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1964

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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Spectrophotometric Study of Aqueous Solutions of Iodopolyvinyl Borate

(Presented by Academician I. I. Chernyaev, 12 IX 1963)

In the patent literature ($^{1-3}$) there are a few brief data on the preparation of films from solid oriented iodine-containing polyvinyl borates. It is known that they possess increased strength in comparison with films made from iodopolyvinyl alcohol. In 1949, West (^{4}) reported that aqueous dispersions of polyvinyl borate, obtained by the interaction of polyvinyl alcohol with a solution of boric acid, react with iodine in the same way as amylose solutions, giving a blue coloration.

Fig. 1. Absorption spectra of aqueous solutions (220-400 mμ).
1 –0.024% J_2, 0.25% PVA; 2 –the same + 0.5% H_3BO_3; 3 –the same + 4% H_3BO_3. Layer thickness 0.0509-0.4107 cm

The study of mixed compounds of iodine and boron with high polymers and the elucidation of the mechanism of the reaction of their formation is, from our point of view, of great theoretical interest and may have a much broader practical significance than that noted in the foreign literature. The inclusion of iodine in the molecules of high polymers, in particular polyvinyl alcohol, gives colored complexes containing iodine in the oxidation state +1, which explains their biological activity (^{5}). It may be supposed that the behavior of boron in forming a complex with high polymers is analogous to that of iodine, which under these conditions enhances its antiseptic action and loses its toxicity (^{6}).

For these reasons we decided to carry out a study of the absorption spectra of the systems: 1) J_2—H_3BO_3—PVA—H_2O and 2) J_2—KJ—H_3BO_3—PVA—H_2O.

Experimental Part

The solutions under study were prepared in twice-distilled water from twice-sublimed crystalline iodine of chemically pure grade, potassium iodide of chemically pure grade, and boric acid of the same grade. The polyvinyl alcohol was manufactured by the Yerevan "Polyvinyl Acetate" plant.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

Spectrophotometric studies were carried out at room temperature on an SF-4 spectrophotometer in the range 220-800 mμ.

As we found (^{5}), formation of an iodine complex with polyvinyl alcohol (PVA) without the participation of iodide—in contrast to the iodine-starch reaction—does not occur. This is confirmed by Fig. 1, 1. If, however, a small amount of H_3BO_3 is added to an aqueous solution of iodine with polyvinyl alcohol, then, as is seen from Fig. 2, 2, a broad absorption band already appears in the visible region with $\lambda_{\max} \sim 650$ mμ, whereas in the ultraviolet

region only a slight increase in optical density is observed. Increasing the concentration of H_3BO_3 to 4 g/100 ml causes a sharp increase in the optical density of the band with $\lambda_{\max} \sim 660$ m . At the same time, in the ultraviolet region of the spectrum the absorption band with $\lambda_{\max} \sim 288$-290 m disappears completely (Fig. 1, 3). But the band with $\lambda_{\max} \sim 350$ m , as is seen from the same Fig. 1, 3, does not disappear and is expressed quite distinctly. Thus, with the aid of H_3BO_3, the complex ion J_3^- is incorporated into the polymer with the formation of a blue complex, similarly to what occurs in the formation of the iodine-starch complex (^{6}). It should be noted that the incorporation of the J_3^- ion into the polymer molecule is also confirmed by the fact that in the absence of the high polymer the absorption band with $\lambda_{\max} \sim 288$-290 m , even at a high concentration of H_3BO_3, undergoes no changes, and the absorption spectrum of the system J_2—H_3BO_3—H_2O is no different from the absorption spectrum of the system J_2—H_2O.

Fig. 2. Absorption spectra of aqueous solutions (400-800 mμ). 1—0.024% J_2, 0.25% PVA; 2—the same + 0.5% H_3BO_3; 3—the same + 4% H_3BO_3. Layer thickness 0.1003 cm.

As we have shown (^{5}), the absorption band with $\lambda_{\max} \sim 288$-290 m is a very stable element of the absorption spectrum of the system J_3—KJ—PVA—H_2O and is preserved at a ratio of 0.0635 g J_2 per 1 g polyvinyl alcohol.

Fig. 3. Absorption spectra of aqueous solutions of iodopolyvinyl alcohol and iodopolyvinyl borate. 1—1% PVA, 2—1% PVA, 3% H_3BO_3, 3—0.25% PVA, 3% H_3BO_3. Concentration in all solutions: J_2—0.1%, KJ—0.3%. Layer thickness 0.0063-0.0113 cm.

Since in the spectrum of the system J_2—H_3BO_3—PVA—H_2O the band with $\lambda_{\max} \sim 288$-290 m is absent at known quantitative ratios of the components, it is of interest to investigate in this direction the system J_2—KJ—H_3BO_3—PVA

$-H_2O$. As is seen from Fig. 3, 1, in the absorption spectrum of the system J_2–KJ–PVA–H_2O there are 4 bands with $\lambda_{\max}$ 226 mμ, $\lambda_{\max} \sim$ 288-290 m , $\lambda_{\max} \to$ 350 m , and $\lambda_{\max} \sim$ 600 m . When a sufficient amount of H_3BO_3 is added to this solution, $\lambda_{\max} \sim$ 288-290 m disappears completely (Fig. 3, 2). Thus, the presence of potassium iodide in the solution does not disturb the previously described mechanism of complex formation. However, the incorporation of J_3^- into the complex composition, associated with the disappearance from the absorption spectrum of the band with $\lambda_{\max} \sim$ 288-

290 mμ is possible only at a sufficient concentration of PVA. As can be seen from Fig. 3,3, with the same content of J_2, KJ, and H_3BO_3 in the solution as in Fig. 3,2, but with the PVA concentration lowered to 0.25 g/100 ml, the absorption band with $\lambda_{\max} \sim$ 288-290 mμ is clearly expressed. It should be noted that in the presence of KJ, the addition of H_3BO_3 to the solution causes a shift of the band with $\lambda_{\max} \sim$ 610 mμ toward longer wavelengths.

Let us summarize what has been said: 1) H_3BO_3 can replace iodides in the color iodine-polyvinyl alcohol reaction; 2) with such replacement, in the adsorption spectrum of the solution there is observed a shift of the absorption band from $\lambda \sim$ 610 mμ to λ660-680 mμ; 3) at sufficient concentrations of H_3BO_3 and PVA, in the absorption spectra of the systems: 1) J_2 $-H_3BO_3$ –PVA $-H_2O$ and 2) J_2 –KJ $-H_3BO_3$ –PVA $-H_2O$, the band with $\lambda_{\max} \sim$ 288-290 mμ, corresponding to J_3^-, disappears, while the band with $\lambda_{\max} \sim$ 350 mμ is retained; 4) boron enters into a complex with the anion J_3^-.

Botanical Institute named after V. L. Komarov
Academy of Sciences of the USSR

Received
10 IX 1963

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Note: Figure translations are in progress. See original paper for figures.