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Abstract

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SPECTROPHOTOMETRIC STUDY OF AQUEOUS SOLUTIONS OF IODINE-POLYVINYL ALCOHOL

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As is known, blue coloration with iodine is given not only by starch or amylose, but also by many other inorganic and organic compounds of varied chemical structure. These include calcium hydroxide ([1]) and zirconium hydroxide ([2]), oleum ([3],[4]), potassium acetate ([5]), basic lanthanum acetate ([6]–[8]) and praseodymium acetate ([9]), substituted flavone ([10]) and coumarin ([11]), narcine ([12]), cortisone ([13],[14]), cholic acid ([15]), nylon, polyvinyl borate ([16]), benzamide, piperine ([17]), and many others.

In 1926, Frey and Stark ([18]) found that polyvinyl alcohol also gives a blue coloration upon interaction with iodine. In 1933, Miller and Bracken ([19]) reported that a blue coloration is formed only with completely deacetylated polyvinyl alcohol, whereas an alcohol containing 10% or more polyvinyl acetate units gives a raspberry coloration with iodine. In 1936, a paper by Galley appeared on the sorption of iodine by polyvinyl alcohol ([20]). The patent literature ([21]) gives brief data on the preparation of iodine-polyvinyl alcohol in solutions.

Iodine-polyvinyl alcohol, along with iodinated starch and iodine-amylose, is of special interest, since it possesses valuable biological properties ([22]) (antimicrobial and therapeutic action, nontoxicity). As shown in ([23]), these properties of iodine and high-polymer iodine solutions are associated with their color.

Taking this circumstance into account, and also the almost complete absence in the literature of experimental data on the interaction of iodine with polyvinyl alcohol, we decided to apply an investigation of the absorption spectra of aqueous solutions of iodine-polyvinyl alcohol in the range 220–800 mμ to the study of this reaction.

Experimental Part

Solutions of iodine-polyvinyl alcohol were obtained from polyvinyl alcohol manufactured by the "Polyvinylacetate" plant (Yerevan), containing 2.9% residual acetate groups. Solutions of iodine-polyvinyl alcohol of 0.5–1.0% concentration were prepared in twice-distilled water by the action of a calculated amount of iodine in a potassium iodide solution. Chemically pure iodine was subjected to double sublimation. Spectrophotometric studies were carried out at room temperature on an SF-4 spectrophotometer. The addition of iodine to polyvinyl alcohol was investigated by us over the range from 0.05 g of I_2 per 1 g of polyvinyl alcohol to 4.3 g of I_2 per 1 g of polyvinyl alcohol (Fig. 1). The curve obtained has the form of a Freundlich adsorption isotherm.

The electronic absorption spectrum of an aqueous solution of pure polyvinyl alcohol in the range 220-800 mμ has one absorption band with a maximum at 278 mμ. The absorption spectrum of an aqueous solution of iodine-polyvinyl alcohol is characterized in the indicated range by four bands

absorption, with maxima at 226, 288, 350, and 620 mμ (Fig. 2). When the iodine concentration in the solution is increased, in the absorption spectrum of the iodine-polyvinyl alcohol solution the maximum at $\lambda = 620$ mμ is shifted somewhat toward shorter wavelengths. The absorption spectrum of an iodine-polyvinyl alcohol solution is completely analogous to the absorption spectra of aqueous solutions of iodinated starch and iodinated amylose, obtained by the action on these polymers of iodine in an iodide solution. In contrast to starch and amylose, it is not possible to obtain the iodine complex of polyvinyl alcohol without the participation of iodide, for example by the action of an alcoholic iodine solution. Therefore the maximum at $\lambda = 226$ mμ, belonging to the hydrated anion J^-, is constantly present in the absorption spectrum of an aqueous iodine-polyvinyl alcohol solution. The maximum at $\lambda = 288$ mμ, belonging to the complex anion J_3^-, is also constant and at the same time very stable with respect to the action of excess polyvinyl alcohol. Whereas the maximum at $\lambda = 288$ mμ in the absorption spectra of aqueous amylose solutions

Fig. 1. Dependence of the optical density of solutions of iodine-polyvinyl alcohol at constant polyvinyl alcohol concentration and varying iodine concentration for $\lambda = 600$ mμ. Thickness of the solution layer 0.011 cm. Concentration of polyvinyl alcohol in the solutions 0.5 wt.%.

Fig. 2. Absorption curves of aqueous solutions of iodine-polyvinyl alcohol. Thickness of the solution layer 0.0063 cm.
A –polyvinyl alcohol concentration 0.1 wt.%, C_{J_2}: a –0.001 N, –0.002 N, –0.004 N, –0.008 N, –0.01 N, –0.016 N.
B –polyvinyl alcohol concentration 0.5 wt.%, C_{J_2}: a_1 –0.005 N, $_1$ –0.01 N, $_1$ –0.02 N, $_1$ –0.04 N, $_1$ –0.05 N, $_1$ –0.08 N.

disappears already at a ratio of 0.2 g J_2 per 1 g amylose, in solutions of iodine-polyvinyl alcohol it is retained at a ratio of 0.0635 g J_2 per 1 g polyvinyl alcohol.

The maximum at $\lambda \sim 600$-620 mμ, as is known, is observed in blue aqueous iodine solutions in the presence of high polymers and, evidently, is connected with the center of the blue coloration. The maximum at $\lambda \sim 350$ mμ is constantly observed in aqueous iodine solutions colored yellow or reddish. In the absorption spectra of blue aqueous solutions of iodine-polyvinyl alcohol that we investigated, as well as of natural high polymers, the maximum at $\lambda \sim 620$

Fig. 3. Absorption curves of an aqueous iodopolyvinyl-alcohol solution decolorized by heating and by addition of sodium thiosulfate.

Figure 1: Fig. 3. Absorption curves of an aqueous iodopolyvinyl-alcohol solution decolorized by heating and by addition of sodium thiosulfate.

mμ is invariably accompanied by a maximum at 350 mμ. To solve the question of which color centers these two absorption maxima are associated with, we carried out a study of the absorption spectra of decolorized solutions of iodine-polyvinyl alcohol. After destruction of the cent-

When the blue coloration is destroyed by heating the iodopolyvinyl-alcohol solution to 70°, the liquid assumes a yellow coloration. This coloration is subsequently retained when the solution is cooled to room temperature for a time sufficient to obtain the spectrum. As is evident from Fig. 3, three maxima are observed in the absorption spectrum of the heated solution: at 226, 288, and 350 mμ. Thus, destruction by heating of the center of the blue coloration leads to the disappearance of the absorption maximum at 620 mμ, whereas the maximum at $\lambda = 350$ mμ is retained. Upon cooling, the solution again acquires a blue coloration, and the maximum at $\lambda = 620$ mμ again appears in its absorption spectrum (Fig. 3).

Fig. 3. Absorption curves of an aqueous solution of iodopolyvinyl alcohol decolorized by heating and by addition of sodium thiosulfate. Polyvinyl alcohol concentration 0.5 wt.%, iodine concentration 0.05 wt.%. Thickness of the solution layer: **A** –0.0063 cm, **B** –0.1 cm. **a** –solution before decolorization, **b** –solution decolorized by heating, **c** –solution decolorized by addition of $Na_2S_2O_3$, **d** –solution decolorized by heating and, upon cooling, restored in color.

When sodium thiosulfate acts on the yellow solution obtained as a result of heating the iodopolyvinyl-alcohol solution, the latter is completely decolorized; moreover, in its absorption spectrum the maxima at 288 and 350 mμ disappear. The maximum at $\lambda = 226$ mμ, belonging to the hydrated anion J^-, is not only retained but increases (Fig. 3), as should be expected from the reaction of $Na_2S_2O_3$ with iodine. When an excess of $Na_2S_2O_3$ acts on the blue iodopolyvinyl-alcohol solution, the solution is instantly and completely decolorized; moreover, in the absorption spectrum of such a colorless solution the single absorption maximum at $\lambda = 226$ mμ is retained. In contrast to an iodopolyvinyl-alcohol solution decolorized by heating, a solution decolorized with sodium thiosulfate restores neither yellow nor blue coloration.

Decolorization of a yellow aqueous iodine solution with thiosulfate entails the simultaneous disappearance of two maxima in the absorption spectrum of the solution: at 288 and 350 mμ.

To clarify the nature of these absorption maxima, we studied the absorption spectra of dilute aqueous solutions of JCl, as well as J_2 in a cold potassium iodide solution. Both of these solutions have a yellow coloration. In the absorption spectra of these solutions a sharply expressed maximum at $\lambda = 350$ mμ was found, whereas the maximum at $\lambda \sim 288$–290 mμ was completely absent. It follows from this that the yellow

the coloration of these solutions is associated with the presence in the absorption spectrum of a maximum at $\lambda = 350$ mμ, and that the maximum at $\lambda \sim 288$–290 mμ has no relation whatever to the center of the yellow coloration. These data are in complete agreement with the results obtained in the study of the absorption spectra of colorless aqueous solutions of KJO_3 and KJO_4. In these spectra we found appreciable absorption only of radiation at $\lambda \sim 250$ mμ, which, with respect to the anion JO_3^-, had been shown earlier by Otry and Connik ([27]). The maximum at $\lambda = 350$ mμ was completely absent from the absorption spectra of solutions of KJO_3 and KJO_4.

The absorption maximum at 226 mμ, belonging to the hydrated anion J^-, characterizes the absorption spectrum of colorless iodide solutions and has no relation to the color centers, just as the maximum at 288–290 mμ, belonging to the complex anion J_3^-. This, in our opinion, can explain the fact that neither iodide solutions ([24]) nor a triiodide solution J_3^- ([25,26]) exhibit antimicrobial action. The absorption maximum at 350 mμ belongs to JO^-, which participates in the formation of the color center of yellow aqueous iodine solutions. The maximum at 620–625 mμ is associated with the color center characteristic of iodine solutions in the presence of high polymers, including polyvinyl alcohol.

As shown in ([23]), iodine incorporated into the molecule of high polymers exhibits a higher antimicrobial effect than in the form of JO^-. It follows from this that the center of the blue coloration possesses an independent individual antimicrobial effect alongside the center of the yellow coloration. The antimicrobial action of blue solutions of iodine-high polymers is the result of the combined action of JO^- and the blue complex. Destruction of these color centers by sodium thiosulfate upon complete decolorization of the solutions is accompanied by the disappearance from their absorption spectra of maxima at $\lambda \sim 350$ mμ and at $\lambda \sim 620$ mμ, and entails a complete loss of antimicrobial activity of the solutions. This conclusion is consistent with the data given in ([22,23]) concerning the properties of J^+. The antimicrobial properties of compounds containing J^+ have been used by one of us to obtain therapeutic preparations. Iodopolyvinyl alcohol has shown, for example, a pronounced positive therapeutic effect in such diseases as acute and chronic tonsillitis, ozena, otitis, candidiases of the mucous membranes, dysentery, and a number of others, and also as a blood substitute.

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