Some Properties of Polyoxyethylene Dodecyl Ether over a Wide Range of Polyoxyethylene Chain-lengths

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There have been a number of studies of the properties of polyoxyethylated non-ionic surfactants in relation to their polyoxyethylene chain-lengths. Most of these studies have, however, been limited to the non-ionic surfactants with relatively short polyoxyethylene chains; little attention has been paid to the surfactants with considerably long polyoxyethylene chains. Their properties depend to a large extent on the average number of oxyethylene units present. It is, therefore, desirable to have data for non-ionic surfactants over a wide range of the chain-lengths of polyoxyethylene in order better to understand the effect of chain-length on their properties.

The author[1,2] has previously shown the relationship between the properties of polyoxyethylene dodecyl ether, such as its micellar molecular weight, its solubilization and its viscosity, and its polyoxyethylene chain-lengths above the critical micelle concentration.

The present paper will deal with the purification of a non-ionic surfactant, including the determination of its molecular weight, and chromatographic and infrared spectral studies, from short up to quite long polyoxyethylene chains. It is always of importance, when one studies the properties of a polyoxyethylated non-ionic surfactant, to purify the sample, i. e., to remove polyethylene glycol, a by-product of the addition reaction, from the sample. In addition, this paper will deal with the surface tension of aqueous solutions and with the solubilization of oil-soluble dye, on the basis of which the variation in critical micelle concentration with polyoxyethylene chain-length will be discussed.

Experimental

Materials.—Polyoxyethylene dodecyl ethers (abbreviated to PODE), $C_{12}H_{25}O(CH_2CH_2O)_pH$, were prepared from dodecyl alcohol of a high purity. The average degrees of the polymerization of ethylene oxide, p, in these samples are listed in Table I. The purification of the samples and the determination of their molecular weights were carried out as will be described below. Polyethylene glycol (abbreviated to PEG), the molecular weight of which was approximately 4000, was obtained from the Carbide and Carbon Chemicals Co.

The Purification of PODE.—The purification of the samples was carried out by the extraction method by countercurrent partition,[3] using water-saturated *n*-butanol and *n*-butanol-saturated water, in order to remove PEG, a by-product of the reaction.

The purification by liquid chromatography was also attempted for this purpose by using alumina (200 mesh powder for chromatographic analysis) as an adsorbent. Two different solvent systems were used, one a mixture of *n*-butanol and water, the other acetone alone. However, the former was somewhat disadvantageous in the sense that it affords only a small amount of purified sample at one time, and the latter was not satisfactory. Thus, the attempt at purification by liquid chromatography was abandoned.

It was confirmed, by testing through paper chromatography, that the samples purified by the extraction method contained no detectable free PEG. The development was carried out by applying a mixture of *n*-butanol, acetone and water (4 : 1 : 5 by volume[4]). The evaporation of the developer was followed by visualization in the Dragendorff reagent.

The Determination of Molecular Weights.—The molecular weights of PODE were determined by the freezing point depression of their benzene solutions by means of the Beckman method with the usual precautions. The molecular weights were also determined by the anhydrous acetic acid-pyridine method, which is commonly used for measuring hydroxyl values.

Infrared Absorption Spectra.—Infrared measurements were performed on a Shimadzu Type IR-27 spectrometer using a sodium chloride prism. The infrared spectra of PODE were recorded in a liquid or solid state, the PODE with a longer polyoxyethylene chain being solid.

Surface Tension.—Surface tensions were measured by the drop weight method with a tip 5.03 mm. in diameter in a thermostat of 30±0.1°C. The observed values were corrected by using the correction factor of Harkins and Brown. The duration time after the formation of a drop was 0.5∼5.0 min., depending on the concentration of the solutions. Under these conditions there was no appreciable change in the surface tension.

Solubilization. — Yellow-OB, an oil-soluble dye used as a solubilizate, was purified by repeated

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[1] F. Tokiwa, This Bulletin, 35, 1737 (1962).

[2] F. Tokiwa, ibid., 36, 222 (1963).

[3] K. Nagase and K. Sakaguchi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), 64, 635 (1961).

[4] K. Hattori and K. Konishi, ibid., 64, 1195 (1961).

recrystallization from an ethanol-water mixture. Solubilizations were run in a water bath at a constant temperature of 30±0.1°C for 24 hr. to attain equilibrium, the method described in a previous paper[2] being employed. The amounts of solubilized dyes were determined by optical density measurements using a spectrophotometer, Shimadzu model B-60.

Results and Discussion

Molecular Weights and R_f-Values.—In Table I the molecular weights of the original PODE, obtained from the gain in weight by the addition of ethyhlene oxide, are compared with those of the purified PODE estimated from the freezing-point depressions and the terminal hydroxyl values.* Essentially, the molecular weights obtained from the freezing-point depressions should be equal to those obtained from the hydroxyl values, since both of these molecular weights are number-average molecular weights. The values shown in Table I indicate that they are nearly in agreement with each other and, at the same time, verify that PODE molecules do not form micelles in benzene over a considerably wide range of polyoxyethylene chain-lengths.

The variation in R_f-value with the polyoxyethylene chain-length, i. e., the value of p, is show in Fig. 1-a for the purified PODE and the original PODE containing a small amount of PEG (approximately 5%). Figure 1-b also illustrates the variation in R_f-value with the HLB-value for these samples. The R_f-values decrease with increasing values values of p or HLB. The values of purified PODE are slightly higher than those of the original PODE. On the other hand, the R_f-value of the PEG contained in original PODE seems

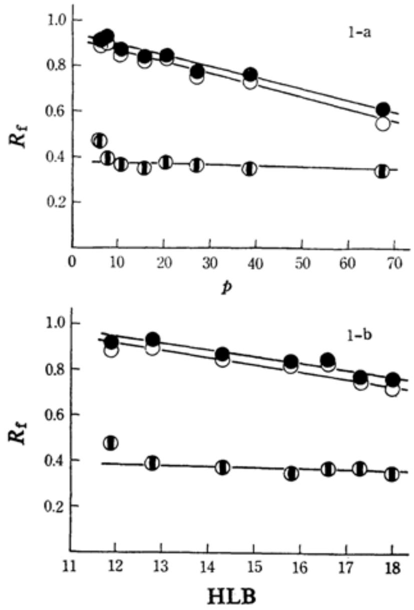

Fig. 1. Relationship between the R_f-value and the p-value (1-a) or the HLB-value (1-b) for purified (●) and original PODE (○), and PEG(◐).

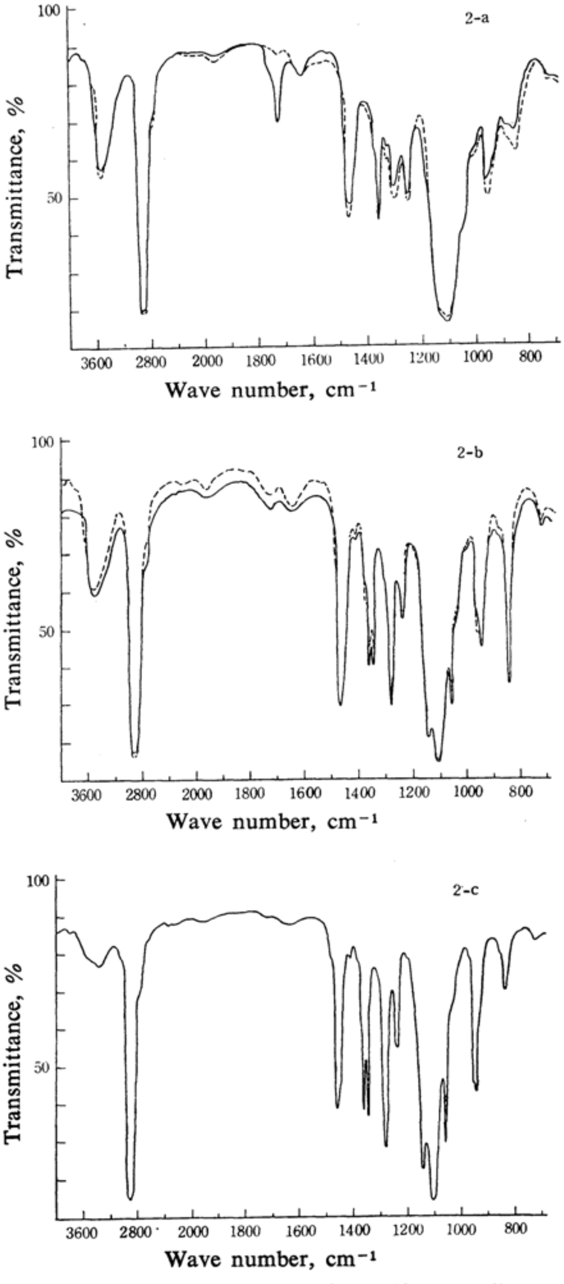

Fig. 2. Infrared spectra of purified (solid curve) and original PODE (dashed curve) for p=10.6 (2-a) and p=20.4 (2-b), and PEG (2-c).

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* The hydroxyl value is the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of a one gram sample.

TABLE I. MOLECULAR WEIGHTS AND CRITICAL MICELLE CONCENTRATION OF PODE AS A FUNCTION OF POLYOXYETHYLENE CHAIN-LENGTH

Sample[a]	Molecular weight		CMC (mol./l. $\times 10^4$)	
	from freezing pt. depresion	from hydroxyl value	from surface tension	from solubilization
PODE- 6.2	640 ($\bar{p}$= 6.2)	468 ($\bar{p}$= 6.4)	—	0.8
PODE- 7.6	501 (= 7.2)	510 (= 7.4)	2.0~3.2	0.9
PODE-10.6	645 (=10.4)	625 (=10.0)	—	1.2
PODE-15.8	870 (=15.5)	857 (=15.2)	2.0~3.5	1.8
PODE-20.4	1070 (=20.0)	1110 (=21.0)	—	2.1
PODE-27.1	1330 (=26.0)	1380 (=27.1)	3.0~4.5	2.5
PODE-38.6	1810 (=37.0)	1790 (=36.5)	4.0~6.0	3.6
PODE-67.3	—	—	—	5.7

a) The numbers listed after PODE represent the average numbers of oxyethylene units per molecule, which were obtained from the gain in weight by the addition of ethylene oxide.

to be nearly independent of the value of p or HLB.

Infrared Spectra and Surface Tension. — The infrared spectra of purified PODE are compared with those of original PODE. Some of these spectra are shown in Fig. 2, together with the spectrum of PEG. The spectra of the purified samples are identical with those of the original samples except for one absorption band. With purified PODE, a relatively strong absorption appeared at 1725 cm^{-1} up to the PODE value of $p=15.8$, as may be seen in Fig. 2-a. However, the original PODE and the purified PODE with p-values larger than 20.4 either showed no appreciable absorption at all or had a very weak absorption at 1725 cm^{-1}.

All the absorptions in the region of the frequencies lower than 1500 cm^{-1} have already been assigned by Davison.⁵⁾ The absorption at 1725 cm^{-1} suggests the presence of carbonyl groups in the molecule of purified PODE, since carbonyl absorption is commonly observed around this frequency.⁶,⁷⁾ The ether bonding in polyoxyalkylene compounds is known to be not very stable in the presence of heating, light, oxidizing agents, and so on.⁸⁻¹¹⁾ It is possible, therefore, to assume that a certain change occurs through autoxidation⁹,¹⁰,¹²,¹³⁾ at the ether bonding in the PODE molecule during the course of purification, thus forming carbonyl group in the molecule, whatever the detailed mechanism is. Nemoto¹³⁾ has suggested that the ether bonding of polyoxyethylated non-ionic surfactants is attacked by autoxidation.

Carbonyl absorptions will arise from the –COOH, –COOR, –CHO and $\rangle$CO groups. If the above assumption is right, there is a possibility of finding one or more of these groups in the purified PODE. In fact, the acid values and the ester values** of all the PODE showing carbonyl absorptions were found to have a range of 10~14 and 11~16 respectively; these values are considered to be rather smaller than those expected from the intensity of the absorption observed. Qualitative tests with 2,4-dinitrophenyl hydrazine¹⁴⁾ and benzidine showed the presence of a trace of carbonyl groups, suggesting that the samples contain aldehyde and/or ketone groups. Thus, the reason why such a remarkable absorption appeared at 1725 cm^{-1} with purified PODE could be explained partially by the above data. However, the reason why this absorption was observed exclusively in the case of the PODE with p values smaller than 15.8 is not explainable clearly. Research is continuing to learn more about this problem.

The surface tensions of aqueous solutions of (a) original and (b) purified PODE and (c) the purified PODE to which 5% of PEG had been added to make the sample original were measured for the purpose of learning the effect of the carbonyl group, which was found in purified PODE, on the surface activity. Typical surface tension vs. concentration curves are shown in Fig. 3. The surface tension of PODE solutions is characterized by a sharp initial decrease, followed by a gradual flattening. The inflection of the curve corresponds

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5) W. H. T. Davison, *J. Chem. Soc.*, **1955**, 3270.

6) L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," Methuen, London (1958), p. 132.

7) G. Delzenne and G. Smets, *Makromol. Chem.*, **18/19**, 82 (1956).

8) C. E. Schweitzer, R. N. MacDonald and J. O. Punderson, *J. Applied Polymer Sci.*, **1**, 158 (1959).

9) S. L. Madolsky and S. Strauss, *J. Polymer Sci.*, **36**, 183 (1959).

10) C. W. McGray, Jr., ibid., **46**, 51 (1960).

11) L. E. St. Pierre and C. C. Price, *J. Am. Chem. Soc.*, **78**, 3432 (1956).

12) W. G. Lloyd, ibid., **78**, 72 (1956).

13) Y. Nemoto and T. Imai, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **62**, 483 (1959).

** The definition of these values is similar to that of the hydroxyl value described already.

14) O. L. Brady, *J. Chem. Soc.*, **1931**, 756.

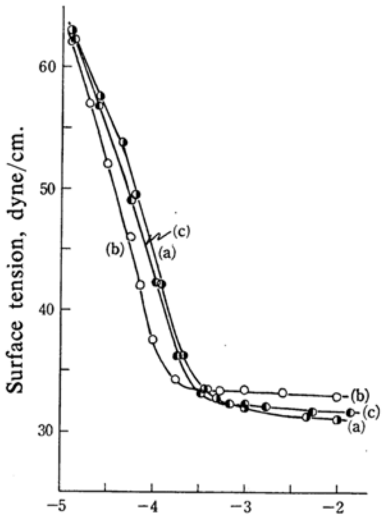

Fig. 3. Surface tension vs. concentration curves of aqueous solutions of PODE with $p=7.6$ at 30°C; (a) original PODE, (b) purified PODE and (c) the purified PODE to which 5% PEG was added.

to the critical micelle concentration (CMC); it is not so sharp as that of the ionic surfactant because of the distribution of the molecular weights of PODE.

With the PODE with a p value of 7.6, curve c is more similar to curve a than to curve b, as may be seen in Fig. 3. This indicates that PEG has a tendency to make the surface tension higher below the CMC. However, no significant difference in surface tension among the curves of a, b and c could be observed. It could be considered, therefore, that the carbonyl group found in the purified sample by infrared absorption influences the surface activity not very strongly.

The Critical Micelle Concentration.—Figure 4 illustrates the solubilization curves, in which the amounts of solubilized dye are plotted against the concentrations of PODE. The solubilization behavior of PODE is somewhat different from that commonly observed for ionic surfactants. With ionic surfactants, scarcely any solubilization takes place until the concentration of surfactant reaches the CMC,[16] while in the case of PODE the amounts of dye solubilized increase gradually with the increasing concentration, even below the CMC. This may be explained by the following. The sample of PODE has a certain distribution of molecular weights, and some solubilization can take place in the region of the surfactant concentration which is lower than the CMC. A much more complicated micellar equilibrium, but which is fundamentally of the same type, appears to occur in non-ionic surfactant solutions.

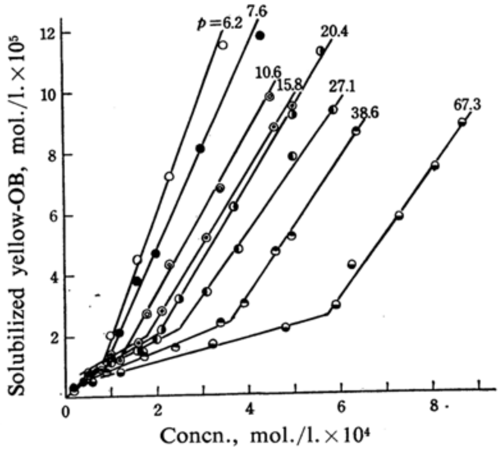

Fig. 4. Solubilization of yellow-OB vs. concentration of PODE curves at 30°C.

Solubilization is generally regarded as an effect which begins to be noticeable at the CMC. The break point in the solubilization vs. concentration curve corresponds to the CMC. Table I shows the CMC values of PODE in relation to the chain-length of polyoxyethylene; they increase with the increase in the values of p. The CMC's obtained from the solubilization were relatively sharp as compared with those obtained from the surface tension. The CMC values of PODE are of an order of 10^{-4} mol., in agreement with the results of other investigations of polyoxyethylated surfactants.[17,18]

Concerning the relationship between the CMC value and the polyoxyethylene chain-length, Nakagawa and Kuriyama have already proposed a theory,[19] which is satisfactorily comparable with experimental results over a relatively limited range of chain-lengths, using methoxy polyoxyethylene decyl and dodecyl ethers.[17] Hsiao et al.[18] have also reported that, with aqueous solutions of Igepals (condensate products of alkyl phenol with ethylene oxide), the rate of increase in CMC values is given by the expression:

$$\ln(\mathrm{CMC}) = k + aR$$

where a and k are constants, and where R

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[15] E. Funakubo, "Identification of Organic Compounds," Yoken-do, Tokyo (1954), p. 326.

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

[17] T. Nakagawa, K. Kuriyama and K. Tori, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 1573 (1957).

[18] L. Hsiao, H. N. Dunning and P. B. Lorenz, *J. Phys. Chem.*, **60**, 657 (1956).

[19] T. Nakagawa and K. Kuriyama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 1568 (1957).

represents the mole ratio of oxyethylene to phenol.

According to Hsiao et al., the logarithm of the CMC value given in Table I was plotted as a function of the polyoxyethylene chain-length, as is shown in Fig. 5-a. Such a straight line as he obtained was not obtained in the present experiment. However, if the ordinate is expressed on an ordinary scale, as is illustrated in Fig. 5-b, the relation between the CMC and p value seems to be rather linear; it can be written by:

$$\mathrm{CMC}=(0.30+0.083p)\times 10^{-4}$$

This equation indicates that the effect of the oxyethylene unit in the hydrophilic chain on the CMC value is not so marked as that of the methylene unit in the hydrophobic chain. It was reported that the CMC value is approximately doubled by decreasing the number of methylene groups in the hydrophobic chain by one.[15] This is in interesting contrast to the solubility phenomena, where an oxyethylene unit is equivalent to one methylene unit.[20]

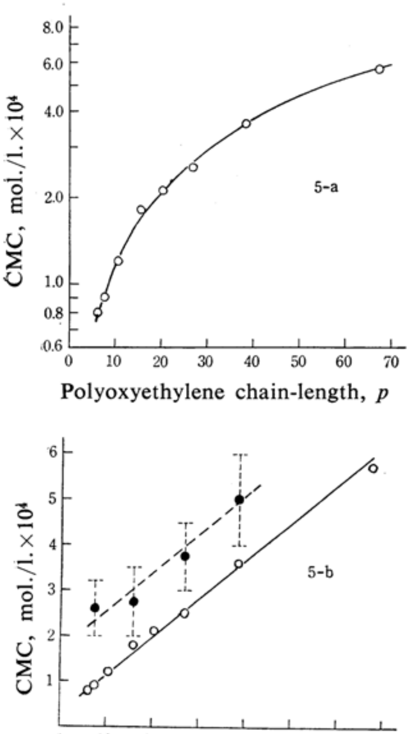

Fig. 5. The relationship between critical micelle concentration and polyoxyethylene chain-length; the ordinate is expressed in a logarithmic scale (5-a) and in decimal scale (5-b) (the dotted line represents the data from surface-tension measurements).

Summary

The fundamental properties of polyoxyethylene dodecyl ether (PODE) with different polyoxyethylene chain-lengths (p) have been studied over a wide range of p values. The molecular weights of the PODE, purified by the extraction method using water-saturated n-butanol and n-butanol-saturated water, have been determined by both the freezing point depressions of benzene solutions and the hydroxyl values of PODE; the molecular weights as determined by the different methods are in nearly complete agreement with each other. The R_f-values of the original samples containing small amounts of PEG are slightly lower than those of the purified samples, and the PEG contained in original samples show an almost constant R_f-value, irrespective of the p value.

The infrared spectra of purified PODE have been compared with those of the original ones. The spectra of the purified PODE with p-values smaller than about 16 exhibited a carbonyl absorption at 1725 cm^{-1}. However, the reason for this could be established only partially. The effect of the carbonyl group found in the above PODE on the surface tension of aqueous solutions was not observed distinctly.

The solubilization behavior of PODE differs somewhat from the behavior of ordinary ionic surfactants, and some solubilization can take place in the region of the surfactant concentration which is lower than the CMC. There appears to be a simple relationship between the CMC values, obtained from solubilization vs. concentration curves, and the p values of PODE over a wide range of p values.

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20) M. N. Fineman, G. L. Brown and R. J. Myers, *J. Phys. Chem.*, 56, 963 (1952).