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The Iodine Affinity of Polyvinyl Acetate and Its Derivatives

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Polyvinyl acetate (PVAc)¹⁾ and its derivatives, such as partially saponified PVAc²⁾, and polyvinyl alcohol (PVA),³⁾ are known to form colored complexes with iodine. The complex reaction of PVA with iodine has been reported on by several investigators, and various mechanisms have been suggested to explain the reaction. Zwick⁴⁾ proposed a helical complex structure, such as has been described in the case of amylose.⁵⁾ On the other hand, Tebelev *et al.* pointed out that complex iodine is taken up into the interstices between the aggregated PVA molecules.⁶⁾ In order to clarify the mechanism of the complex formation between these polymers and iodine, stoichiometric studies of the binding of iodine to the polymers are required. In the present paper, accordingly, we will attempt to clarify whether or not it is possible to determine the iodine affinity of PVAc and its derivatives by the potentiometric titration method.

Experimental

Materials. Both of the PVA's used were commercial products from the Nippon Synthetic Chemical Industry

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4) M. M. Zwick, *J. Appl. Polym. Sci.*, **9**, 2393 (1965).

5) R. S. Stein and R. E. Rundle, *J. Chem. Phys.*, **16**, 195 (1948).

6) L. G. Tebelev, G. F. Mikulskii, E. P. Korchagina and S. A. Glikman, *Visokomolekul. Soedin.*, **7**, 128 (1965).

Co., Ltd. The NL-05 was used as perfectly saponified PVA, while the GL-05 was used as partially saponified PVAc. The residual acetyl content in the partially saponified PVAc was 11.32 mol%. A PVAc suspension was used as the PVAc sample. The PVAc suspension was prepared both by the suspension polymerization of vinyl acetate and by the addition of the PVAc solution obtained by methanol-solution polymerization to water. The suspension polymerization of vinyl acetate was carried out at 70°C for 1.5 hr, using potassium peroxydisulfate as the initiator. The solid content thus obtained was 14.26%, and the mean particle diameter of the PVAc suspension, as determined by means of an electron microscope, was 0.17 μ. The excess initiator, the byproducts formed by the decomposition of the initiator, and the residual vinyl acetate were removed by dialysis. The degree of polymerization of PVAc was calculated by measuring the intrinsic viscosity in acetone at 30°C, using the following equation first proposed by Nakajima;[7] $[\eta]=7.94\times10^{-4}P^{0.62}$. 0.5 g of commercial starch was dissolved in 100 ml of water, and its supernatant solution was used as the starch sample.

Measurements. A Yanagimoto potentiometric titrimeter equipped with a calomel cell and a bright platinum electrode, type KY-5, was used for the measurement of the iodine affinity of PVAc and its derivatives. The potentiometric titration was carried out as follows at room temperature according to the procedure reported by Bates *et al.*[8] The sample solution (50 ml) containing potassium chloride (0.3728 g) and potassium iodide (0.8300 g) was titrated with a 0.001 N iodine solution prepared by dissolving iodine (0.1269 g), potassium iodide (8.3003 g), and potassium chloride (3.7278 g) in distilled water (1000 ml).

Results and Discussion

PVAc Derivatives. Figure 1 shows the potentiometric titration curves for PVAc derivatives. A blank curve was also obtained in the absence of the polymer sample. The PVA used in our experiment did not exhibit any color reaction with iodine in a dilute aqueous solution. The titration curve for the PVA was the same as that for a blank. The color reaction of the partially saponified PVAc with iodine was red-violet, and the complex solution possessed an absorption peak at 480—490 mμ. The iodine potentials of the titration curves for the partially saponified PVAc decreased with the increase in the concentration of the polymer, and the titration curves were all similar in type to those of amylopectin reported by Bates *et al.*[8] Consequently, the increase in iodine bound to partially saponified PVAc appears to be proportional to the increase in the concentration of free iodine.

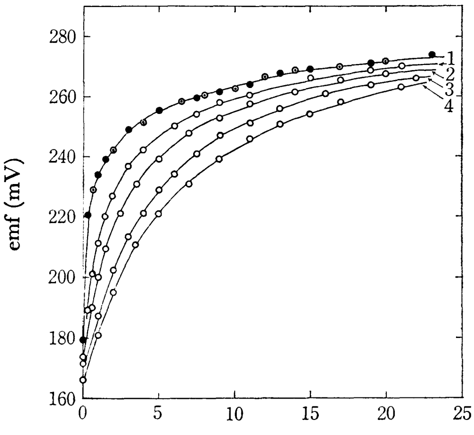

Fig. 1. Titration curves for PVA and partially saponified PVAc.
●: Blank, ⊙: PVA, 0.1500 g, ○: Partially saponified PVAc, 1: 0.0500 g, 2: 0.1000 g, 3: 0.1500 g, 4: 0.2000 g.

PVAc Suspension. The color of the iodine-PVAc suspension complex was the same red-violet as that of the iodine-partially saponified PVAc complex, and the absorption maximum was at 490—500 mμ. Figure 2 shows the potentiometric titration curves for the PVAc suspension, together with those for starch. The curves in Fig. 2 were obtained by the titration of PVAc and of starch in varying amounts. The curves for PVAc, as well as those for amylose, had horizontal parts for the iodine potentials, indicating that all the added iodine was consumed in the complex formation. Therefore, according to the calculation method of the iodine affinity suggested by Bates *et al.*,[8] it is possible to determine the amounts of iodine consumed in the complex formation with PVAc. As is shown in

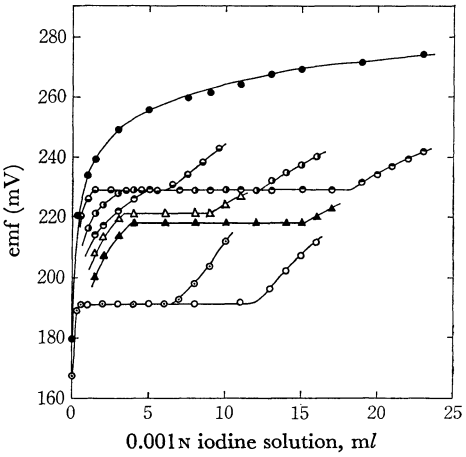

Fig. 2. Titration curves for PVAc and starch.
●: Blank.
PVAc sample of suspension polymerization: ($\bar{P}$=3640)
◒: 0.0100 g, ◑: 0.0200 g, ◓: 0.0300 g.
PVAc sample suspended polymer in water ($\bar{P}$=510): △: 0.0150 g, ▲: 0.0250 g.
Starch: ⊙: 0.0158 g, ○: 0.0252 g.

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[7] A. Nakajima, *Kobunshi Kagaku*, **6**, 451 (1949).

[8] F. L. Bates, D. French and R. E. Rundle, *J. Amer. Chem. Soc.*, **65**, 142 (1943).

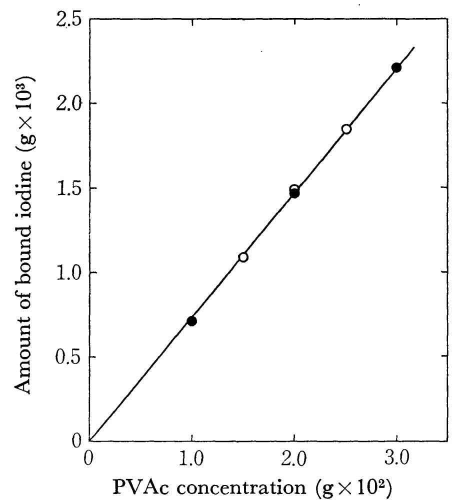

Fig. 3. Relationship between PVAc concentration and amount of bound iodine.

●: PVAc sample of suspension polymerization ($\bar{P}$=3640)

○: PVAc sample suspended polymer in water ($\bar{P}$=510)

Fig. 3, a linear relationship was obtained between the amount of iodine bound to PVAc and the PVAc concentration, regardless of the form of PVAc suspended in water, and the iodine affinity of PVAc (grams of iodine consumed by 100 g of PVAc) was found to be 7.3. All the iodine potentials of the horizontal parts for PVAc were higher than those for starch. It is already clear from the experimental results that amylose of a low molecular weight requires a higher iodine potential for a complex formation. However, there have not yet been any reports concerning the reason for this. In the case of PVAc, it is impossible to consider the relationship between the potential of a horizontal part and the degree of polymerization, because the spectrum of the complex is not influenced by the degree of polymerization.9) Since the complex reaction of the partially saponified PVAc with iodine is also based on the number of the vinyl acetate units existing continuously in the polymer chain,10) the mechanism of the complex formation of the partially saponified PVAc must be essentially identical with that of PVAc. When we compare Figs. 1 and 2, PVAc and partially saponified PVAc can be seen to indicate a remarkable difference in the titration curves. This seems to be because only PVAc among the samples examined was a heterogeneous system, since water is a nonsolvent for PVAc. Further, more detailed studies will be necessary to confirm the above results.

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