Organoboron Compounds. IV. The Dyeing Property of Polyvinyl n-Butylboronate with Congo Red*

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Recently Fujino and Fujimoto reported on the dyeing properties of two kinds of polyvinyl alcohol films1), one of which had previously been heat-treated and the other, formalized. They showed that the dye sorbed by films decreases in quantity with the extent of formalization. In a previous paper2), the present authors reported on the reaction of polyvinyl alcohol with *n*-butylboronic acid and on some properties of the products, showing that it is possible to prepare some films with various esterification grades. Generally it is considered that the force binding dye molecules to polyvinyl alcohol is chiefly due to the hydrogen bond and some mechanical retention. If the binding force comes into play by co-ordination, even in the absence of mordants, it will strengthen the bond between the dye molecule and the substrate. The aim of this investigation consists in the point mentioned above. Since it is well known that the boron atom can coordinate easily with such negative atoms as oxygen, nitrogen and halogens, the dyeing capacity of polyvinyl boronate is expected to become large. In a previous communication3) the authors showed that the quantity of the dye sorbed by films increases with the increasing esterification grade and that the apparent diffusion coefficient also corresponds to the esterification grade. The authors have observed some facts regarding the property of polyvinyl *n*-butylboronate films dyed with Congo red, the former containing boron atoms and the latter, nitrogen atoms.

Experimental

Substrates.—Boronate films were prepared, as described in a previous paper2), by pouring a carbon tetrachloride solution of polyvinyl *n*-butylboronate with different esterification grades on a surface of mercury and then drying it for several days at room temperature. The films were all cut in pieces 1 cm.×2 cm. The thickness was about 0.1 mm. Congo red was purified according to Robinson and Mills' method4).

Dyeing Procedure.—The films with different esterification grades were immersed into a Congo red solution at various temperatures. Then the sample were taken out one by one at definite intervals, well washed with cold water, and desorbed with a pyridin-water mixture. The amounts of dye sorbed by the samples were measured with a photo-electric colorimeter.

Measurement of the Heat of Sorption by Microdesorption Method.—The samples having various esterification grades were previously dyed with Congo red and immersed into water kept at 20, 40 and 60°C according to the method which was proposed by Gilbert and Rideal5); after reaching equilibria, the desorbed dye was measured by a photo-electric colorimeter.

Results and Discussion

In dyeing experiments, it is generally necessary to record the time needed to reach the equilibrium of sorption. The sorption rate here was always faster than that of the polyvinyl alcohol film prveiously studied by Fujino and Fujimoto1). Figure 1 shows the relation between the rate and the temperature obtained with samples of the same esterification grade. Above 60°C the samples swelled for the first 10 hr. and later partially dissolved owing to

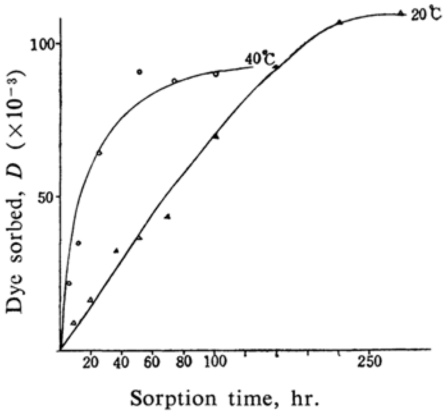

Fig. 1. Dye sorbed and absorption rate.

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* I, This Bulletin, 34, 1107 (1961); II, ibid., 33, 1741 (1960); III, *Waseda Applied Chem. Soc. Bulletin, (in Japanese)* 28, No. 5, 28, (1961).

1) K. Fujino and N. Fujimoto, *J. Soc. Textile and Cellulose Industries, Japan,* 15, 138, 217 (1959).

2) S. Kato, Y. Tsuzuki and S. Kitajima, This Bulletin, 34, 1107 (1961).

3) S. Kato and Y. Tsuzuki, ibid., 33, 1741 (1960).

4) C. R. Robinson and H. A. Mills, *Proc. Roy. Soc.,* **A131**, 576 (1931).

5) G. A. Gilbert and E. K. Rideal., ibid., **A182**, 335 (1944).

the hydrolysis of the samples; therefore, the rate curves above 60°C were all neglected.

With samples of different esterification grades (E_g), differences in sorption were also observed. At the same time the quantity of the dye sorbed corresponds to the value of E_g, the data of which are given in Table I.

TABLE I. RELATION BETWEEN THE QUANTITY OF THE DYE SORBED AND ESTERIFICATION GRADE (E_g)

No. of sample	E_g, %	Dye sorbed (g./g. dry film) $\times 10^2$ 20°C	40°C	Activation energy kcal./mol.
B-1	75.4	5.6	4.7	17.4
B-2	80.6	7.9	6.0	16.1
B-3	85.6	10.9	9.2	13.0

Esterification grade (E_g) can be estimated from the boron content of the products by the following equation:

$$E_g = (133.74 \times \mathrm{B}\%)/(16.41 - \mathrm{B}\%)$$

Heat of Sorption.—In order to learn whether co-ordination takes place or not in this dyeing mechanism, the measurement of the heat of sorption was desirable. In the case of cellulose fiber and Vinylon, the heat of sorption was estimated to be about 10 to 20 kcal./mol.[6] According to Laubengayer and Condike[7], the heat of formation of the complex between trimethylboron and ammonia is 41.3 kcal./mol. This value seems to represent the energy of the B-N bond. The heat of sorption can be measured by means of the microdesorption method, which is quite convenient and can be used smoothly*. The results were shown in Fig. 2.

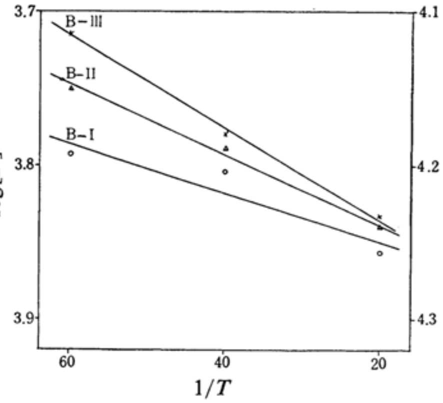

Fig. 2. Temperature dependance of the desorption of dye in equilibrium.

The slopes of the three lines in Fig. 2 represent the heat of sorption. These values apparently correspond to E_g. The values obtained are, however, not so high as those observed with cellulose and Vinylon fibers, as can be seen in Table II.

TABLE II. THE HEAT OF SORPTION AND ESTERIFICATION GRADE

No.	% E_g	Heat of Sorption (HS) kcal./mol.	HS/E_g
B-1	75.4	15.9	0.21
B-2	80.6	22.5	0.23
B-3	85.6	30.1	0.35

In order to study this problem, deeper infrared spectra were taken with dyed as well as undyed films, the data of which are shown in Fig. 3.

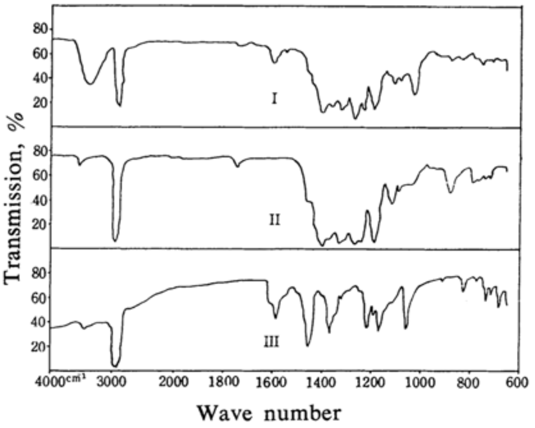

Fig. 3. Infrared spectra.
I Film dyed with Congo red
II Film not dyed
III Congo red in Nujol

The absorption band at 1580 cm^{-1} can be assigned to the azo bond, that at 3420 cm^{-1} to the bonds of amino group, and many bands below 1300 cm^{-1} in III to those of the aromatics[8]. Among the bonds of the boron atom linked with such negative atoms as oxygen, nitrogen and halogens, the B-N bond is the strongest, so bonding can be expected to occur with the azo and amino groups. The weak band at 3510 cm^{-1} may be regarded as due to a free type of hydroxyl group in II, and this absorption peak and that of the amino group at 3420 cm^{-1} shift to a lower frequency after the dyeing with Congo red, while the absorption band of the azo group shifts to a slightly higher frequency. From these results, it is considered that the bonding between the boron

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[6] T. Vickerstaff, "Physical Chemistry of Dyeing", 2nd. ed, Oliver and Boyd, London (1954), p. 229.

[7] A. W. Laubengayer and G. F. Condike, *J. Am. Chem. Soc.*, **70**, 2274 (1954).

* Ref. 4 traced by A. Yabe and A. Uchida, *J. Soc. Org. Synth. (in Japanese)*, **13**, 601 (1955).

[8] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", Methuen & Co., London (1958), p. 272.

atom and the nitrogen atoms may take place, for the most part, at the amino group in the dye molecules. Of course, the hydrogen atom of the amino group in the dye molecule can make a hydrogen bond with the oxygen atom⁹⁾ in polyvinyl *n*-butylboronate; hence, the presence of the broad band at 3400 cm^{-1} in the spectrum of I can be ascribed to two factors, one of which is the formation of the hydrogen bond between the amino group of the dye and the oxygen atom of polyvinyl *n*-butylboronate, and the other is the co-ordination of the boron atom to the nitrorgen atom of the amino group. The energy of dyeing should become ca. 40 kcal./mol. if all dye molecules are fixed to polyvinyl *n*-butylboronate by co-ordination, but, in fact, the values of the heat of sorption per E_g are not always equal. This means that the dyeing proceeds not only through co-ordination but also through a hydrogen bond.

Another factor which should be considered regarding the results of the relation between E_g and the dyeing property is the destruction of the dense polyvinyl alcohol structure by the treatment with boronic acid. Sakurada and Okada¹⁰⁾ have studied the reaction of boric acid with polyvinyl alcohol by means of X-ray diffraction; on the basis of the diminished fine structure in the diffraction pattern, they concluded that the crystalline part of polyvinyl alcohol is thereby decreased. In the case of the reaction of *n*-butylboronic acid with polyvinyl alcohol the molecular weight and the size of this acid are larger than those of boric acid, so that the crystalline part of polyvinyl alcohol, will diminish with the increasing esterification grade. The results of the estimation of activation energy suggest this consideration. Thus, experimenial results show that the two factors mentioned above overlap. In order to demonstrate the co-ordination, further experiments with various dyes should be carried out. The effects of various reactants on the spectra of the polyvinyl *n*-butylboronate in solution will be discussed later.

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9) M. St. C. Flett, *J. Soc. Dyer and Col.*, **68**, 59 (1952).

10) I. Sakurada and A. Okada, *Chem. High Polymers (Kobunshi Kagaku,)* **15**, 491 (1958).