NOTES

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The Determination of the Iodine Affinity of Poly(vinyl acetate)

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In a previous paper, in which the complex between poly(vinyl acetate)(PVAc) and iodine in the presence of potassium iodide has been investigated, we have reported that the potentiometric titration curve for a PVAc suspension with iodine is of the same type as that for amylose.[1] However, it was found from the results of many experiments that the iodine affinity of PVAc (grams of iodine consumed by 100 g of PVAc) varies widely with the measurement conditions, because the reaction system between PVAc suspended in an aqueous solution and iodine is heterogeneous. Therefore, in the present paper, we wish to attempt a more accurate estimation of the iodine affinity of PVAc in an apparent homogeneous system.

Experimental

Materials. The PVAc samples used here were prepared by the solution polymerization of vinyl acetate in methanol and by the suspension polymerization of vinyl acetate, using benzoyl peroxide and potassium persulfate respectively. The degree of polymerization of the PVAc prepared by solution polymerization was about 500. The iodine, potassium iodide, and sodium thiosulfate were reagents of a guaranteed grade.

Measurements. A methanol solution (1 ml) containing PVAc (1.5×10^{-3}g) prepared by solution polymerization and iodine, the content of which was varied from 0.80×10^{-7} to 20.8×10^{-7} mol, was added to 40 ml of an aqueous solution of potassium iodide (6.42×10^{-3} mol), and the total volume was exactly adjusted 50 ml by adding water.[2] The mixture instantly showed a red-violet color. The colored solution was kept in a water bath thermostated at 15°C for an hour; then the absorbance and the potential values of the solution were measured by the use of a Hitachi-Horiba M-5 pH-meter and a Hitachi 101 spectrophotometer respectively.

The films of PVAc were prepared by casting a methanol solution of PVAc obtained by the solution polymerization and a PVAc suspension produced by the suspension polymerization on the polyethylene film. The films of PVAc thus obtained were dried in a vaccum, dipped in 100 ml of a 0.1N iodine solution (iodine/potassium iodide=1/4 by wt.) for 24 hr at 15°C, and then washed with water for two weeks. The amount of iodine reacted with PVAc was determined by the following method: the film reacted with iodine was dissolved by methanol (50 ml), and then it was titrated with a 0.1N sodium thiosulfate solution.

Results and Discussion

When the mixture of PVAc and iodine in methanol was added to an aqueous solution of potassium iodide, a red-violet complex was immediately formed. This complex was rapidly destroyed by adding sodium thiosulfate, and at that time the solution was transparent, after which it gradually became turbid because of the precipitation of PVAc. It is evident from this finding that, in the method used here, the reaction system of PVAc with iodine is apparently homogeneous.

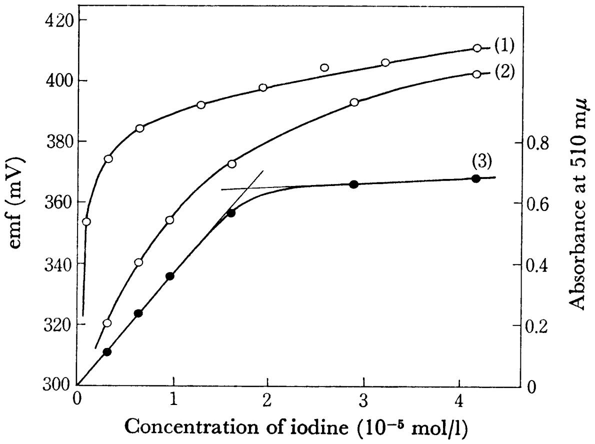

Fig. 1. Plots of emf (○) and absorbance (●) at 510 mμ versus concentration of iodine. PVAc concentration: 0.03 g/l.
(1) Curve of emf in the absence of PVAc,
(2) Curve of emf in the presence of PVAc,
(3) Curve of absorbance at 510 mμ in the presence of PVAc.

The potential values *versus* the concentration of iodine in the apparent homogeneous system are shown in Fig. 1, in which the potential values in solution increased with an increase in the concentration of iodine. This result has some similarity to that for the partially-saponified PVAc, which is easily soluble in water and which reacts with iodine to produce the red-violet complex.[1,3]

In a previous paper,[1] we could see a horizontal part in the potentiometric titration curve for the PVAc with iodine, where the potential values in solution remained constant upon the addition of iodine because the iodine added was consumed in the complex formation with PVAc suspended as particles in water.

Consequently, it is confirmed that the potentiometric titration curve for PVAc with iodine varies with the reaction conditions. On the basis of these data, we can explain the potentiometric titration curves for PVAc with iodine as follows: the fact that the titration curve for PVAc suspended in water is similar to that for

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[1] S. Hayashi, T. Nakabayashi, and K. Yoshida, This Bulletin, **43**, 3292 (1970).

[2] S. Hayashi and C. Kawamura, *Kogyo Kagaku Zasshi*, **72**, 2491 (1969).

[3] S. Hayashi, C. Nakano, and T. Motoyama, *Kobunshi Kagaku*, **20**, 303 (1963).

Table 1. Iodine affinities of PVAc in film

Samples			Results		
Area (cm^2)	Weight (g)	Thickness[a)] (mm)	Degree of swelling in area[b)]	Degree of swelling in weight[c)]	Iodine affinity
PVAc obtainecd from solution polymerization					
3.15	0.4833	1.28	5.1	6.6	13.5
3.42	0.4562	1.10	3.8	6.2	13.4
4.01	0.4900	1.02	3.8	6.5	13.1
3.80	0.4554	0.99	4.0	6.3	13.2
3.96	0.4595	0.97	3.8	6.5	13.1
7.29	0.4135	0.47	4.0	6.9	10.6
8.12	0.4054	0.42	3.9	7.0	9.8
9.25	0.3154	0.28	4.4	7.3	8.2
PVAc obtained from suspension polymerization					
3.42	0.4935	1.44	1.8	4.8	12.6
4.14	0.4437	0.89	2.4	6.3	14.0
5.28	0.4797	0.76	2.0	6.7	15.7
6.60	0.4918	0.62	2.7	5.4	12.9
10.73	0.4914	0.38	2.9	4.4	10.7
11.22	0.3075	0.27	3.1	3.9	4.7

a) Thickness was calculated from area and weight by assuming that specific gravity of PVAc is 1.20.

b) Degree of swelling in area

$$=\frac{\text{Area of swelling film}}{\text{Area of original film}}$$

c) Degree of swelling in weight

$$=\frac{\text{Weight of swelling film}}{\text{Weight of original film}}$$

amylose indicates a heterogeneous reaction based on the diffusion of iodine into the PVAc particles suspended in water, without regard to the formation of a helical complex of a polymer with iodine postulated in the case of amylose.[4)]

The relationship between the absorbance and the concentration of iodine in the apparent homogeneous system is shown in Fig. 1. When the amount of PVAc was kept constant, the maximum absorption was obtained by adding more than about 2.5×10^{-5} mol/l of iodine for 3.48×10^{-4} mol/l of monomer units in PVAc. This shows that PVAc has a stoichiometric relation with iodine. According to Bates *et al.*,[5)] results of Fig. 1 show the iodine affinity of PVAc to be 12.2. This value is considerably larger than the value of 7.3 obtained in the heterogeneous system.[1)] Furthermore, from Fig. 1, the molecular extinction coefficient of iodine in the complex was estimated to be 42200 l/mol·cm.

The iodine affinities of PVAc in film are summarized in Table 1. The swelling of a film began as soon as the film assumed a red-violet color; eventually it grew to several times the original film. When a thin film was used as a sample, it was observed that some of the polymers disperse into water from the film as the complex forms during a period of washing. On the other hand, when a thick film was used as a sample, no loss of polymers was observed, and the iodine affinities of PVAc were about the same. This indicates that, if the reaction conditions, such as the reaction time and the concentration of iodine, are given satisfactorily, the iodine affinities of PVAc are almost all the same, independent of the properties of the PVAc originating from the polymerization conditions. Consequently, the largest cause for the error in the iodine affinity of PVAc found by the potentiometric titration in the heterogeneous system[1)] appears to be the insufficiency of the reaction conditions in its system. The average value of the iodine affinities of PVAc in film, except for the thin films, was 13.5. This value is in good agreement with that found from Fig. 1. Accordingly, the iodine affinity of PVAc obtained in the apparent homogeneous system is thought to be reasonable.

The stoichiometry indicates that one molecule of iodine reacts with about 24 vinyl acetate units in PVAc. However, in the absence of direct evidence, the arrangement of iodine molecules in the complex between PVAc and iodine can not be illustrated. Further work is now in progress.

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4) R. E. Rundle, J. E. Foster, and R. A. Baldwin, *J. Amer. Chem. Soc.*, **66**, 2116 (1944).

5) F. L. Bates, D. French, and R. E. Rundle, *ibid.*, **65**, 142 (1943).