# *The Polymer-like Property of a Non-ionic Detergent Having a Long Polyoxyethylene Chain*

By Fumikatsu TOKIWA

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Generally, detergent molecule is composed of one large hydrophobic portion and one hydrophilic portion to render the molecule amphipathic. In the case of non-ionic detergents of the polyoxyethylene series, it is possible to start with a substance such as long chain alkyl alcohol and progressively to introduce a controlled number of ether groups by means of ethylene oxide, thereby conferring on it any desired hydrophilic property. The various properties of non-ionic detergent depend, of course, on the number of ethylene oxide groups. In addition, it is possible to consider that the " polymer-like property ", not directly related to the hydrophilic property, will appear in the detergent molecule when the polyoxyethylene chain becomes sufficiently long.

Isemura et al.[1] have shown from the surface tension data of a detergent-like compound, poly-DL-alanine dodecylamide, that at low concentrations the slope of the surface tension vs. concentration curve is the steepest for a certain degree of polymerization and is more gentle when the degree of polymerization is larger than this value; they ascribed this effect to the polymer-like property of poly-DL-alanine dodecylamide. Furthermore, Maruta[2] has observed that the surface tension and foaming power of a non-ionic detergent show, respectively, a minimum and a maximum value at a definite chain-length of polyoxyethylene; he has inferred that these phenomena are also due to the polymer-like behavior of the detergent.

In this paper an attempt is made to interpret tentatively the behavior of a non-ionic detergent with a long polyoxyethylene chain by taking into account the polymer-like property of the detergent. The lengthening of the polyoxyethylene chain of a non-ionic detergent not only increases the hydrophilic property of the molecule but also gives the molecule a polymer-like property. The present paper deals with the nature of the non-ionic detergent with relation to the chain-length of polyoxyethylene. It deals especially with the solubilization and viscosity in connection with the ultracentrifugal data[3] reported previously.

## Experimental

**Materials.**—The detergents studied are polyoxyethylene dodecyl ethers (abbreviated to PODE),

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[1] T. Isemura, S. Ikeda, F. Tokiwa and J. Noguchi, This Bulletin, **34**, 1236 (1961).

[2] I. Maruta, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **83**, 861, (1962).

$C_{12}H_{25}O(CH_2CH_2O)_nH$, which have been prepared from dodecyl alcohol of a high purity. The samples of PODE used are the same samples as those used in a previous investigation[3]. The degree of the polymerization of ethylene oxide, *p*, of these samples are listed in Table I, where the number written after PODE represents the value of *p*, i. e., the average number of oxyethylene groups per molecule. Polyethyleneglycol[3] (abbreviated to PEG) (Carbowax-4000), the molecular weight of which was approximately 4000, was obtained from the Carbide and Carbon Chemicals Co.

Yellow-OB, an oil-soluble dye which was used as a solubilizate, was purchased from the Wako Pure Chemicals Co. and was purified by repeated recrystallization from an ethanol-water mixture.

**Measurements of Solubilization.** — In order to attain equilibrium, the solubilizations were run in a water bath at a constant temperature of 30±0.1°C for 20 hr. The desired amounts of yellow-OB were taken in test tubes, and then appropriate volumes of detergent solutions of various concentrations were pipetted in. The tubes were sealed and fastened to a revolving drum in the water bath. After equilibrium had been attained, the unsolubilized yellow-OB was filtered off.

This filtration was followed by dilution of an aliquot of the filtrate with ethanol to a final mixture of 7 : 3, by a volume ratio of ethanol to water, ethanol being introduced to prevent precipitation of insoluble matter. Colorimetric measurements were made with a Shimadzu Model B60 spectrophotometer to determine the amount of dye solubilized in terms of optical density at a wavelength of 445 mμ.

**Measurements of Viscosity.** — The viscosities of detergent solutions were measured with an Ostwald-type viscometer at 25±0.01°C. The efflux time for pure water was 141.2 sec.

## Results

**Solubilization.**—The solubilization of yellow-OB vs. the concentration of PODE curves are illustrated in Figs. 1 and 2, where *S* is the extent of the solubilization of yellow-OB. The value of *S* decreases with the increasing length of the polyoxyethylene chain at each concentration of PODE, if an abscissa is expressed in grams per 100 ml. of solution, as is shown in Fig. 1. However, if the abscissa is expressed in moles per liter of solution, as is illustrated in Fig. 2, the value of *S* is seen to increase with an increasing *p* value until the maximum value corresponding to PODE of $p \fallingdotseq 27$ is reached while it is seen to decrease beyond this maximum. PEG shows no sign of solubilizing power.

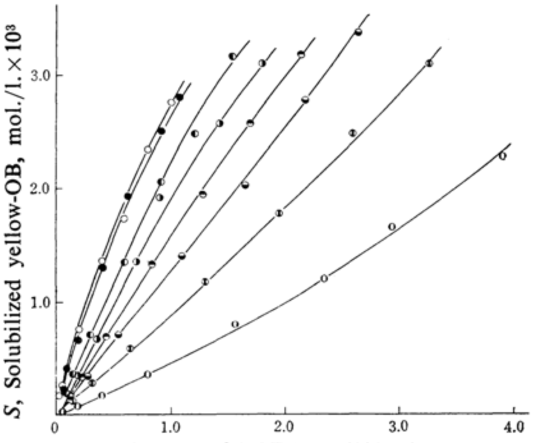

Fig. 1. Solubilization of yellow-OB vs. concentration of PODE curves at 30°C (I).

○ *p*= 6.2 ● *p*= 7.6 ◐ *p*=10.6
◑ *p*=15.8 ◓ *p*=20.4 ◒ *p*=27.1
⦶ *p*=38.6 ◍ *p*=67.3

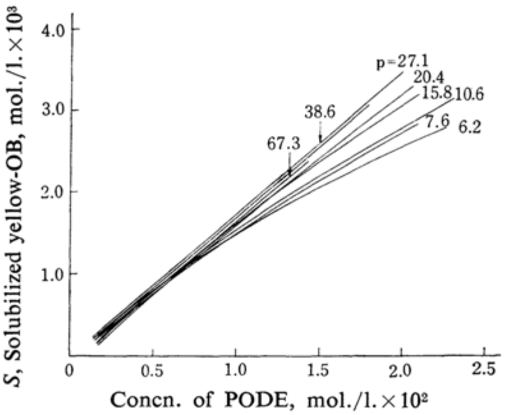

Fig. 2. Solubilization of yellow-OB vs. concentration of PODE curves at 30°C (II).

**Viscosity.** — Figure 3 shows the $\eta_{sp}/c$ vs. $c$ curves for each PODE in aqueous solutions, where $\eta_{sp}$, $c$ and $\eta_{sp}/c$ represent a specific viscosity, a concentration and a reduced viscosity, respectively. The curves run linearly with $c$, except for the PODE of the smallest *p* value, as is shown in Fig. 3. In the case of the PODE where $p=6.2$, its viscosity can not be measured with the viscometer used in the region of higher concentrations because of an extraordinarily high viscosity. This may be attributed to the low cloud-point of this sample. PEG also showed a linear relation.

Intrinsic viscosity, $[\eta]$, was obtained by extrapolating the linear plots of $\eta_{sp}/c$ to $c=0$. The values of $[\eta]$ for PODE having various polyoxyethylene chains are summarized in Table I. The intrinsic viscosity increases with the increasing chain-length except in PODE in which $p=7.6$. An anomaly found in the value of $[\eta]$ in PODE where $p=7.6$, whose slope of the $\eta_{sp}/c-c$ curve is fairly steep, may also be

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[3] F. Tokiwa and T. Isemura, This Bulletin, 35, 1737 (1962).

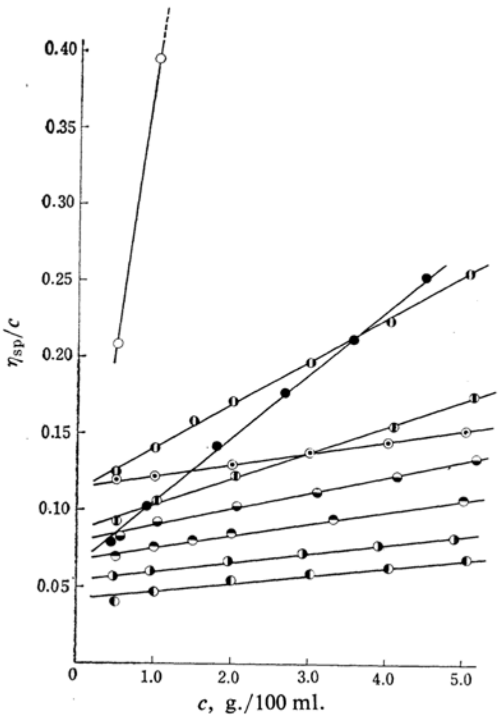


Fig. 3. Reduced viscosity vs. concentration curves of PODE and PEG at 25°C.
○ $p=6.2$ ● $p=7.6$ ◐ $p=10.6$
◑ $p=15.8$ ◓ $p=20.4$ ◒ $p=27.1$
⦶ $p=38.6$ ⦶ $p=67.3$ ⊙ PEG

TABLE I. CHARACTERISTICS OF PODE (AND PEG) AS A FUNCTION OF POLYOXYETHYLENE CHAIN-LENGTH

| Sample | Cloud-point, °C | $n$ | $[\eta]$ | $k'$ | $\phi/c$ |
|---|---|---|---|---|---|
| PODE- 6.2 | 34.5 | 0.76 | — | — | — |
| PODE- 7.6 | 44.6 | 0.85 | (0.065) | (9.88) | — |
| PODE-10.6 | 76.5 | 0.92 | 0.042 | 2.95 | 1.78 |
| PODE-15.8 | >100 | 0.95 | 0.054 | 2.05 | 2.12 |
| PODE-20.4 | — | 0.98 | 0.068 | 1.72 | 2.61 |
| PODE-27.1 | — | 1.04 | 0.080 | 1.73 | 3.00 |
| PODE-38.6 | — | 1.11 | 0.087 | 2.25 | 3.48 |
| PODE-67.3 | — | 1.20 | 0.113 | 2.20 | 4.52 |
| PEG | — | — | 0.114 | 0.59 | — |

caused by the relatively low cloud-point of this sample.

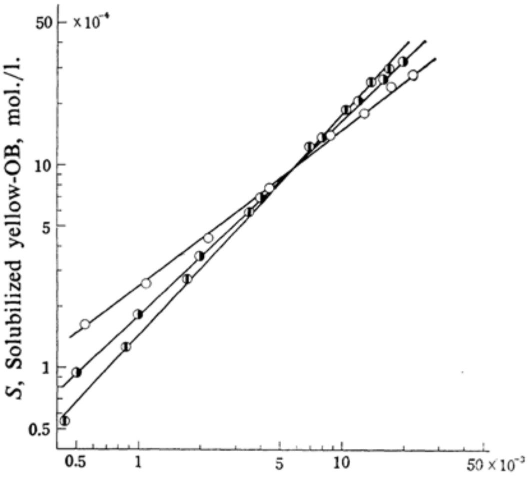
## Discussion

At a given molar concentration, the number of the molecules per micelle decreases and, at the same time, the number of micelles increases with the increasing length of the polyoxyethylene chain[3-5]. Therefore, the amount of dye solubilized by PODE is expected to increase with the polyoxyethylene chain-length, if the concentration of PODE is expressed by moles per liter of solution. In fact, the polyoxyethylene chain-length is responsible for the solubilizing power up to the PODE where $p \fallingdotseq 27$ at high concentrations, while the amount of dye solubilized decreases as the $p$ value exceeds this value. When the polyoxyethylene chain of PODE becomes quite long, the nature due to the polyoxyethylene chain predominates over that due to the alkyl chain and the characteristics of PEG become obvious; thus the effect of the alkyl chain is reduced and a polymer-like property appears in the molecule. This might be the reason why PODE where $p \fallingdotseq 27$ has the maximum solubilizing power. This is also supported by the observation that PEG shows no solubilization.

Solubilization isotherms above the critical micelle concentration for the oil-soluble dyes can in some instances be fitted to the general form[6,7]:

$$S = Kc^n \tag{1}$$

where $K$ and $n$ are constants. If the data of the solubilization shown in Fig. 2 are replotted in a logarithmic scale, straight lines are obtained for all cases, irrespective of $p$ value, some of which are illustrated in Fig. 4. We thus confirm that Eq. 1 holds in the present experiment. The values of the constant, $n$, which can be estimated from the slope of the straight line, are listed in Table I.



Concn. of PODE, mol./l.

Fig. 4. Log-log plots of solubilization vs. concentration.
○ $p=6.2$ ◑ $p=15.8$ ⦶ $p=38.6$

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[4] T. Nakagawa and K. kuriyama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nipon Kagaku Zassi*), **78**, 1568 (1957).

[5] T. Nakagawa and H. Inoue, ibid., **79**, 345, 348 (1958).

[6] A. M. Schwartz, J. W. Perry and J. Berch, "Surface Active Agents and Detergents", Interscience Publishers, New York (1958), p. 442.

[7] A. M. Mankowich, *J. Colloid Sci.*, **14**, 131 (1959).

As is seen in Table I, the value of $n$ increases with the $p$ value and is greater than unity for PODE of $p>27$. This indicates that solubilization curves plotted in a ordinary scale change from convex to concave upward from around $p=27$. Since the $n$ values are smaller than unity for ordinary detergents7), the behavior of PODE of $n<1$ in solubilization may also be interpreted as PODE acting as an ordinary detergent8), though the reason for this action is not clear. On the other hand, the case of an $n$ value larger than unity implies that the solubilizing power increases with acceleration as the concentration of the detergent increases, although the amout of increase is not very much. A similar tendency was observed in the solubilization curve of polysoap9).

This presumably indicates that there occurs some interaction, which seems to promote the solubilization, among different micelles or aggregates of the detergent, as will be described below. Evidence for some kinds of interaction will be provided by the Huggins' $k'$ and by an effective volume of PODE calculated from the viscosity and other data10,11), and it is inferred that the interaction might have some relation to the increment of polyoxyethylene chain-length.

As for the interactions among different aggregates of PODE, the initial slopes of the $\eta_{sp}/c$ against $c$ plots expressing these interactions depend both on the extension of aggregates and on the affinity between aggregate and solvent relative to the aggregate-aggregate and solvent-solvent affinities11-13). It has been shown that these two factors can be resolved by expressing the slope as a product of $[\eta]^2$ and a quantity $k'$12). The value of $k'$ can thus be computed by means of Huggins' familiar equation12):

$$\eta_{sp}/c=[\eta]+k'[\eta]^2c \tag{2}$$

Although no completely quantitative theory concerning Huggins' constant $k'$ is available for such colloidal solutions as a PODE solution, the $k'$-value can be assumed to be a measure of aggregate-solvent affinity11). By the use of the $k'$-value, which leads to a tentative interpretation of some observed effects of the polyoxyethylene chain on the viscosity of PODE solutions, information concerning the interaction among aggregates or the polymer-like behavior of PODE will be obtained.

The fifth column of Table I shows the dependence of the $k'$-value upon the polyoxyethylene chain-length. The $k'$-value at first decreases and then somewhat increases with the increasing $p$ value; it then decreases again, finally approaching the $k'$-value for PEG, with the exception of a high $k'$-value for PODE in which $p=7.6$, which is caused by an anomalous aggregation. It is noticeable that the increase in $k'$-value exists in the region of larger $p$ values in spite of increasing hydrophility. This indicates either that the aggregate-aggregate affinity increases more than the hydrophility of PODE, which increases with the $p$ value, or that the affinity increases with the hydrophility, when polyoxyethylene chain becomes sufficiently long. Furthermore, this suggests probably that some interaction occurs among different aggregates by the help of long polyoxyethylene tails, being ascribed to the polymer-like property of the detergent having a long hydrophilic tail.

On the other hand, it is worth while to consider the viscosity data in the light of the theoretical viscosity equation proposed by Guth and Simha14):

$$\eta_r=1+2.5\phi+14.1\phi^2 \tag{3}$$

This equation is applicable to the dispersion systems of spherical particles, where $\eta_r$ is a relative viscosity and $\phi$ is a volume fraction of the particle. The use of Eq. 3 in the present experiment involves the assumption that the aggregates of PODE are spherical5). From

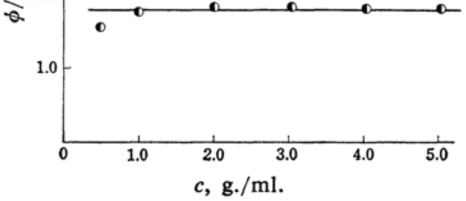

Fig. 5. Effective volume vs. concentration curves of PODE at 25°C.
● $p=7.6$ ◐ $p=10.6$ ◑ $p=15.8$
◒ $p=20.4$ ◓ $p=27.1$ ⦶ $p=38.6$
◍ $p=67.3$

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8) M. E. L. McBain and E. Hutchinson, "Solubilization", Academic Press, New York (1955), p. 147.

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

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

11) U. P. Strauss, N. L. Gershfeld and E. H. Crook, ibid., **60**, 577 (1956).

12) M. L. Huggins, *J. Am. Chem. Soc.*, **64**, 2716 (1942).

13) D. A. I. Goring and A. Rezanowich, *J. Colloid Sci.*, **15**, 472 (1960).

14) E. Guth and R. Simha, *Kolloid-Z.*, **74**, 147 (1936).

Eq. 3 the volume fraction, $\phi$, was computed, and the effective volume, $\phi/c$, shown in Table I denotes the volume occupied by one gram of the detergent in the solution.

The value of $\phi/c$ is nearly independent of concentration and increases with the increasing polyoxyethylene chain-length, except in the case of PODE in which $p=7.6$, as is shown in Fig. 5. Nakagawa and Inoue[5] have obtained results corresponding to the present ones in the same way, using methoxy polyoxyethylene alkyl ether, in a relatively limited extent of chain-length.

The author has previously shown from the data of ultracentrifugal experiment[3] that the aggregation number, i. e., a number of molecules per aggregate, is highly dependent on the chain-length of polyoxyethylene and decreases with an increase in the chain-length. Considering this result in connection with the values of $\phi/c$, therefore, we may say that the number and effective volume of aggregates at a given concentration of PODE increase with the polyoxyethylene chain-length. In concentrated solutions, thus, chances for different aggregates to approach and/or contact each other might be more frequent with the increasing chain-length. The interaction among different aggregates, caused by these chances, is presumably that which results in the polymer-like property of the non-ionic detergent with a long polyoxyethylene tail. From this point of view, the experimental finding that the value of $n$ is slightly greater than unity in the case of PODE with a sufficiently long polyoxyethylene chain, can be attributed to the polymer-like behavior of PODE.

## Summary

The solubilization and viscosity of polyoxyethylene dodecyl ether (PODE) solutions were studied as a function of the polyoxyethylene chain-length ($p$). The solubilization is in accordance with the isotherm $S=Kc^n$, where $S$ is the extent of solubilization, $c$, the concentration of detergent, and $n$ and $K$, constants. The value of $n$ increases with the $p$ value and is slightly greater than unity for PODE of $p>27$. The $k'$-value calculated from Huggins' equation, which is dependent on the $p$ value, decreases at first with the $p$ value and then somewhat increases in spite of the increasingly hydrophilic nature. The effective volume, $\phi/c$, of PODE, which is nearly independent of $c$ except for the case of PODE in which $p=7.6$, increases regularly as the $p$ value becomes larger. On the basis of these results, the polymer-like property of PODE of a considerably large $p$ value and the interaction among aggregates of PODE were discussed in connection with ultracentrifugal data reported previously.

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*Research Laboratory*
*Kao Soap Co., Ltd.*
*Sumida-ku, Tokyo*