

Poly(vinyl Alcohol)-Iodine Complexes

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Synopsis

The poly(vinyl alcohol)-iodine blue color reaction in dilute aqueous solution has been investigated, and extinctions at the absorption maximum have been measured as a function of the concentrations of polymer, iodine, iodide ions, and boric acid. Depending upon the reaction conditions, the main absorption maximum can be made to appear at any wavelength between 580 and 700 $m\mu$, with the longest wavelengths and highest extinctions per vinyl alcohol group showing up at high boric acid concentrations. Poly(vinyl alcohol) samples from various sources displayed, under identical reaction conditions, great differences in staining intensities. This can be ascribed to differences in the regularity of the polymer chain structures. To account for the behavior of poly(vinyl alcohol) towards iodine under a wide variety of reaction conditions, as well as for a number of irreversible or only slowly reversible phenomena, a model for the mechanism of the PVA-iodine complex formation is proposed involving a dual process of helix formation and intramolecular helix association. There is evidence to indicate that at full iodine saturation of the polymer, 12 vinyl alcohol residues supported by one boric acid molecule form a single turn of a helix which enwraps one iodine atom, out of a long polyiodide chain nested in the interior of a poly(vinyl alcohol) helix.

INTRODUCTION

The blue colored complexes of poly(vinyl alcohol) with iodine have often been likened to those of amylose and iodine.¹⁻⁸ However, while the latter have been extensively studied during the past decades (for a recent review see Senti and Erlander⁹), much less attention has been paid to the former until very recently. This state of affairs may in no small degree have been influenced by such authorities in the field of starch research as Rundle and his co-workers, who had originally rejected the idea that these two types of complexes were essentially of the same kind. According to these authors,¹⁰ "Amylose is unique not in staining blue with iodine, but in staining blue in such dilute solutions that molecular dispersion of amylose seems to be approached. In most, if not all, other blue complexes aggregates of molecules are required, and quite probably the iodine molecules are arranged between neighboring molecules. The amylose-iodine complex is different in that a single molecule envelopes a parallel array of iodine molecules. It seems likely that the unique structure of the amylose-iodine

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complex is the explanation for its unique behavior in solution." As an example of such "other" blue complexes, Rundle specifically names the staining by iodine of poly(vinyl alcohol) and cellophane film, and that of cellulose fibers.

Amylose was, indeed, the first polymeric molecule discovered to exist in a helical shape even in solution.¹¹ The dimensions of the interior channel surrounded by the amylose helix are such that iodine molecules can be snugly accommodated, and strongly held, in these channels. In recent years, however, many more polymeric materials, both of natural and synthetic origin, have been found to assume helical molecular shapes under specific conditions.¹² Today, even such simple polymers as polytetrahydrofuran are suspected of forming helices in some solvents,¹³ and helix-coil transitions have also been reported taking place in films.¹⁴

Recognizing that helix formation may be a much more common feature with polymers in solution than hitherto thought, it seems worthwhile to re-examine the case of those poly(vinyl alcohol)-iodine complexes. Their relatively low binding energy and, therefore, the need for higher iodine concentrations to form the blue complexes may speak as much for the single macromolecular envelope as against it. If a poly(vinyl alcohol) chain has no tendency of its own to assume a helical shape spontaneously in the absence of iodine, the entropy decrease that would have to accompany helix formation in the presence of iodine could easily account for the diminished stability of the poly(vinyl alcohol) (PVA) complexes as compared to those of amylose.

Another reason for the slow progress in the elucidation of the PVA-iodine reaction may lie in the fact that experimental work with these complexes is beset by a number of complications. Color development is slow,¹⁵ reaching maximum intensity sometimes only after several days and fading off again after that. Intensity measurements in different runs conducted under seemingly identical conditions do not coincide.¹⁶ Hysteresis effects have been encountered when complex formation is allowed to take place at reduced temperature, and the solutions are brought back to room temperature.⁵ Phenomena of this sort, however, have also been observed with amylose.

Previous Work in This Field

The blue color reaction of PVA with iodine was observed by Herrmann and Haehnel,¹⁷ who were the first to synthesize poly(vinyl alcohol), and by Staudinger and co-workers¹⁸ as early as 1927. Bockmühl and Midden-dorf¹⁹ noted a few years later that the blue color would still show up with a PVA concentration as low as 2×10^{-2} base mole/l., but that this might take several hours or days. According to these authors,¹⁵ the color developed faster when the iodine was reacted *in statu nascendi* by allowing iodic acid and iodide ions to come together in the presence of poly(vinyl alcohol).

In 1936 Gallay¹ measured the amount of iodine that is carried along by PVA when it is precipitated from iodine solutions of various concentrations.

He also observed that the blue color would only appear when the iodine concentration exceeded a certain minimum.

West²⁰ reported that in the presence of boric acid, poly(vinyl alcohol) and iodine formed the blue complex at a much greater dilution of the reactants than in the absence of boric acid. The absorption maximum of the PVA-iodine-boric acid complex was found to lie at 670 $m\mu$ (as against 590 $m\mu$ for the starch-iodine complex and 628 $m\mu$ for the amylose-iodine complex). Moreover, the heat of addition of iodine to PVA in the presence of boric acid was found to be surprisingly high (20 kcal./mole), and practically equal to values measured for amylose-iodine complexes. Monte-Bovi et al.²¹⁻²³ proposed the use of the system PVA-boric acid as an indicator in iodometry in place of starch because of the former's high sensitivity and the stability of its solutions.

Miller and Brakken² noted that the blue color did not develop with a poly(vinyl alcohol) containing 10% or more of acetate residues, but that a crimson color shows up instead, as is also displayed by completely unhydrolyzed poly(vinyl acetate) in aqueous alcoholic solution when iodine is added.

Yoda,²⁴ who studied absorption spectra of PVA solutions containing various ratios of PVA:I₂, found that the maximum in the absorption spectrum of the PVA-iodine complexes lies at 600 $m\mu$ for highly hydrolyzed PVA, at 480 $m\mu$ for PVA of a low degree of saponification, and that there were two peaks, at both 480 and 600 $m\mu$, in intermediate cases.

Since 1954, Schildknecht³⁻⁵ has studied iodine complexes of partially and fully hydrolyzed poly(vinyl alcohol) and of ethylene vinyl alcohol copolymers in the absence and presence of boric acid. He found, *inter alia*, that with fully hydrolyzed PVA the rate of color formation, as well as the final intensity, could be considerably enhanced by the addition of salts and by decreasing the temperature. Schildknecht thought that the effect of the added salt might be to assist the PVA molecule in taking up a helical shape to form a channel type of inclusion complex. This, however, was not reflected in a change in viscosity, which he expected should take place concurrently with color development.

Kontos²⁵ measured the absorption spectra of PVA-boric acid-iodine complexes in the range of 250 and 800 $m\mu$ prepared at different concentrations of the various components. Of the three maxima at 288, 353, and 680 $m\mu$ which he observed, the one at 288 $m\mu$ always decreased as the one at 680 $m\mu$ increased upon complex formation. At the same time, the maximum at 353 $m\mu$ increased at low iodide concentration, but decreased at high iodide concentration.

In 1958 an extensive program was launched in Russia under the leadership of Ushakov and Mokhnach⁷ with the aim of evaluating the therapeutic properties of various PVA-iodine complexes. According to these authors, iodine in its highly polarized form, as it is believed to exist in the colored compounds, has potent antibacterial properties which are lost as soon as discoloration takes place for whatever reason. Since then, the

complexes have been biologically tested in a variety of physical forms, as precipitates, crosslinked gels, films,²⁶ and fibers.²⁷ Vinyl alcohol copolymers were synthesized, and the influence of the comonomer upon iodine binding was examined. The presence of 5% maleic acid in the PVA chain, for instance, was reported to increase complex stability 40-fold.

Mokhnach and Zueva²⁸ studied iodo-poly(vinyl alcohol) in aqueous solution at a number of concentrations. The fully developed complex showed four absorption peaks: at 226, 288, 350, and 620 $m\mu$. When the blue color was made to vanish by heating, only the 226, 288, and 350 $m\mu$ peaks remained. Upon reduction with thiosulfate, all but the 226 $m\mu$ peak disappeared. The complex could also be decomposed by very prolonged dialysis.²⁹

The same authors recently observed³⁰ that, in the presence of sufficient boric acid, the blue colored complex is also formed from poly(vinyl alcohol) and iodine alone with no addition of potassium iodide. In this case, the absorption maximum appears between 660 and 680 $m\mu$, instead of at 610 $m\mu$ as is usual when boric acid is absent and potassium iodide is added instead.

Glikman et al.³¹ noted that the intensity of the blue color depended both upon the absolute starting concentrations, and on the PVA:iodine ratio. Measuring the rate of color development, they found that the color intensity K as a function of time t after mixing the components could be described by the formula

$$K = t/(a + bt)$$

where a and b are constants. The authors made the interesting observation that, of two poly(vinyl alcohols) showing the same final absorption spectrum, the initial rate of color formation of the one was twice as large as that of the other. They, therefore, proposed to use the initial rate of color development as a means to characterize different PVA samples.

Several years ago, Imai and Matsumoto³² discovered that the PVA-iodine interaction is sensitive to the molecular weight and the steric regularity of the polymer molecule. Longer and more stereoregular poly(vinyl alcohols) will display higher color intensities under the same reaction conditions than polymers with short chains and random molecular configuration. Since then, the PVA-iodine coloration has been used as one of the indicators by which PVA's of similar molecular weights prepared under different conditions have been compared with regard to their molecular fine structure.^{16, 33-35}

In our studies on the fiber-forming properties of a number of PVA products,³⁶ we have likewise used the PVA-iodine color reaction for the characterization of our polymers. In our procedure we prepared for every poly(vinyl alcohol) a series of dilute solutions of different concentrations of the polymer, all containing the same concentration of iodine and potassium iodide, and measured the extinction at 610 $m\mu$, after the solutions had been allowed to stand for 24 hr. at room temperature. Plotting the extinc-

TABLE I
 Poly(vinyl Alcohol) Products Used in this Investigation, the Fiber-Forming Properties of Which were Studied Previously^a

Designation	PVA product	Manufacturer	Viscosity (4% soln.), cpoise	Volatiles, %	Ash, % ^a	Degree of polymerization	Ester groups, mole-%	1,2-Glycol groups, mole-%	Iodine value, (mole/l.) ⁻¹	Gelling tendency	Starting vinyl ester
A	Mowiol N 70/98	Hoechst, Germany	20	5.5	2.7	1400	0.2	1.3	1.6	Low	Acetate
B	Polyviol W 28/20	Wacker, Germany	28	5.2	1.3	1900	1.2	1.3	1.1	Low	Acetate
C	Elvanol 75/51	DuPont, U.S.A.	51	5.5	1.2	2400	2.6	1.3	1.8	Low	Acetate
D	Elvanol 72/60	DuPont, U.S.A.	60	4.6	1.2	2750	0.65	1.2	2.6	Low	Acetate
E	Elvanol 71/30	DuPont, U.S.A.	30	4.9	1.3	1800	0.65	1.2	2.4	Low	Acetate
K	PVA-H	Kurashiki, Japan	30	7.9	5.7	1750	0.2	1.2	4.1	Medium	Acetate
F	NH-1030	Norsk Hydro, Norway	15	14.9	0.1	1030	0.2	0.6	11.8	High	Formate
G	NH-1800	Norsk Hydro, Norway	51	5.5	0.05	1800	0.3	0.6	13.8	High	Formate
H	CL-TNO 3500	Own lab preparation	65	11.1	0.6	3500	0.2	0.6	16.8	High	Formate

^a After treatment with sulfuric acid.

tions versus polymer concentration for the products listed in Table I gave a series of straight lines passing through the origin, each line joining the points belonging to one particular product. This is shown in Figure 1.

The values of the tangents of these lines were then taken to characterize the various polymers in what we called the "iodine values" listed in Table I.

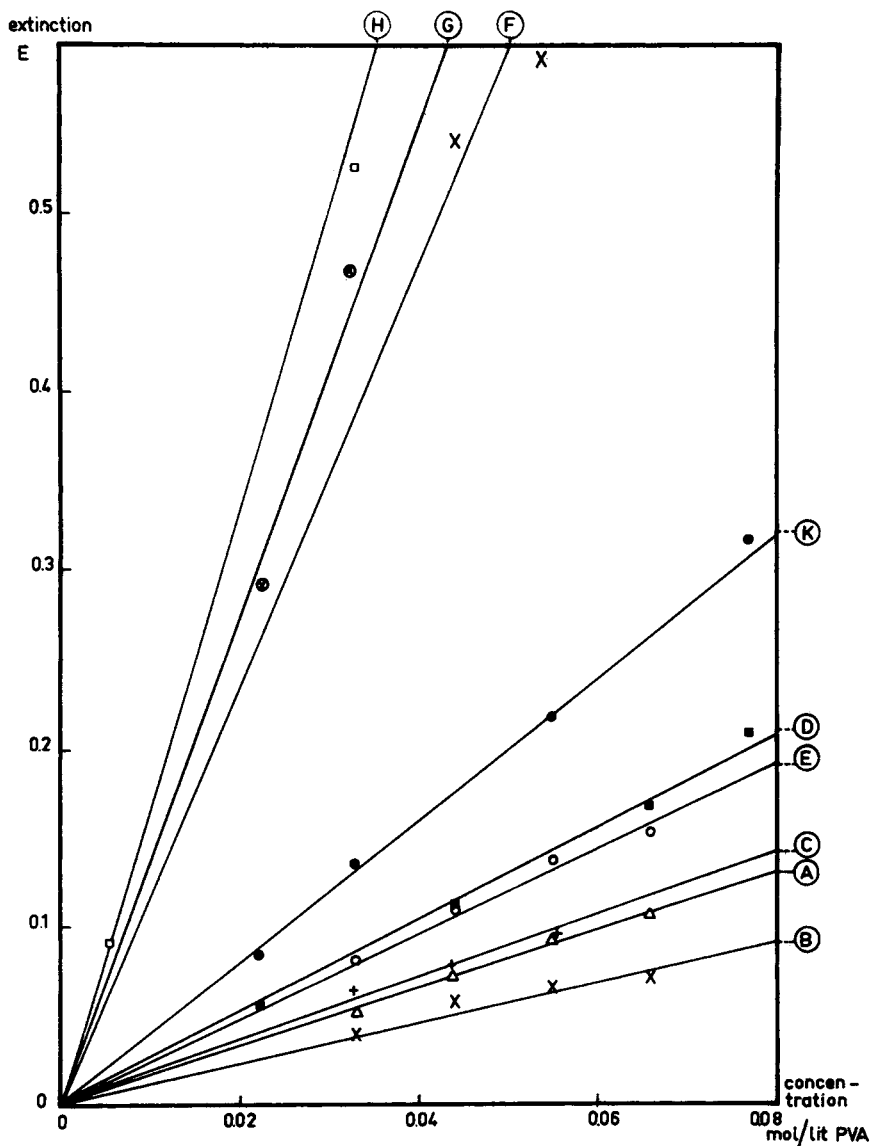


Fig. 1. Extinctions at $610\text{ m}\mu$ for different PVA samples, 24 hr. after the addition of iodine, as a function of the concentration of PVA. The samples are those listed in Table I. For experimental conditions see Table II.

The linear dependence on polymer concentration as shown in Figure 1 indicated two things: firstly, that under the conditions employed very little of the iodine in the solutions is actually bound to the polymer, so that almost no change in the iodine concentration of the solution surrounding the polymer takes place as more polymer is added (in the given PVA concentration range) and, secondly, that the color reaction most probably involved single PVA molecules and not polymer aggregates as suggested by Rundle.

We, therefore, undertook a more systematic study of color intensity as a function of the concentrations of those polymers differing in stereoregularity listed in Table I, and of the concentrations of iodine, iodide ions, and boric acid, sometimes at several temperatures. Unfortunately, by the time the blue color is fully developed, the PVA-iodine complexes are no longer in a dynamic equilibrium with their surrounding solutions. A thermodynamic analysis of the results with the aim of obtaining quantitative values for the energy and entropy changes taking place during the iodine complexing reaction is, therefore, not permissible here in the same way as it had been done for the rapidly reacting amylose.^{9,37,38} In spite of these obstacles, however, the information gained from these measurements was able to throw some light on the mechanism of the reaction between iodine and poly(vinyl alcohol).

EXPERIMENTAL

Preliminary Study

Before we could get this reaction satisfactorily under control, we encountered a great deal of scatter in the results of our extinction measurements. This was quite apart from the difficulty reported by Rosen and co-workers¹⁶ in reproducing the absolute values of color intensity at different times under the same experimental conditions. We, therefore, undertook a preliminary qualitative study of parameters that might influence the PVA-iodine color reaction with the aim of tightening control on the experimental conditions used in our subsequent quantitative studies. The following factors were found to be likely causes for fluctuation in results, if special attention is not paid to them, particularly in cases where color intensities are measured after 24 hr., at which time many compositions have not reached their maximum intensity values yet.

Air. The contact with air causes a premature fading of the color of the PVA-iodine reaction mixture. Half-filled test tubes show a light rim near the surface of the solutions. Air should, therefore, be excluded.

Light. Exposure to light, especially sunlight, causes color fading.

Temperature. The final color intensity, and still more the rate of color development are, over a wide range of concentrations, very temperature sensitive. Thermostatting is, therefore, absolutely necessary. Once a complex has been formed at a reduced temperature, its redecomposition at a small temperature increase is extremely slow.

Concentration. Mixing the reactants can become a problem, when working at a high concentration of one of the components. In such cases some colored complex is often formed almost instantaneously. Since the reactants are usually added from still more concentrated solutions, some complex is bound to be formed near the surface of the added drops before homogenization has been achieved. The reaction product thus formed will, however, not adjust itself in a reasonable time to the concentration conditions prevailing shortly afterwards. In this way considerable distortions of the final results may ensue. Temporary concentration fluctuations may thus form another source for scattering of measured values. One way around this difficulty may be to liberate the iodine (in the nascent state) by adding acid to a neutral PVA solution containing iodide and iodate ions after the essential components have been homogeneously dispersed first.

Boric acid at a concentration slightly above 0.2*M* causes gelation of poly(vinyl alcohol) solutions.^{39,40} Boric acid should, therefore, never be added from a more concentrated solution than that to a PVA solution already containing iodine. The gel forming near the surface of the boric acid drops will immediately stain and not disperse again.

Order of Addition of Reactants. The example just mentioned shows that the order of addition of the reactants is in some cases important. When the components have to be mixed and made up to a constant volume, the order of addition recommended is: PVA, water, (boric acid), KI-I₂ solution, or PVA, water, KI, KIO₃, (boric acid), sulfuric acid. Vigorous stirring for rapid dispersion is always indicated.

Time. Extinction measurements can, of course, be commenced at any time after mixing the components. However, because of its strong temperature dependence, tracing the initial rate of color development requires the use of thermostatted cuvettes, while these can be dispensed with when the color is fully developed.

When measuring intensities after several days, one must watch out for the onset of fading after the intensity maximum has been reached. Different polymers attain their intensity peaks after different time intervals, and also the rates of fading vary between the PVA's. A reduction in temperature, as a rule, slows down the intensity drop-off.

It has been our experience that at most concentrations the polymers have reached intensities within a few per cent of the maximum after 2 days at 8°C., while fading was still negligible under these conditions even for the most rapidly staining compositions.

Aging of PVA Solutions. The iodine color reaction was found to be sensitive to the state of aggregation of the poly(vinyl alcohol) in solution. Solutions prepared by boiling for at least 2 hr. in order to attain complete molecular dispersion, as recommended by Matsumoto,⁴¹ and used fresh, produced higher color intensities under otherwise identical reaction conditions than PVA solutions stored for some time in the cold. This is especially so with the more stereoregular polymers, which have a larger tendency to associate again than the irregular PVA.⁴² Such a tendency to reassociate

is even more drastic in the case of amylose, where retrogradation can lead to an almost complete loss of the capacity to take up iodine.⁴³

Nascent Iodine. Iodine liberated from iodide ions and iodic acid, in the presence of PVA, has been reported to bring about a faster color development than when a KI-I₂ solution is reacted with PVA at the same concentration.¹⁵ We did not verify this claim, but we found no significant difference with regard to the strength of the fully developed color after the intensity increase has ceased, as to whether the iodine had been reacted *in statu nascendi* or not. As already mentioned, liberating the iodine *in situ* makes it possible to have the color reaction started with the essential components in the desired dilution.

Electrolytes. Electrolytes enhance the blue color formation at low concentrations, or in the absence of boric acid. This is true both for electrolytes with salting-out effects upon poly(vinyl alcohol),⁴⁴⁻⁴⁶ such as sodium chloride⁵ or sodium sulfate, and for those with salting-in effects, such as sulfuric acid or potassium iodide.

Polymers

The poly(vinyl alcohols) used in our experiments were taken from the list of products shown in Table I. When the difference in reactivity owing to steric regularity was to be considered, two PVA brands, e.g., B and G, were selected to represent a random and a more regularly built polymer, respectively. More than two types of PVA from Table I were employed in an experimental series, when also intermediate cases seemed to be of interest. The letters A, B, C, etc., used in the figures to designate a particular poly(vinyl alcohol) refer to the lettering of the polymers in Table I.

Solutions

The reaction solutions in which the development of the blue PVA-iodine complex took place, were prepared in two ways.

In the first procedure, 50 cc. portions of the reaction mixtures were made up in 100 ml. Erlenmeyer flasks with vigorous stirring from stock solutions of PVA (0.27-0.027 base mole/l.), water, boric acid (0.52 mole/l.), and KI-I₂ (4:1) (0.02 mole/l. iodine or less). They were at once transferred into test tubes, which were filled to the rim and covered with rubber caps, so that no air became occluded. The test tubes were stored for two days at 8°C. (unless otherwise stated) in the dark before they were allowed to return to room temperature for spectrophotometric measurements. In an experimental run with this procedure, the concentrations of all but one of the reactants was the same in all the test tubes, while the concentration of one other reactant was systematically varied.

In the second procedure, 50 cc. portions of the reaction mixtures were made up from stock solutions of PVA, water, potassium iodide (0.12 mole/l. or less), potassium iodate (0.024 mole/l. or less), boric acid, and sulfuric acid (1*N*), and stored and measured as above.

When all the reaction mixtures are given the same initial iodide concentrations, the addition of increasing amounts of iodate to successive samples has the effect of increasing the iodine concentration while decreasing the iodide concentration along a line of compositions. On the other hand, by increasing both the amount of iodide and iodate added to successive samples correspondingly, the iodine concentration only can be made to change.

The range over which the concentrations of the components in the reaction solutions have been varied in this study, and wherefrom the most characteristic results are reported in this paper, is as follows: PVA, 10^{-2} – 10^{-1} base mole/l.; I_2 , 3×10^{-5} – 3×10^{-3} mole/l.; KI, 10^{-4} – 10^{-2} mole/l.; H_3BO_3 , 0.02–0.2 mole/l.; H_2SO_4 , 10^{-3} – $10^{-1}N$.

The concentrations of the components as added to the reaction solutions in the experiments for which the results are shown in Figures 1–13 are listed in Table II.

TABLE II
Concentration of Components as Added in the Experiments for Which the Results Are Shown in Figures 1–13

Figure	Curves	PVA, base mmole/l.	I_2 , mmole/l.	KI, mmole/l.	KIO_3 , mmole/l.	H_3BO_3 , mmole/l.	H_2SO_4 , mmole/l. ^a
1	All	20–80	1.6	6.4	—	—	—
2	I	2.7	0–2.4	7.2	—	—	40
2	II	2.7	0–1.2	3.6	—	42	60
2	III	2.7	0–1.0	0.9	—	83	60
2	IV	2.7	0–0.8	0.9	—	166	60
2	V	2.7	0–0.7	0.9	—	208	60
3	B2, G2	2.7	0–2.9	3.6	—	21	60
3	B16, G16	2.7	0–2.0	0.9	—	166	60
4	All	2.14	0.8	6.4	—	21–208	—
5	All	16.2	—	1.2	0.03	50–150	20
6	H	0–4	0.8	6.4	—	125	—
7	I	1.62	—	0.9	0–0.3	166	20
7	II	1.62	—	1.8	0–0.5	166	20
7	III	1.62	—	3.6	0–1.05	166	20
7	IV	1.62	—	7.2	0–1.05	166	20
7	V	1.62	—	14.4	0–1.05	166	20
8	K	16.2	—	0.45	0–1.35	166	660 Ac ^b
9	B; G	16.2	—	0.45	0–1.35	166	660 Ac ^b
10	All	54	—	0.60	0.09	94	20
11	All	—	—	0.533	0.066	—	20
12	1; 2	16.2	—	0.51	0.081	10	20
12	3; 4	16.2	—	0.51	0.081	166	20
13	All	2.7	—	$15 + 5c_{KIO_3}$	0–1	—	60

^a In mmole/l. hydrogen ions; also HCl used occasionally.

^b Acetic acid.

Spectrophotometric Measurements

The entire absorption spectrum of the colored solutions between 200 and 700 $m\mu$ was only taken in a number of those cases where the heights of the

intensity peaks over the whole range were of the same order of magnitude. This was the case with high boric acid and low iodide and iodine concentrations.

With all other reaction mixtures only the position of the absorption maximum in the visible region was located, and the extinction E measured at the maximum, with the use of 2, 5, or 10 mm. cuvetts, depending on the color intensity.

From the formula $I/I_0 = 10^{-Ea}$, the extinction E which is independent of the cell dimensions, has been plotted against the concentration of that component which was varied in each particular experimental run.

If we may assume that there is only one complexed species of iodine, the value of E can be split into two factors:

$$E = \epsilon_{I_2(\text{comp})}c_{I_2(\text{comp})}$$

where $\epsilon_{I_2(\text{comp})}$ is the molar extinction coefficient of iodine in the complex, and $c_{I_2(\text{comp})}$ its concentration. Any knowledge or assumption concerning the value of the extinction coefficient would then give us the concentration of the iodine bound by the polymer.

RESULTS AND DISCUSSION

Position of the Absorption Maximum in the Visible Region

The position of the absorption maximum of the PVA-iodine complex in the visible region has variously been reported as lying between 595 and 620 $m\mu$ ^{16,24,28,32} in the absence of boric acid, and around 670 $m\mu$ ^{20,25,30} when boric acid is present.

We have found that the absorption maximum of the PVA-iodine complex can be made to appear anywhere between 580 and 700 $m\mu$ with one and the same poly(vinyl alcohol), depending on the conditions employed. In the absence of boric acid and at high iodide concentrations ($>10^{-2}$ mole/l.), the maximum will be produced at the shortest wavelength moving up to 620 $m\mu$ as the iodide concentration is decreased. In the presence of boric acid, the absorption maximum may lie anywhere between 620 and 700 $m\mu$, depending on the concentration of the boric acid. Longest wavelengths are shown at boric acid concentrations above 0.15 mole/l. at low iodide ion concentrations ($<5 \times 10^{-4}$ mole/l.).

Because of this continuity in the shift of the absorption maximum, it seems likely that one deals here with the same sort of complex over the whole range of wavelengths, and that essentially the same mechanism underlies complex formation, whether boric acid is present or not. In the representations that are to follow we will, therefore, treat side by side cases where boric acid has and has not been added.

Dependence on Iodine Concentration

Figure 2 shows the results of a number of spectrophotometric titrations of PVA B with iodine, each one conducted at a different concentration of

boric acid, starting with a boric acid concentration of zero. It can be seen that with the increase in boric acid concentration, the amount of iodine required to bring about a certain color intensity becomes progressively smaller. At the same time, the absorption maximum shifts to longer wave lengths, as has already been stated.

The titration curve of the solution free from boric acid clearly shows the existence of a threshold concentration of iodine below which no color formation takes place. A similar threshold, but smaller in magnitude, is also present at the lower boric acid concentrations.

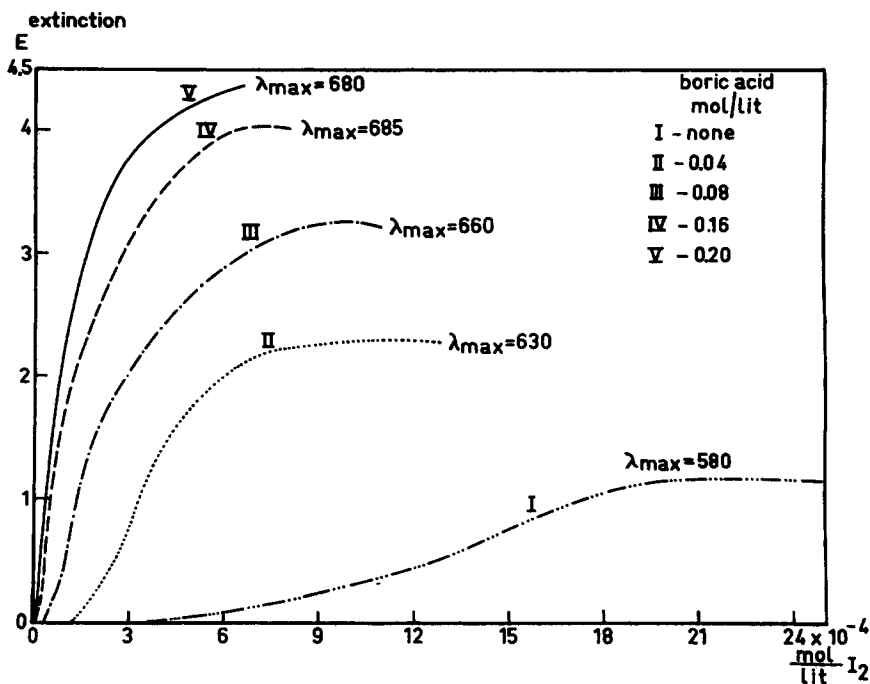


Fig. 2. Spectrophotometric titration of PVA B with iodine at various boric acid concentrations. E is the extinction at the respective absorption maximum.

To answer the question whether more iodine is complexed by the polymer as more boric acid is added, in other words, whether $c_{I_2(\text{comp})}$ increases with boric acid concentration, would require the knowledge of the various extinction coefficients $\epsilon_{I_2(\text{comp})}$ of complexed iodine at the wavelengths between 580 and 700 $m\mu$. These coefficients are not known for poly(vinyl alcohol), but they have been determined in the case of amylose. If we accept the contention⁴⁷⁻⁴⁹ that the channel of the amylose helix constitutes nothing else but a nonspecific matrix that stabilizes linear polymers of iodine as do other channel hosts, we may be permitted to apply the extinction coefficients of iodine in a polyiodide chain, irrespectively of what the stabilizing matrix is made of, and hence also to the complex with poly(vinyl alcohol).

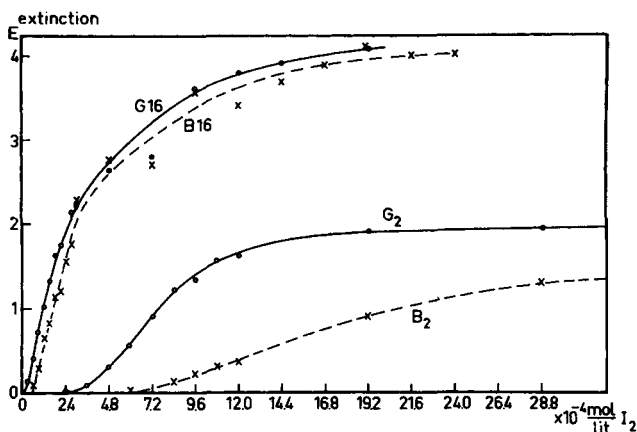


Fig. 3. Influence of stereoregularity on complex formation. Spectrophotometric titrations with iodine of two different types of poly(vinyl alcohol) (G and B) at high (0.16 mole/l. = index 16) and low (0.02 mole/l. = index 2) boric acid concentration. E is the extinction at the respective absorption maximum. $PVA = 27 \times 10^{-4} M$.

Rundle and co-workers⁵⁰ reported the molar extinction coefficient for iodine in the blue complex with amylose to be 25,400 at 580 $m\mu$, increasing gradually to 43,000 as the absorption maximum shifts to 628 $m\mu$. Murakami,⁶ on the other hand, expects, on theoretical grounds, the absorption intensity per iodine molecule to be approximately constant at all wavelengths at a value of roughly 44,000. He explains the lower values found by Rundle for shorter wavelengths as being due in these cases to incomplete binding of the iodine present. $\epsilon_{I_2(\text{comp})}$, according to Murakami, is thus a constant for all wavelengths.

Seen from this point of view, the leveling-off heights of the curves in Figure 2 indicate, therefore, a nearly four times larger binding capacity of PVA for iodine at high boric acid level compared to that in the absence of boric acid. If the molar extinction coefficients of Rundle are applied, the ratio of binding capacities between the two extremes is only slightly larger than 2.

As in the absence of boric acid, so at a relatively low boric acid concentration (0.02M), poly(vinyl alcohols) of high steric regularity (such as PVA G) show stronger iodine binding than do PVA's with a more random molecular structure (such as PVA B). At high boric acid concentrations (> 0.16M), this difference is almost completely suppressed, as is shown in Figure 3.

Dependence on Boric Acid Concentration

Figure 4 shows spectrophotometric titration curves for three different PVAs. Here extinction at the absorption maximum is plotted against concentration of boric acid at constant total iodine and PVA concentrations.

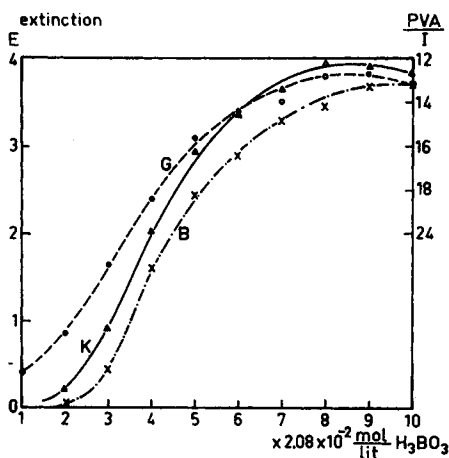


Fig. 4. Spectrophotometric titration of three different poly(vinyl alcohols) with boric acid in the presence of excess iodine. Extinction E is measured at the absorption maximum which shifts with the boric acid concentration. See Table II for experimental details.

As with other plots, every point on these curves is the result of a different experiment, and the blue color was allowed to develop for two days at each particular boric acid concentration.

Sigmoidal shaped curves of this kind have in recent years become associated with coil-helix transitions in natural and synthetic polymers, where such transitions were brought about by changes in the chemical environment or the temperature of the macromolecule in solution.⁵¹⁻⁵⁴ Peticolas¹¹ has shown that a similar curve is followed when the extinction of an amylose-iodine complex at $600\text{ m}\mu$ is set out against temperature. By increasing the temperature, the amylose helix is gradually destroyed, and with it, the iodine channel complex.

In our experiments, the situation may be such that with the PVA and iodine concentrations prevailing, the polymer is nearly all random coiled, and thus absorbs very little iodine. As the boric acid concentration is raised, helix formation takes place progressively, giving rise to increased iodine binding. How boric acid may act on a molecular level to bring this about, will be discussed further on in this paper.

Two more features shown by the curves in Figure 4 might be pointed out. The relative difference in iodine binding strength between PVA's of different degrees of stereoregularity is again seen to be more pronounced at low boric acid concentration, which also makes for a low degree of occupation of the polymer's potential binding sites. At high boric acid level, all poly(vinyl alcohols) seem to converge to the same high color intensity. At still higher boric acid concentrations, intensities tend to drop off again as gelation of the polymer sets in. With the more stereoregular PVA's this occurs at a somewhat lower boric acid level than with the others.

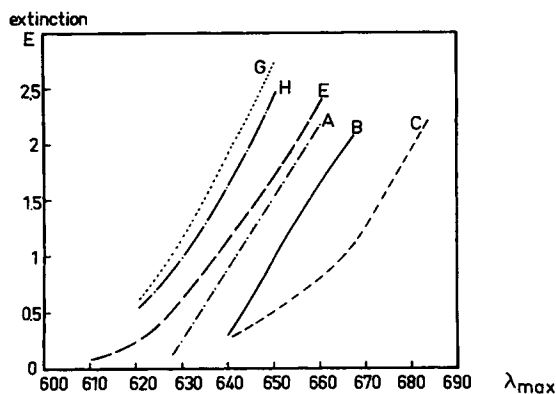


Fig. 5. Behavior of different poly(vinyl alcohols) in the transition region (between 0.05 and 0.15 mole/l. boric acid), where the greatest shift of the absorption maximum towards longer wavelengths takes place. Extinction E at the absorption maximum is plotted against the wavelength of the absorption maximum. (See Table II for concentrations of the reactants.)

If we might be permitted to apply once again the value of $\sim 44,000$ for the molar extinction coefficient of iodine in the blue complex (at λ_{\max} between 670 and 690 $m\mu$) we could, from Figure 4, make an estimate of the limiting binding capacity of poly(vinyl alcohol) for iodine, as far as such binding contributes to color formation.

With the highest extinction value in Figure 4 being approximately 3.9, we have:

$$E = \epsilon_{I_2(\text{comp})} c_{I_2(\text{comp})} = 3.9 = 44,000 c_{I_2(\text{comp})}$$

The highest concentration of complexed iodine is thus approximately:

$$c_{I_2(\text{comp}) \max} = 0.89 \times 10^{-4} \text{ mole/l.}$$

With a PVA concentration of 21.4×10^{-4} base mole/l., the limiting ratio of VA: I_2 will be:

$$VA/I_2 = 21.4 \times 10^{-4} / 0.89 \times 10^{-4} \cong 24$$

$$VA/I \cong 12$$

The limiting capacity thus seems to be 12 vinyl alcohol residues per iodine atom, as can also be read off the right-hand scale in Figure 4.

Of the 8×10^{-4} mole/l. originally added to the solution, more than 7×10^{-4} mole/l. remains unbound by the polymer. Other experiments have shown that, under the conditions prevailing here, this "equilibrium" concentration of iodine is sufficient to keep the PVA near its iodine saturation value. In fact, no other conditions of iodine and iodide ion concentrations or temperature could be found that could raise the color intensity significantly beyond an extinction value of 3.9, when the PVA concentration was 21.4×10^{-4} base mole/l. The poly(vinyl alcohol) must, thus, be considered saturated with respect to blue staining iodine.

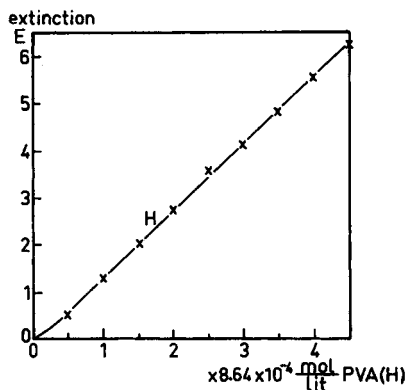


Fig. 6. Extinction at $670 \text{ m}\mu$ vs. concentration of PVA H at high boric acid level in the presence of excess iodine (Table II).

Concurrently with the increase in color intensity as the boric acid level is raised, there is the shift of the absorption maximum from the 620 to the $690 \text{ m}\mu$ region. Here again, different PVA's show differences in behavior, especially around the inversion points of the curves in Figure 4. If in this transition region we plot color intensities at the absorption maximum against the wavelength of that maximum (Fig. 5), we find that the more stereoregular PVA's trail behind the sterically irregular ones in shifting towards longer wavelengths.

Dependence on Polymer Concentration

The linear dependence of color intensity on polymer concentration in dilute solution when sufficient iodine is present has already been demonstrated in Figure 1. While these measurements were taken in the absence of boric acid and at a low degree of iodine binding, experiments with other ratios of the components show the same linear dependence on polymer concentration. A case representing the other extreme to the conditions employed in Figure 1 is that of the high molecular stereoregular PVA H complexing iodine at high boric acid level to about 85% of its maximum capacity; this is shown in Figure 6. Here, too, dependence on polymer concentration is strictly linear. This once more indicates that complex formation between PVA and iodine at this dilution involves only single polymer molecules.

Dependence on Iodide Concentration

Mokhnach and Zueva²⁸ have shown that iodide ions are indispensable to the formation of the blue complex with PVA, as is the case with aqueous solutions of amylose.^{55,56} The precise role that iodide ions play in either of these complexes is not completely understood.

Because of the limited solubility of iodine in water, in the absence of iodide ions, the concentration of these ions cannot altogether be freely

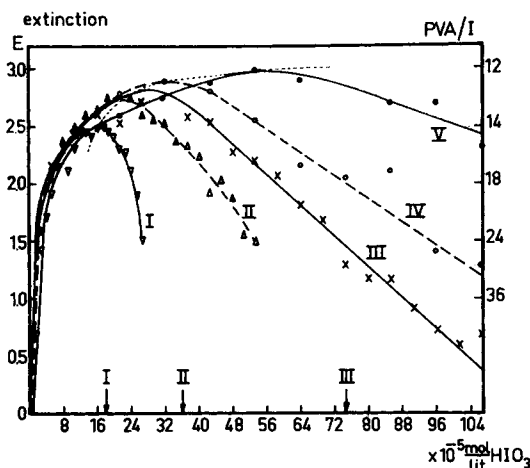


Fig. 7. Spectrophotometric titration with iodate of PVA G solutions (at high boric acid level) having a given initial iodide ion concentration. Curves I to V differ in the magnitude of this initial iodide ion concentration, which is doubled from curve to curve from I to V. (For details see Table II.) At every point of the abscissa there is a certain total iodine concentration, while going up in the direction of the ordinate the iodide ion concentration changes from curve to curve.

varied without also affecting the iodine concentration. In order to be able to change the iodide ion concentration right up to the limit of iodine solubility, we adopted here the second procedure described in the experimental section, starting off with a given iodide concentration and oxidizing this in successive samples by increasing amounts of iodic acid. In this way, the iodine-iodide ratio is changed all the time until all iodide ions are oxidized. The influence of such a procedure upon the color intensity is shown in Figure 7 for the stereoregular PVA G at high boric acid level for several experimental runs, each one starting with a different initial iodide ion concentration.

It can be seen from Figure 7 that the curves with the higher iodide ion starting concentrations also reach higher intensity peaks than those with lower iodide starting concentrations; however, the concentration of free iodine necessary to produce this maximum extinction is also larger, the larger the iodide ion starting concentration.

To produce the intensity peak, a different iodide to iodine ratio is necessary for each of the curves in Figure 7. This ratio varies almost 30-fold, from $I^-:I_2 = 0.22:1$ in curve I to 6:1 in curve V.

For amylose-iodine complexes, various situations are recorded in the literature where the color intensity increases,⁵⁷ decreases,⁵⁰ or passes through a maximum⁵⁸ as a function of iodide ion concentration. This seems to depend either on the iodine concentration or on the degree of saturation of the amylose molecule.

For poly(vinyl alcohol), Figure 7 suggests that here, too, the iodide ion concentration may have a different effect in different regions. Unfortu-

nately, the ascending parts of the curves in Figure 7 cannot be drawn with enough certainty to show clearly the influence of iodide ions in the low iodine concentration region.

As mentioned earlier, the iodide ion concentration has an influence upon the position of the absorption maximum. The latter shifts gradually from $695\text{ m}\mu$ at the intensity peak of curve *I* to $660\text{ m}\mu$ at the peak in curve *V*.

The function of the iodide is probably twofold. A small amount of iodide ions, at least, is required to start a polyiodide chain which is responsible for the blue color. Apart from this, iodide ions quite generally are known to have a strong influence upon the conformation of a poly(vinyl alcohol) molecule.^{44,45} According to Buc,⁴⁶ iodide ions at the concentrations considered here will break intermolecular hydrogen bonds between PVA molecules, and possibly also some hydrogen bonds between distant segments of the same molecule, while leaving intact hydrogen bonds between adjacent OH groups. (With regard to amylose Kerr⁵⁵ writes: "Iodide ions may assist in the formation of the required helical configuration from the normal, more or less extended shape.")

We were at first surprised to find that a blue color was still developing when an excess of iodate was added, more than enough to oxidize all iodide ions. The three arrows along the abscissa in Figure 7, indicated by *I*, *II*, and *III*, show the points for the corresponding curves where an equivalent of iodic acid was present to oxidize all the iodide. When, in the region to the right of the arrow of each curve, the order of addition of the reactants was reversed, in other words, when iodide, iodate, and dilute sulfuric acid were mixed first and poly(vinyl alcohol) added afterwards, no color development would take place, as expected.

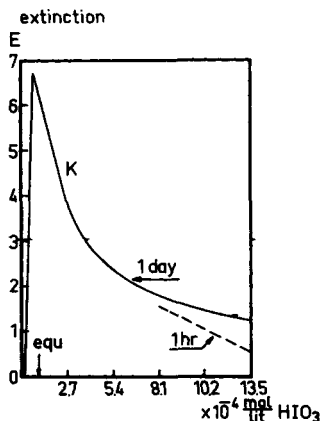


Fig. 8. Extinction of PVA K solutions (high boric acid level) at their absorption maximum of $680\text{ m}\mu$. The arrow shows the point where an equivalent amount of iodate was present to oxidize all iodide ions. The blue color developed to some degree, even in the face of a large excess of iodate.

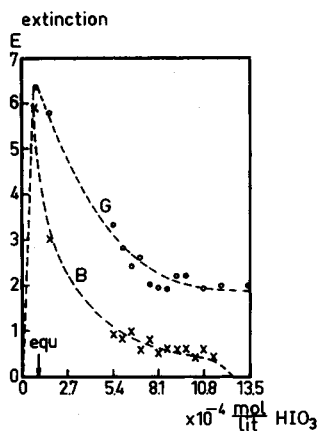


Fig. 9. Extinction of two types of PVA (B and G) differing in stereoregularity, when the blue color is developed in the presence of an excess of iodate. $\lambda_{\max} = 670 \text{ m}\mu$.

To examine this phenomenon more closely, we extended the range of excess iodate added, this time using a less stereoregular PVA K. The experimental conditions employed were such that some blue coloration always showed up immediately when the acid was added, although the color intensity kept on increasing for more than a day. The results are given in Figure 8, which shows that even a tenfold excess of iodic acid was not enough to prevent the appearance of a blue color.

The development of the blue color in the face of an excess of iodic acid can be understood to occur in the following way. As iodide ions alone, or molecular iodine alone, will not produce the blue color reaction with PVA, the complex must be formed during the short interval in the oxidation of the iodide ions that a transient mixture of both iodide ions and iodine molecules is present in the solution. Once a blue complex has formed, iodide ions that participate in the polyiodide chain seem to be protected against oxidation, at least at the iodic acid concentration employed in these experiments. The higher the iodate concentration in the beginning, the shorter will be the time that a transient iodine-iodate ion mixture stays in existence. We would, therefore, expect that with increasing initial iodate concentration color intensities should decrease, as is indeed shown by Figure 8.

The proposed mechanism which involves two competing reaction velocities, that of complex formation and that of iodide oxidation, made us suspect that poly(vinyl alcohols) differing in stereoregularity should come out with different color intensities under identical reaction conditions if they differed in their velocity of complex formation, and this in spite of the fact that at the high boric acid level employed in these experiments, there would be practically no difference in the "equilibrium," color intensity between these PVA's, when the color reaction is allowed to proceed to completion in the continuous presence of both iodide ions and molecular iodine

in the surrounding solution. Figure 9 shows that the expected difference indeed exists between such polymers as PVA B and PVA G, with the more stereoregular polymer displaying a higher intensity in the face of excess iodic acid than the random polymer. This is in accordance with the observation by Ushakov and co-workers cited above³¹ that PVA's with equal final color intensities can still differ substantially in their initial rates of color development.

Irreversible and Slowly Reversible Phenomena

Color Fading. An aqueous iodine-iodide solution shows a number of absorption peaks which are characteristic of the species shown in Table III.^{59,60}

TABLE III

Species	λ_{\max} , m μ	Molar extinction coefficient
I ⁻	222-226	13,000*
I ₃ ⁻	287.5	40,000
I ₃ ⁻	353	26,400
I ₂	460	746

* Data of Kontos.²⁶

The PVA-iodine complexes have at least two maxima, the one between 580 and 700 m μ already discussed, and another maximum around 355 m μ .^{26,28} The latter practically coincides with the second maximum belonging to the I₃⁻ anion. The short wave peak of the iodine complex becomes apparent at medium to high boric acid levels, when the iodine-iodide equilibrium concentration becomes of the same order of magnitude as the concentration of the complexed iodine. For such cases we found that the combined absorption maximum at 355 m μ can be related to the heights of the peaks at 287.5 m μ (for free I₃⁻), and in the 650 m μ band (for complexed iodine) by the equation:

$$E_{355} = 0.66E_{287.5} + 0.17E_{\max\ 650\ \text{band}}$$

for solutions stored up to two days at 8°C. Thus, a constant ratio exists between the extinctions of the two peaks due to the PVA-iodine complex, at least initially. We might, therefore, complete the Table III as shown in Table IV.

TABLE IV

Species	λ_{\max} , m μ	Molar extinction coefficient
I ₂ (comp)	~355	7,500
I ₂ (comp)	650-700	44,000

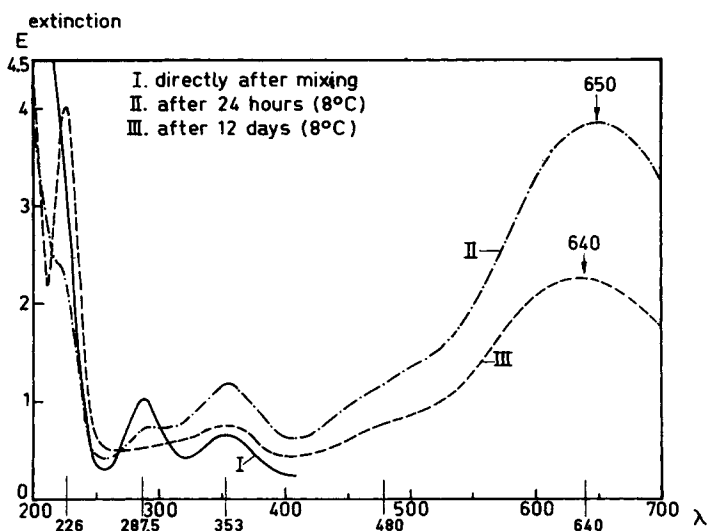


Fig. 10. Spectrum of PVA (K)-iodine-boric acid complex at various times after mixing the reactants.

With these coefficients and the knowledge of the equilibrium constant of the reaction $I^- + I_2 \rightleftharpoons I_3^-$ ⁵⁹ in solution surrounding the complex, one could hope to draw up, from spectrophotometric measurements alone, a material balance of the distribution of iodine and iodide ions between the complex and the outside solution, provided there is only one complexed iodine species.

In practice, neither in the case of PVA nor in that of amylose such attempts of material balancing have been successful in accounting for all the iodine and iodide ions. For amylose Kuge and Ono³⁷ have, therefore, tried to make a number of *ad hoc* assumptions regarding the existence of different species of bound iodine. Mokhnach^{28,61} presumed that both in the PVA-iodine and in the amylose-iodine complexes hypoiodide ions (IO^-) played an important role, for which the 355 $m\mu$ peak should be characteristic.

Our own observations have indicated that the total concentration of iodide ions, and that of molecular iodine, does not remain constant, and that iodine is slowly reduced, and more iodide ions are formed. This process is probably the cause for the eventual fading of the blue color; it may be already in progress even while the color intensity is still on the increase. Figure 10 shows the absorption spectrum of a PVA-iodine complex in the presence of boric acid at various times after mixing the components.

The changes taking place with time in the region between 200 and 400 $m\mu$ should be compared with those in Figure 11, which shows the spectra at various times of a solution containing likewise iodine, potassium iodide, and sulfuric acid, but no PVA or boric acid. Whatever the changes taking place in the blank experiment over several days, the extinction at 226 $m\mu$

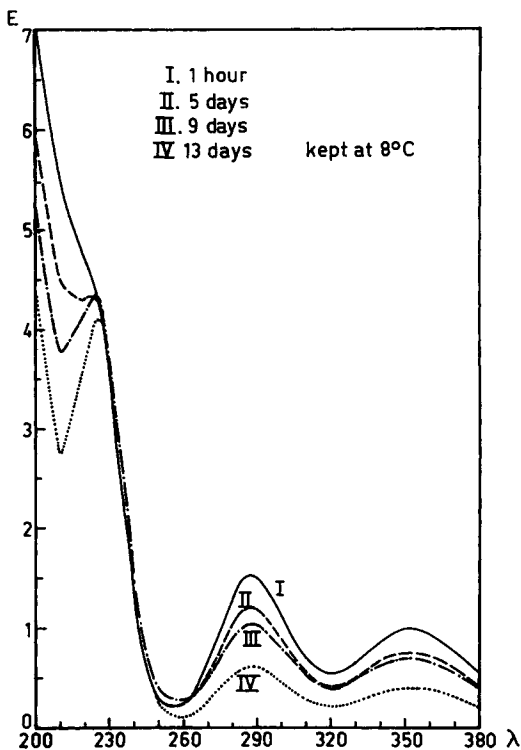


Fig. 11. Spectrum of HI-I₂ solution (~ 0.2 mmole/l.) at various times after preparation of the solution.

characteristic for iodide ions remains practically constant. In the presence of PVA and boric acid (Fig. 10), on the other hand, the intensity at $226\text{ m}\mu$ first decreases as a nearby maximum below $200\text{ m}\mu$ (of unknown identity) loses in significance, and then increases again owing to the formation of additional iodide ions, while the blue color intensity diminishes, and the absorption maximum gradually shifts to shorter wavelengths. (Another blank experiment showed that boric acid alone had no time-dependent influence upon the absorption maximum at $226\text{ m}\mu$.)

A seemingly similar slow reduction of iodine by aqueous alcoholic solutions has been studied by Cantacuzène,⁶⁰ who ascribed this reduction to the presence of aldehyde impurities in the alcohol. Although the possible presence of some aldehyde endgroups or other reducing impurities in our PVA samples cannot be excluded, we feel that for the PVA-iodine reaction an attack of the iodine on the host polymer may be a direct consequence of complex formation itself.

While the oxidizing power of the iodine in solution, as can be measured potentiometrically, is diminished by complex formation owing to a reduction in the concentration of free iodine, the accumulation and localization of the iodine inside the host molecule should, for the same reason alone,

increase its oxidative power towards the polymer. Moreover, the link between the polymer and the iodine may have something of the nature of an electron transfer bond. Cramer considers that the cavity of an inclusion complex is to be regarded as a region of high electron density, so that the cavity behaves as an electron donor.⁶² The activation of the iodine is furthermore reflected in the loosening of the iodine-iodine bond observed by West⁶³ in PVA complexes where the normal bond length of the iodine molecule of 2.7 Å. is increased to 3.10 Å. in the complex. The iodine atoms may be considered, so to speak, already partially reduced, the moment they become settled inside the polymer cavity, and it is not surprising that from time to time an irreversible event of complete reduction should take place. That this does not happen more rapidly may be due to the fact that the oxidation of a secondary alcohol to a ketone requires the coincidence of two simultaneous electron transfers from the polymer to an iodine molecule, accompanied by the ejection into the solution of two protons.

Position of the Absorption Maximum. It has been stated above that the position of the main absorption maximum of the PVA-iodine complexes between 580 and 700 $m\mu$ will depend upon the concentrations of iodide ions and boric acid in the solution. Other factors influencing the position of the maximum to a lesser degree, are the concentrations of the polymer,²⁸ the iodine, and the ratio between the two, as well as the temperature.

However, even at the same composition and temperature; the maximum can be made to appear at different wavelengths, depending upon how the solution has been constituted. Thus, in an experiment for which the absorption spectra are shown in Figure 12, a complex was composed at low boric acid level, so that the maximum developed at 620 $m\mu$ (curve 2). After the color had reached a stationary intensity, more boric acid was added. This then caused an increase in color intensity only, while the absorption maximum remained stationary at 620 $m\mu$ (curve 3). When the entire amount of boric acid was added to a solution of the same composition directly from the start, the maximum appeared at 675 $m\mu$ (curve 4).

In the study of the amylose-iodine reaction, the wavelength of the absorption maximum has been related to the length of the polyiodide chain⁶⁴ and this in turn to the degree of polymerization of the host polymer which stabilizes it.^{9,65} Such a correlation indeed works for relatively short-chain amylose hydrolyzates, but seems to break down for degrees of polymerization above 300.⁶⁶ In fact, Foster and Paschall⁶⁷ have demonstrated with native amylose that with the same polymer, the absorption maximum can be produced either at 635 or at 665 $m\mu$, depending on the way the complex is constituted. It will, thus, appear that above a certain degree of polymerization, several shorter helices along a polymer chain are more stable than one very long one.⁶⁸ Such shorter helices may then gain in stability by lateral association. The backfolding upon themselves of amylose helices belonging to one and the same molecule has recently been demonstrated to occur in amylose monocrystals.^{69,70}

If we are permitted to carry over the picture of the backfolded helices to the case of poly(vinyl alcohol), it would not seem surprising that once the nucleus of a structure has formed with an average helix length corresponding to $620\text{ m}\mu$, it might constitute a template for additional helices to be built on when more boric acid is added.

Decomposition of the Complex upon Dilution or Warming. Decomposition of the complex upon dilution is extremely slow. This can lead to some curious situations, as can be seen by comparing curves 1 and 2 of Figure 12. These show the spectra of two solutions of identical compositions, of which

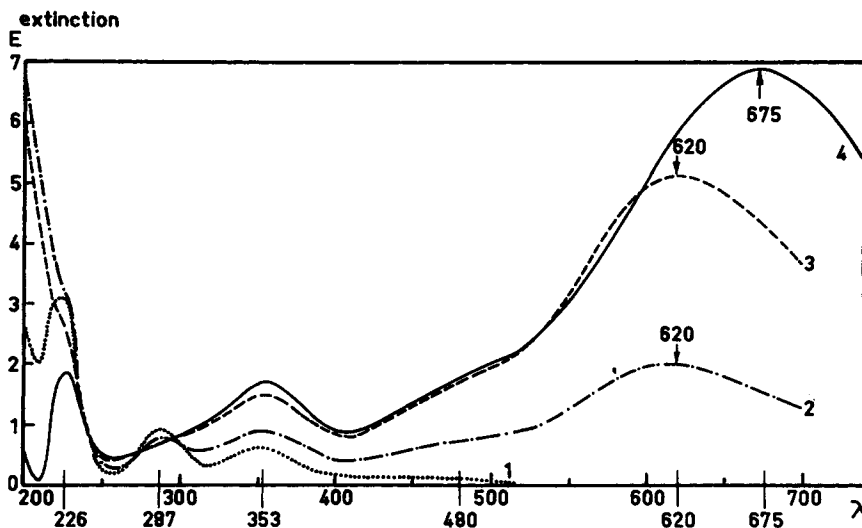


Fig. 12. Spectra of PVA (K)-iodine-boric acid complex solutions: (1), (2) at (the same) low boric acid level; (3, 4) at (the same) high boric acid level. A blue complex was allowed to develop at low boric acid level (0.02 M), after which the solution was diluted with an equal volume of water and measured after 24 hr. (curve 2). When the same solution was diluted with an equal volume of (0.3 M) boric acid instead of pure water, curve 3 was measured after 24 hr. If the total concentration of boric acid was added right from the beginning, curve 4 was obtained. If the first solution was directly diluted with an equal volume of water without awaiting color formation, the solution would be below its threshold concentration, and no color would develop (curve 1).

the one displays a fairly intense blue color and the other none at all. The latter was made up of the required components, and immediately diluted by an equal volume of water, which left the solution below its threshold concentration, where no color developed (curve 1); the second solution was allowed to stand before dilution until the complex had formed, and was measured one day after it, too, was diluted (curve 2). While the PVA-iodine complexes can be decomposed by very prolonged dialysis,²⁹ the fact that decomposition upon dilution is so much slower than the building up of the blue complex supports the suggestion made previously that a secondary structure probably forms after some primary complex is constituted.

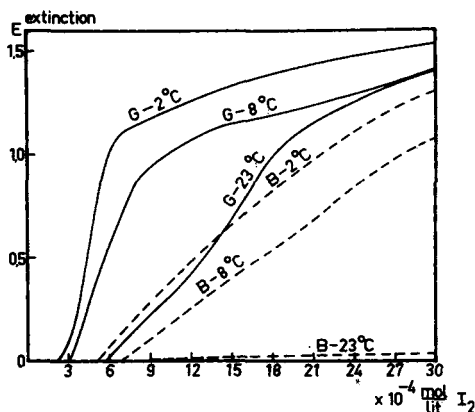


Fig. 13. Extinction at the absorption maximum (580 μ , high iodide concentration, no boric acid) at different total iodine concentrations, when the color was allowed to develop at three different temperatures. Polymers differing in stereoregularity (B and G) display different temperature dependences.

Warming up the blue complex solution presents a similar picture as dilution. While heating to 70°C. will cause the color to disappear rapidly,²⁸ returning a cooled solution to room temperature will not bring about a corresponding adjustment of the color intensity for several months.⁵ This makes it possible to measure, at room temperature, the influence upon color intensity of a lower temperature which prevailed during complex formation.

We found that such influence of temperature upon color intensity was largest in the absence of boric acid, and that under these circumstances marked differences existed between polymers of different degrees of steric regularity. This is demonstrated in Figure 13, which shows spectrophotometric titration curves of the two PVA's, B and G, when complex formation took place at 2, 8, and 23°C. One sees that PVA B shows a greater temperature dependence than PVA G, especially in the vicinity of room temperature.

It will appear that for a polymer with a random configuration, complex formation is accompanied by a larger entropy decrease than for a stereoregular poly(vinyl alcohol). However, since we do not deal here with equilibrium states, a quantitative estimate of entropy differences on the basis of the curves in Figure 13 is not justified thermodynamically.

Mechanism of the PVA-Iodine Reaction

We shall now try to accommodate the great variety of our observations, as well as those of other workers in the field, into an all-embracing qualitative model of the possible mechanism of the PVA-iodine reaction. The picture is to a great extent based upon the recognition of the far-reaching analogy existing between the amylose-iodine and PVA-iodine reactions. Where differences in behavior of the two polymers exist, they are due to the fact that amylose is a rigid, completely stereoregular, and optically active

macromolecule, whereas poly(vinyl alcohol) has a highly flexible chain with a more or less irregular configuration. The direction of the α -glycoside bonds between the glucose rings in amylose gives rise to the occurrence of helical loops in the amylose molecule in solution even in the absence of iodine,⁶⁶ whereas in poly(vinyl alcohol) the formation of a helical structure, if it can be induced, would require a much more radical process of ordering. The larger entropy decrease thus accompanying PVA complex formation, would then manifest itself in a lower binding strength of PVA towards iodine as compared to amylose.

The optical asymmetry of the glucose residue would cause one sense of turning of the amylose helix to be preferred over the other, no such preference can exist in the case of poly(vinyl alcohol), however, so that once helices are induced to form in PVA they will, with equal probability, form in both senses. Short helices that have just begun to grow in close proximity to each other along the same polymer chain will interfere with each other, if their sense of turning happened to be opposite, thus causing early

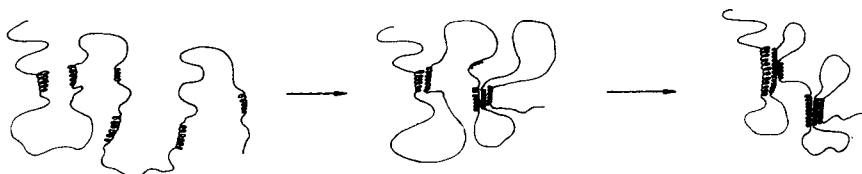


Fig. 14. Proposed model for the mechanism of the PVA-iodine reaction. Shape changes taking place in the poly(vinyl alcohol) molecules before and during color development involve helix formation, helix association, and finally helix recrystallization.

mutual termination at the point of encounter. Thus, PVA helices might hardly be able to grow long enough to accommodate extensive polyiodide chains absorbing in the $600\text{ m}\mu$ band unless some rearrangement takes place subsequently.

In our model we assume, therefore, that a poly(vinyl alcohol) molecule in dilute solution of the reactants is induced to helix formation at a number of isolated, preferably stereoregular sites along the polymer chain when coming into contact with iodine and iodide ions. These helices, however, are not long and stable enough to function on their own as hosts for extensive linear polyiodide chains. Only by grouping together into a cluster of helices, is additional stability attained. As several helices have joined a crude, imperfect cluster, a slow process of "recrystallization" sets in, in which faults in the helices are eliminated, loose segments folded in, and other, still unattached, helices attracted. This process is drawn schematically in Figure 14.

It is during this slow recrystallization stage that the PVA channels in the interior of the helices become long and regular enough for the guest polyiodide chain to link up and thus display its blue color. The color intensity

will continue to rise until the clusters have reached an advanced state of perfection.

The number of clusters that have formed will depend upon a process of nucleation taking place at an early stage of the reaction. The final average number of helices per cluster will be dependent upon the length and flexibility of chain segments and loops between the cluster junction points, and upon the chemical environment. As the final color intensity is a function of the total number of helices existing at the end of the reaction, it will necessarily contain a strong memory element of conditions having prevailed at the beginning of the reaction when nucleation of the clusters occurred. Because of the events following soon afterwards, the system may have never been able to reach a thermodynamically stable state. For, no sooner are the iodine molecules firmly installed and localized, than they commence their slow oxidative attack upon the host molecule, which eventually leads to a fading of the color.

Essentially the same mechanism should prevail at low boric acid concentration, where this acid apparently has the effect of stabilizing and lengthening the individual helix.

At a high boric acid level, and at a high degree of iodine binding, when almost the whole PVA molecule is involved in complex formation, the average length of the helices may essentially be governed by the primary process of the formation of the individual helix only, involving a mechanism of nucleation, helix growth, and termination. Termination here will occur every time that a growing right-hand helix encounters a left-hand one or the end of the molecule. The rate of nucleation may be larger at high iodide ion concentration, causing a shortening of the average helix length, and, with it, a shift of the iodine complex absorption maximum to shorter wavelengths.

The limiting iodine-binding capacity (as far as this contributes to blue staining) of 12 vinyl alcohol residues per iodine atom greatly supports the hypothesis of helix formation in PVA-iodine complexes. It will appear that 12 vinyl alcohol residues make up one turn of a helix, and that two turns are required to complex one iodine molecule. As could be verified with the aid of Stuart models, the geometry of such an arrangement is greatly similar to that of the amylose-iodine complex. In the latter, six glucose residues form one turn of a helix around two iodine atoms. The length of a glucose unit approximately equals that of two vinyl alcohol residues, and the width of the glucose ring lying flat against the iodine core is roughly that of two vinyl alcohol chain segments belonging to successive turns of the helix, being stacked on top of each other (Fig. 15).

Poly(vinyl alcohol) reacting with boric acid is known to gel when slightly more than one boric acid molecule per 12 vinyl alcohol residues is bound by the polymer.³⁹ It will thus appear that the limiting PVA-iodine-boric acid complex composition which is still completely soluble, is that of one boric acid molecule per turn of the helix. The stabilizing effect of boric acid upon the helix may be due to the occasional linking by a boric acid

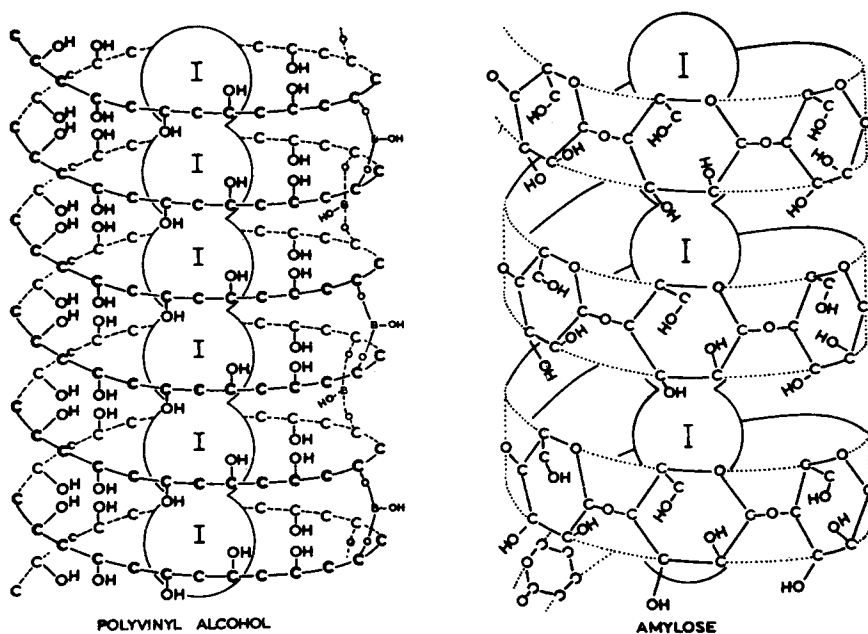


Fig. 15. Model of the proposed poly(vinyl alcohol)-iodine-boric acid helical complex structure (left) compared with the structure of the amylose-iodine complex (right).

molecule of two OH groups belonging to successive turns of the helix, having become close neighbors in the helical conformation of the PVA chain. This is also demonstrated in Figure 15.

To summarize: our model for the mechanism of the PVA-iodine reaction is based on the assumption that helix formation takes place in individual polymer segments, and is accompanied, or followed, by the development of a helix cluster superstructure.

The assumption of the formation of the individual helix is supported by the limiting stoichiometry of the PVA-iodine-boric acid complexes and by the continuity of the phenomena from zero to high boric acid concentrations (sigmoidal curves), and, also, by the apparent necessity of a geometrically well-defined matrix for a linear polyiodide chain to nest in.

The formation (and slow recrystallization) of helix clusters could account for the long time necessary to reach the intensity maxima, for the hysteresis phenomena encountered upon rewarming and diluting, and for the stationary wave length of the absorption maximum, when more boric acid is added, after color development has taken place (template concept). It could also explain why Schildknecht⁵ has found no change in viscosity during the actual color formation. Cluster growth may be governed by the initial local helix concentration and thus may become a function of the molecular weight of the polymer, as observed by Imai and Matsumoto.³² The threshold concentration of iodine necessary for color formation may be connected with the nucleation of clusters.

In drawing up this model and interpreting the experimental results, we have intentionally refrained from drawing any conclusion regarding the precise composition of the polyiodide chain responsible for the blue color, although we have clearly favored the polyiodide chain concept, $I^-(I_2)_n$, in preference to the polytriiodide hypothesis, $(I_3^-)_n$. This problem, as well as the question of what energetic states are involved in the phenomenon of the blue coloration, have repeatedly been discussed in the literature with regard to the amylose-iodine complexes,^{6,56,71,72} but no definite conclusion has been reached so far on either of these questions.⁹

CONCLUSION

Evidence is presented which supports an earlier contention of Schildknecht that poly(vinyl alcohol) in dilute aqueous solution may form helical, unimolecular inclusion compounds with iodine similar to those of amylose. However, whereas amylose in solution normally exists in the shape of partially preformed helices which can rapidly accommodate iodine molecules in their central channel, the randomly coiled PVA chains are only induced to fold up by coming into contact with iodine molecules and iodide ions.

Limiting intensities suggest, in analogy to amylose, that one iodine molecule is complexed by two turns of a PVA helix which can be stabilized by boric acid, each turn consisting of 12 vinyl alcohol residues.

In the absence of boric acid, complex formation is particularly sensitive to the structural regularity of the poly(vinyl alcohol) molecule. This difference in reactivity progressively diminishes as the concentration of boric acid is increased.

The iodine guest molecules seem to be locally activated and to attack and oxidize the host molecule slowly, causing a gradual fading of the blue color.

The two-stage mechanism proposed for the poly(vinyl alcohol)-iodine interaction, i.e., that of helix formation and helix association, can account qualitatively for a variety of peculiar phenomena observed with these complexes. This picture also seems to be supported by recent conclusions of Tobolsky,⁷³ who, from purely thermodynamic reasoning, had predicted the necessary occurrence of intramolecular, helical aggregates in helix-forming polymers, generally.

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Résumé

La réaction entre l'alcool polyvinylique et l'iode en solution aqueuse diluée (qui donne une couleur bleue caractéristique) a été étudiée. Après développement complet de la couleur les extinctions ont été mesurées en fonction des concentrations en polymère, iode, ions iodiques et acide borique. Suivant les conditions de réaction le maximum d'absorption peut apparaître à toute longueur d'onde entre 580 et 700 m μ . Les extinctions les plus fortes (par groupe alcool vinylique), et les longueurs d'ondes les plus élevées correspondent aux hautes concentrations en acide borique. Des alcools polyvinyliques, provenant de sources diverses, présentent de grandes différences d'intensité de coloration pour des conditions de réactions identiques. Ce comportement peut être attribué à des différences de régularité de structure du polymère. Pour expliquer le comportement de l'alcool polyvinylique envers l'iode, dans des conditions de réaction très diverses, aussi bien irréversibles que quasi-irréversibles, on propose un modèle de formation du complexe alcool polyvinylique-iode comprenant un double mécanisme savoir formation de spirale et association intramoléculaire de ces spirales. Il semble que les résultats permettent de conclure qu'en cas de saturation complète du polymère par l'iode, une spire de la chaîne macromoléculaire (formée par 12 groupes d'alcool vinylique et une molécule d'acide borique) renferme un atome d'iode. Celui-ci fait partie d'une chaîne polyiodique qui est donc enveloppée par une spirale d'alcool polyvinylique.

Zusammenfassung

Die blaue Farbreaktion von Polyvinylalkohol mit Jod in verdünnter wässriger Lösung wurde untersucht. Nach voller Entwicklung der Farbe wurde die Extinktion am Absorptionsmaximum als Funktion der Konzentrationen des Polymeren, von Jod, von Jodidionen und von Borsäure gemessen. Je nach den Versuchsbedingungen kann das

Absorptionsmaximum der Komplexe bei allen Wellenlängen zwischen 580 und 700 $m\mu$ erzeugt werden, wobei die längsten Wellenlängen und höchsten Extinktionswerte per Vinylalkoholgruppe bei hohen Borsäurekonzentrationen auftreten. Polyvinylalkohole verschiedenen Ursprungs legten unter den gleichen Umständen grosse Unterschiede in den Farbintensitäten an den Tag, was auf Verschiedenheiten in der Regelmässigkeit des Polymerkettenaufbaus zurückgeführt werden kann. Für den Mechanismus der Polyvinylalkohol-Jodkomplexbildung wird ein Modell vorgeschlagen, dem ein Doppelprozess von Spiralbildung und innermolekularer Assoziation von Spiralen zugrunde liegt. Damit kann das Verhalten von Polyvinylalkohol gegenüber Jod unter verschiedenen Versuchsbedingungen, sowie auch eine Anzahl irreversibler oder nur sehr langsam umkehrbarer Erscheinungen qualitativ erklärt werden. Die Ergebnisse lassen darauf schliessen, dass bei völliger Sättigung mit Jod zwölf Vinylalkoholgruppen mit Hilfe eines Borsäuremoleküls eine Spiralwindung bilden, welche ein Jodatomb umschlingt. Dieses Jodatomb ist ein Teil einer Polyjodidkette, die im inneren Kanal der Polyvinylalkoholspirale eingelagert ist.

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