

THE INTERACTION BETWEEN POLYETHYLENE OXIDE AND SURFACTANT

By

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1. Introduction

Various kinds of water-soluble polymers are used as a sizing agent of textiles. The interaction between polymers and surfactants have been studied previously by many investigators¹⁾²⁾³⁾ The water-soluble polymers used in those studies are polyvinyl alcohol and polyvinyl pyrrolidone which have polar groups. The interaction between sodium lauryl sulfate and ethylene glycol which is polyethylene oxide of low-molecular weight has been investigated by M. N. Jones.⁴⁾

The polyethylene oxides of higher molecular and their derivatives are used as not only a sizing, but also a soil release finishing agent. It is considered, accordingly, of interest to study the interaction between the polyethylene oxide and surfactant.

In the present paper, some results will be reported on the viscometric studies of the polyethylene oxides of molecular weight of 500,000-3,000,000 in aqueous solution of sodium lauryl sulfate or sodium laurate.

2. Experimentals

2.1 Materials

Sodium lauryl sulfate was prepared by recrystallization of a commercial product from ethyl alcohol. Sodium laurate was prepared by neutralization of lauric acid with sodium hydroxide in conductivity water at 90°C. Sodium hydroxide was always used in 2% excess, in order to prevent the hydrolysis of the soap.

Commercial polyethylene oxides were purified by extraction with acetone containing 5% of water. Their molecular weights shown in Table 1 were determined by the viscosity measurements and the calculations with the following equation.⁵⁾

$$[\eta] = 6.4 \times 10^{-5} M^{0.82} \quad (\text{in water at } 35^\circ\text{C})$$

Table 1. Molecular weights of polyethylene oxides.

Brand	$[\eta]^a$ (dl./g)	Molecular weight
PEO-3N	2.8	4.6×10^5
PEO-10N	9.6	20.5×10^5
PEO-18N	16.0	38.3×10^5

a) in water at 35°C

2.2 Viscosity measurements

The viscosities of polyethylene oxide in the solutions of various concentrations of a

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surfactant were measured by a viscometer of Ostwald type at 35°C. The shear stress on the wall of the viscometer was 18 dyn/cm². The effect of the velocity gradient, therefore, may be neglected in this range of stress.⁶⁾

3. Results and Discussion

3.1 The significance of viscosity measurement

If the polymer chain unites with surfactant ions, its shape is expected to be changed. The polymer is extended by Coulombic mutual repulsion of the ions united on the chain. Accordingly, the information regarding the interaction between the polymer and surfactant can be obtained from the intrinsic viscosity.

3.2 Interaction between polyethylene oxide and sodium lauryl sulfate

The reduced viscosities of polyethylene oxide in sodium lauryl sulfate solutions are plotted against the polymer concentration in Figures 1 and 2. As is shown in Figure 1, PEO-18N in water behaves as a nonionic polymer and the curves of the polymer concentration C vs. the reduced viscosity η_{sp}/C are linear. The ionic property of polymers, however, appears in the range of 0.005~0.02 moles of sodium lauryl sulfate concentrations, and the reduced viscosity increases when the concentration of polymer approaches to zero. It is considered that polyethylene oxide molecules are extended by the mutual repulsion of sodium lauryl sulfate ions adsorbed on their chains. While,

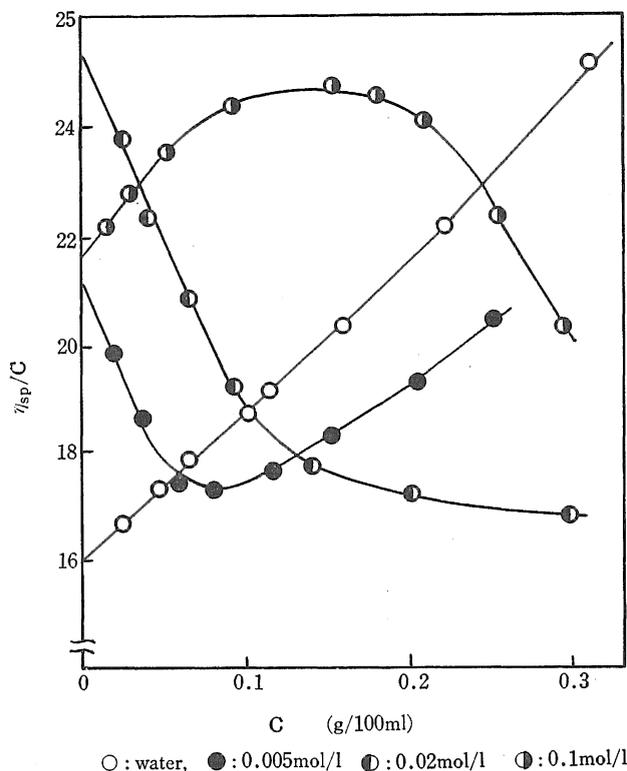


Fig. 1. The reduced viscosity of PEO-18N in sodium lauryl sulfate solution.

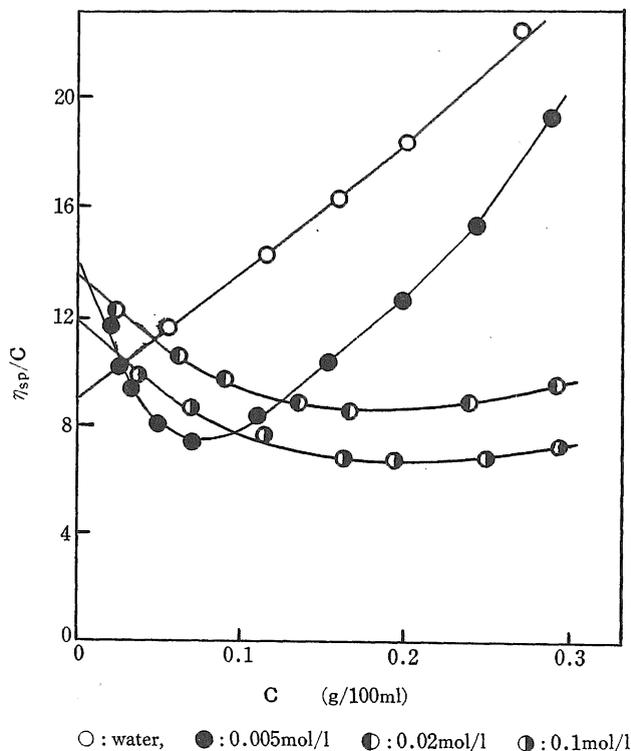


Fig. 2. The reduced viscosity of PEO-10N in sodium lauryl sulfate solution.

the curves of C vs. η_{sp}/C in 0.1 moles solution of sodium lauryl sulfate fall when the polymer concentration approaches to zero. The fact is accounted for a desolvation effect of the counter ion, that is Na ion.

In the case of PEO-10N shown in Figure 2, such a decrease of the reduced viscosity is not noticed in any concentration of sodium lauryl sulfate because of its higher solubility than PEO-18N. PEO-3N gives almost the same curves as PEO-10N.

3.3 Interaction between polyethylene oxide and sodium laurate

The curves of C vs. η_{sp}/C of PEO-10N in the various concentrations of sodium laurate solutions are shown in Figure 3. The electro viscous behavior of an ionic polymer is also be recognized; the increasing of the reduced viscosity in the lower concentrations of the polymer is shown. On the other hand, the decreasing of the reduced viscosity which was not observed even in 0.1 moles solution of sodium lauryl sulfate occurs in 0.05 moles solution of sodium laurate. The fact indicates that the solubility of polyethylene oxide in sodium laurate is less than that in sodium lauryl sulfate. The tendency of the reduced viscosities of PEO-3N and PEO-18N is identical with that of PEO-10N in Figure 3.

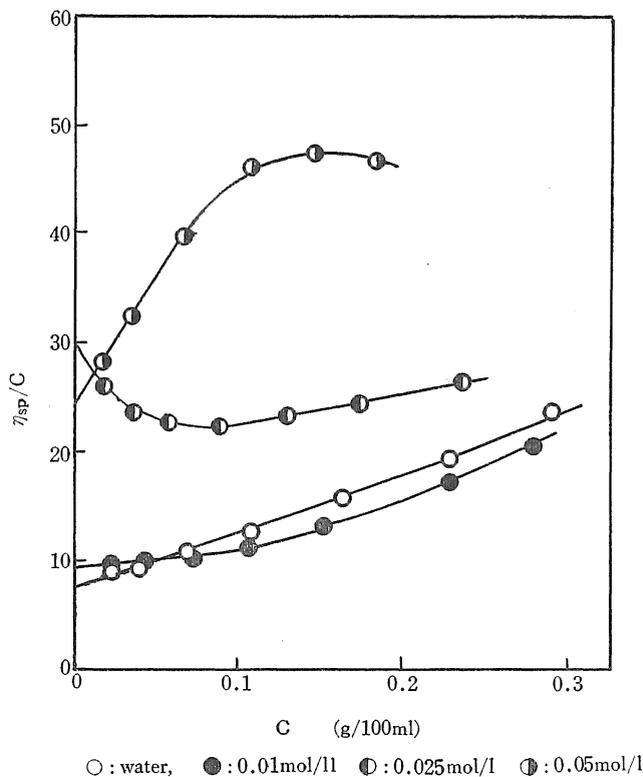


Fig. 3. The reduced viscosity of PEO-10N in sodium laurate solution.

3.4 The intrinsic viscosity of polyethylene oxide in sodium lauryl sulfate solution

The intrinsic viscosity of polyethylene oxide is obtained from the extrapolation of the curves of the reduced viscosity to zero concentration. The relation between the intrinsic viscosity of polyethylene oxide and the concentration of sodium lauryl sulfate is shown in Figure 4. Except for PEO-3N, the values of the intrinsic viscosity have a maximum in about 0.006 moles solution of sodium lauryl sulfate which is its critical micelle concentration. The intrinsic viscosity of PEO-3N also increased rapidly in those concentrations. It is considered that the molecule of polyethylene oxide is most strongly expanded in near the critical micelle concentration of sodium lauryl sulfate.

3.5 The intrinsic viscosity of polyethylene oxide in sodium laurate solution

The relation between the intrinsic viscosity of polyethylene oxide and the concentration of sodium laurate is shown in Figure 5. It indicates roughly agreement with the data given in sodium lauryl sulfate solutions mentioned above. A peak of the intrinsic viscosity appears in the critical micelle concentration of sodium laurate. From a comparison of Figure 4 with Figure 5, it is seen that the maximum values of the intrinsic viscosity in sodium laurate are larger than that in sodium lauryl sulfate. In critical micelle concentration, sodium laurate solution is considered to be superior to sodium lauryl sulfate with regard to the solubility of the polymer.

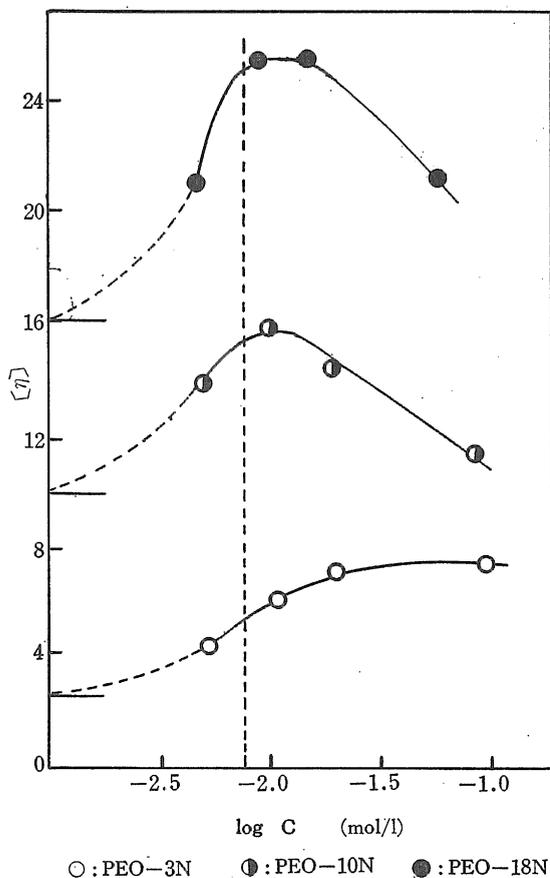


Fig. 4. The relation between the intrinsic viscosities of polyethylene oxide and sodium lauryl sulfate concentrations.

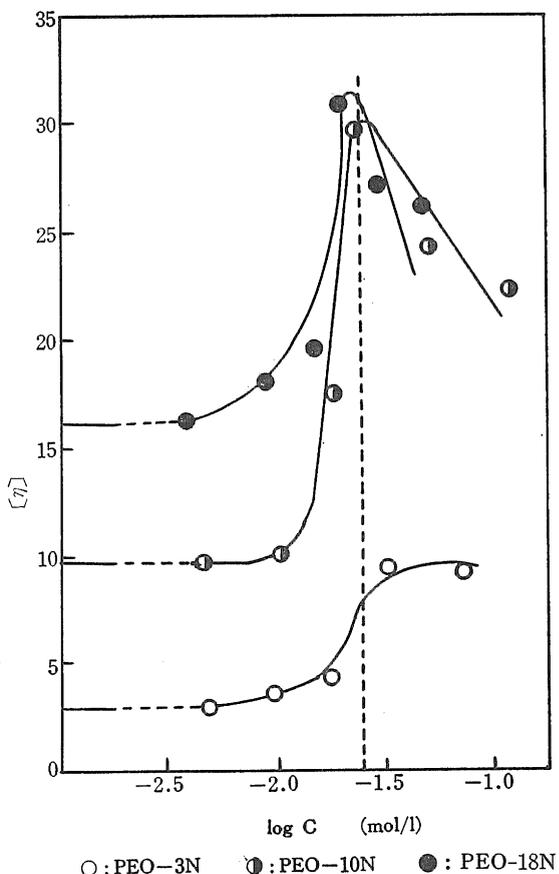


Fig. 5. The relation between the intrinsic viscosities of polyethylene oxide and sodium laurate concentrations.

These results are interpreted in terms of a polymer-surfactant complex or micelle formed by binding between the surfactant ions and the polymer.

Summary

The interaction of surfactant with polyethylene oxide has been investigated by the measurement of viscosity in the aqueous solution.

The three samples of polymer examined in the present paper have the viscosity-average molecular weights of 4.6×10^5 , 2.05×10^6 , and 3.83×10^6 , respectively. Sodium lauryl sulfate and sodium laurate are used as surfactants.

The intrinsic viscosity of polyethylene oxide plotted against the concentration of surfactant shows a maximum peak or a steep curve in near region of critical micelle concentration of the surfactant. From these results obtained, the formation of a polymer-surfactant complex or micelle is surmised.

Acknowledgement

The author wishes to express the deepest appreciation to Dr. Seishi Machida, the professor of the Kyoto University of Industrial Arts and Textile Fibers, for his kind advice in the preparation of the manuscript. Thanks are due to Miss T. Inoue and Miss T. Matsuoka for their assistance in the experimental work.

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