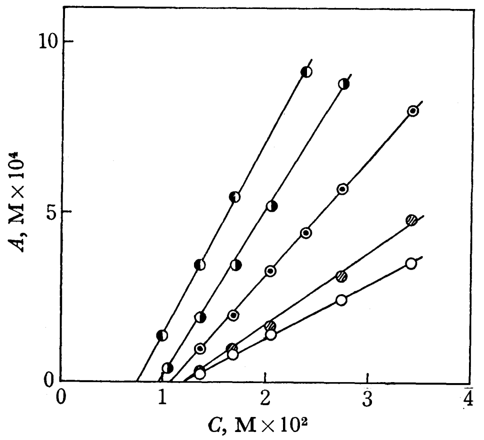

Fig. 1. The curves of the amount of solubilized Yellow OB *vs.* the concentration of NaC$_8\phi$S in the presence of PEG: ○, NaC$_8\phi$S alone; ▨, PEG-5; ⊙, PEG-14; ◑, PEG-35; ◐, PEG-136. The curves in the presence of PEG-2,3,9,20, or 91 are not shown here. The number written after PEG expresses the average degree of polymerization.

polymer–surfactant complex is formed by binding the surfactant molecules onto the long chain of the polymer molecule.[1–9] Further, it has been imagined that the binding of the surfactant molecules is not uniform along the polymer chain, but discrete, forming clusters or aggregates on it in such a manner as in micelle formation.[1,2,7–9] If this is the case, Yellow OB should be solubilized in these clusters. Such a solubilization mechanism in the complex is apparently analogous to that in the micelle of the surfactant alone. However, this mechanism itself can not account for such high solubilizing powers of the PEG–NaC$_8\phi$S complex, as may be seen in Fig. 1.

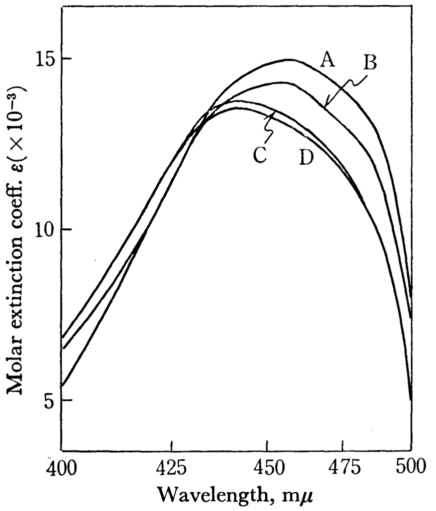

Fig. 2. The absorption spectra of Yellow OB in PEG alone (curve A), and in the aqueous solution of NaC$_8\phi$S (curve D), NaC$_8\phi$S–PEG-5 (curve C) or NaC$_8\phi$S–PEG-136 (curve B) at 1.0% NaC$_8\phi$S and PEG concentration.

Figure 2 shows the absorption spectra of Yellow OB in PEG alone as well as in aqueous solutions of NaC$_8\phi$S, NaC$_8\phi$S–PEG-5, and NaC$_8\phi$S–PEG-136. The spectra with NaC$_{12}$S and NaC$_{12}$S–PEG are almost the same as those shown in Fig. 2, though not specifically shown. With the NaC$_8\phi$S–PEG-136 complex, the shape of the Yellow OB spectrum and its absorption maximum, $\lambda_m$, are very similar to those observed with PEG alone. With the NaC$_8\phi$S–PEG-5 complex, on the other hand, the spectrum closely resembles the spectrum in the NaC$_8\phi$S solution. These results indicate that the solubilization behavior of NaC$_8\phi$S–PEG-136 toward Yellow OB is different from that of NaC$_8\phi$S–PEG-5. In the former case, the solubilization seems to occur in the PEG atmosphere of the complex, while in the latter case, it occurs mainly in the hydrocarbon part of the NaC$_8\phi$S micelle. The results also suggest that there are at least two different types of complexes, that is, the "polymeric" PEG–NaC$_8\phi$S complex and the "oligomeric" PEG–NaC$_8\phi$S complex.

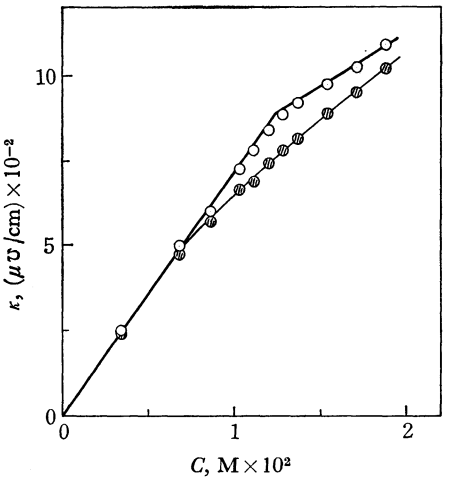

Fig. 3. The electrical conductivity *vs.* concentration curves for NaC$_8\phi$S in the absence and presence of PEG: ○, NaC$_8\phi$S–PEG-5; ▨, NaC$_8\phi$S–PEG-136. The bold line indicates the curve for NaC$_8\phi$S alone.

Figure 3 shows the conductivity *vs.* concentration curves for NaC$_8\phi$S in the absence and in the presence of PEG. There is no difference between the curves for NaC$_8\phi$S alone (bold line) and NaC$_8\phi$S–PEG-5 (open circle), while the curve for NaC$_8\phi$S–PEG-136 is different from that for NaC$_8\phi$S–PEG-5. This gives another piece of evidence for the existence of the two types of complexes.

To explain the solubilizing power of the complex being much greater than that of the surfactant micelle alone, we here propose new models of the polymer–surfactant complex, different from the model hitherto accepted,[1,2,7–9] based on the above spectral and conductivity data. The following models seem to be plausible for this explanation. The PEG polymer in the form of a random coil would be bound by the surfactant molecules with the hydrophilic group orientating to the aqueous phase; this model is analogous to the structure of polysoaps or proteins in an aqueous solution.[13,14] Probably, the solubilization of Yellow OB may take place in the region of a complex rich in PEG. The PEG itself is a very good solvent for this

---

[13] T. Nakagawa and H. Inoue, *Kolloid-Z. Z. Polymere*, **195**, 93 (1964).

[14] C. C. Bigelow, *J. Theoret. Biol.*, **16**, 187 (1967).

dye. An increase in solubilization on the addition of PEG can thus be explained by this mechanism. On the other hand, the PEG oligomer is gathered on the surface of the surfactant micelle in such a manner that polar substances, such as glycerol and dimethylphthalate, are adsorbed on the surface of the micelle.[15,16]

*Boundary between Oligomer and Polymer in Complex Formation.* The radius of a randam-coil polymer in solution, *i.e.*, the radius of gyration, is proportional to $n^{1/2}$ when the excluded volume effect of the polymer is negligible[17] and where $n$ is the degree of polymerization of the polymer. This condition may be satisfied in the present case.[18] Thus, the average volume of the polymer coil will be proportional to $n^{3/2}$.

It seems reasonable to assume that the solubilization capacity of the polymeric PEG–surfactant complex is proportional to the volume of the polymer coil, provided that the solubilization of Yellow OB occurs in the region of this polymer coil, as has been already described. Thus, the solubilizing power of the complex is expected to be proportional to $n^{1/2}$, since the number of the polymer molecules is inversely proportional to $n$ at a constant weight concentration.

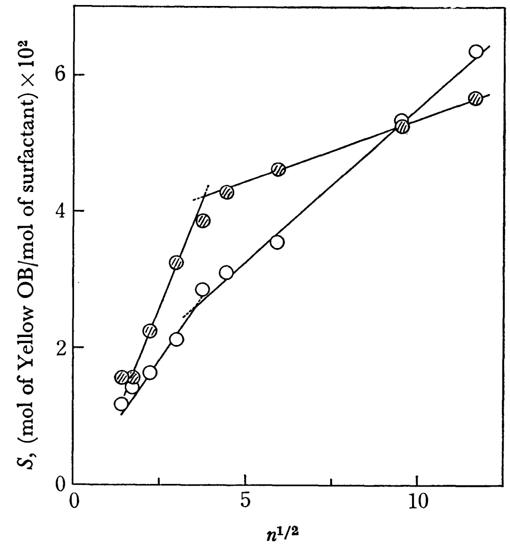

Fig. 4. The solubilizing power of surfactant–PEG-$n$ complex plotted against $n^{1/2}$; ○, $NaC_{12}S$–PEG-$n$; ◍, $NaC_8\phi S$–PEG-$n$.

In Fig. 4, the solubilizing power, $S$, of the $NaC_8\phi S$–PEG complex, obtained from the slope of the straight line shown in Fig. 1, is plotted against $n^{1/2}$. This figure also includes the $S$ *vs.* $n^{1/2}$ plot for the $NaC_{12}S$–PEG complex. In both cases, it should be noted that there is an inflection point around $n=10$—15. This point or region may be interpreted as a boundary between the two different types of polymer–surfactant complexes, or as a transition from oligomeric to polymeric PEG.

According to the thermodynamics of micelle formation, the following equation may be written:[19]

$$\mu_M^\circ = \mu_m^\circ + RT\ln C_0 \qquad (1)$$

where $\mu_M^\circ$ and $\mu_m^\circ$ are the standard chemical potentials of a surfactant in the micelle phase and in the monomer phase respectively, and where $C_0$ is the critical micelle concentration of the surfactant. Analogously to Eq. (1), we may write this equation:

$$\mu_c^\circ = \mu_m^\circ + RT\ln C_C \qquad (2)$$

for the formation of the polymer-surfactant complex. Here, $\mu_c^\circ$ refers to the standard chemical potential of the surfactant in the complex phase, and $C_C$ is the surfactant concentration of complex formation at which the solubilization begins. Eliminating $\mu_m^\circ$ from Eqs. (1) and (2), we obtain:

$$\mu_c^\circ - \mu_M^\circ = RT\ln(C_C/C_0) \qquad (3)$$

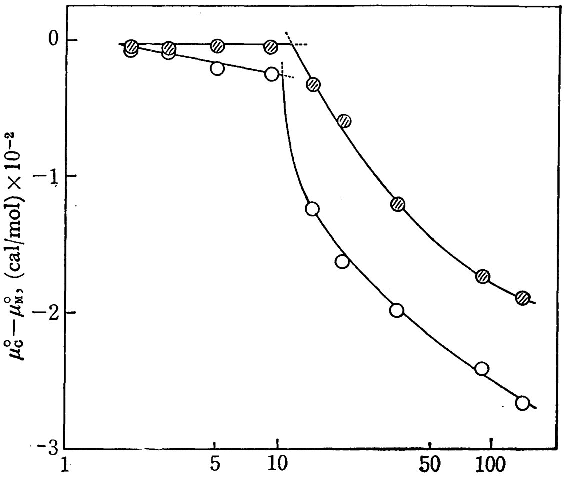

Fig. 5. The value of $(\mu_c^\circ-\mu_M^\circ)$ plotted against $n$: ○, $NaC_{12}S$–PEG-$n$: ◍, $NaC_8\phi S$–PEG-$n$.

The value of $(\mu_c^\circ-\mu_M^\circ)$ calculated from $C_C$ and $C_0$ by means of Eq. (3) is plotted against $n$ in Fig. 5. The curves of $(\mu_c^\circ-\mu_M^\circ)$ *vs.* $n$ for both the $NaC_8\phi S$–PEG and $NaC_{12}S$–PEG complexes have an inflection at $n=10$—15. In the oligomeric region, the value of $(\mu_c^\circ-\mu_M^\circ)$ is nearly independent of $n$ and $\mu_c^\circ$ is equal to $\mu_M^\circ$, which suggests that the complex formation takes place simultaneously with, or just after, the micelle formation. In the polymeric region, on the other hand, the value of $(\mu_c^\circ-\mu_M^\circ)$ decreases with the increase in $n$. This implies that the complex becomes more stable as $n$ increases. Probably, these results could be explained as showing that the surfactant molecules are bound more easily onto the PEG polymer with a larger $n$ because of the lower electrical repulsion of their ionic heads on the complex surface.

---

15) K. Shinoda, T. Nakagawa, T. Isemura, and B. Tamamushi, "Colloidal Surfactants," Academic Press, New York (1963), p. 140.

16) P. H. Elworthy, A. T. Florence, and C. B., Macfarlane, "Solubilization by Surface Active Agents," Chapman and Hall, London (1968), p. 68.

17) B. P. Flory, "Principles of Polymer Chemistry," Cornell University Press, New York (1953), Chap. 10.

18) F. E. Bailey, Jr., and J. V. Koleske, "Nonionic Surfactants," ed. by M. J. Schick, Marcel Dekker, New York (1967), p. 815.

19) p. 51 in Ref. 16.