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An enormous number of works have been devoted to the study of the color reaction of starch with iodine over the century and a half that have passed since its discovery ([1,2]). However, the results of these studies are wholly out of proportion to the effort expended. If the structure of the iodine–starch complex may with some probability be spoken of as an inclusion compound, then at present nothing is known about the mechanism of the iodine–starch reaction.

Meanwhile, this question is not only of theoretical interest, but also has great practical significance. As early as 100 years ago ([3]) the medicinal properties of iodized starch were known, but because it was used as an external agent, its advantages over other iodine preparations remained unnoticed. In 1942 ([4]), iodized starch was for the first time successfully administered internally for the treatment of human dysentery. Thus its non-toxicity with this method of administration and its obvious advantages in comparison not only with other iodine preparations, but also with antibiotics and sulfanilamides, were first demonstrated.

To understand the biological activity of iodized starch, it is important to identify the form of iodine that is incorporated into the macromolecule. In this connection, the study of the mechanism of the iodine–starch reaction is of special interest.

For this purpose we carried out a spectrophotometric study of the interaction of starch with iodine in aqueous solutions.

Experimental Part

Solutions of iodized starch were prepared in twice-distilled water from ordinary starch of the "Goslaborsnabzhenie" grade by the action of a calculated amount of iodine. The iodine preparation, chemically pure grade, was subjected to double sublimation. Spectrophotometric studies were carried out at room temperature on an SF-4 spectrophotometer in the range 220–800 mμ.

As shown by literature data ([5—8]) and by our studies ([9,10]), in the absorption spectra of blue iodine solutions in the presence of starch and certain other macromolecules, an absorption band is observed in the visible region with

Fig. 1. Absorption spectra of aqueous solutions: 1 –J_2–H_2O; 2 –starch–H_2O; 3 –J_2–H_2O–starch. In all solutions the concentration of J_2 is 0.008%, starch 0.5%; layer thickness 0.2–1 cm

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$\lambda_{\max}$580—620 mμ. This band is often accompanied by another absorption band in the ultraviolet part of the spectrum with $\lambda_{\max}$350—360 mμ.

We studied the appearance of these bands in the absorption spectrum of an aqueous solution of iodized starch against the background of the absorption spectra of the individual components of the complex.

As can be seen in Fig. 1, curve 1 represents the absorption spectrum of a 0.008% aqueous solution of iodine, in which there are three absorption bands with $\lambda_{\max}$288—290, $\lambda_{\max}$350—354, and $\lambda_{\max}$460 mμ, belonging respectively to J_3^-, JO^-, and J_2 (J_2 here and below is an abbreviated expression for $n \cdot H_2O\,[J^+ \ldots J^-]$). Curve 2, characterizing

absorption in the UV region of a 0.5% aqueous starch solution, reveals only a continuous absorption edge with a small optical-density value in the far ultraviolet. After the iodine solution had been mixed with the starch solution, we investigated the absorption spectrum of the resulting blue solution. As curve 3 shows, the absorption bands at λ 288–290 and λ 460 mμ disappeared, while the band at λ 350–360 mμ showed a sharp increase in optical density. At the same time, in the visible part of the spectrum a pronounced absorption maximum appeared at λ 600 mμ, characteristic of the iodine-starch complex. Thus, the addition of starch to an aqueous iodine solution leads to the disappearance of iodine in the form of J_3^- and J_2, with formation of the system: JO^-—H_2O – iodine-starch. It follows from this that, in the presence of starch, J_2 molecules dissociate with formation of complex ions J_3^- and JO^-, of which only the former participates in formation of the complex. The complex anion JO^- does not

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interact with the polymer, as a result of which its concentration increases as J_2 is split, as indicated by the sharp rise in optical density at λ 350–360 mμ.

If this interpretation of the results of our experiment is correct, the following assumption may be made. At a relatively low concentration of starch in an aqueous iodine solution, when its amount is insufficient for complete absorption of the J_3^- anion formed as a result of the dissociation of J_2, the spectrum of the solution should contain 4 maxima: at λ 288–290 mμ (J_3^-), λ 350–360 mμ (JO^-), λ 460 mμ (J_2) and λ 600 mμ (iodine-starch complex). If, further, we

Fig. 2. Absorption spectra of aqueous iodine-starch solutions at constant J_2 concentration of 0.02% and varying starch concentration: 1 —at 0.03%; 2 —at 0.05%; 3 —at 0.07%; 4 —at 0.1%. Layer thickness 0.4—0.5 cm

Figure 2: Fig. 2. Absorption spectra of aqueous iodine-starch solutions at constant J_2 concentration of 0.02% and varying starch concentration: 1 —at 0.03%; 2 —at 0.05%; 3 —at 0.07%; 4 —at 0.1%. Layer thickness 0.4—0.5 cm

gradually increase the starch concentration, while retaining in the solution the initial concentration of J_2, the absorption bands at λ 288—290 and λ 460 mμ should disappear from the spectrum of the solution, with a simultaneous increase in optical density at λ 350—360 and λ 600 mμ.

As Fig. 2 shows, the experiment fully confirms this assumption. Curve 1 demonstrates four clearly expressed absorption bands with maxima at λ 288—290, λ 350—360, λ 460 and λ 600 mμ. On curve 2 the band with λ_{max} 288—290 mμ is already absent, which indicates the disappearance of the complex anion J_3^- as a result of an increase in starch concentration. Curve 3 demonstrates the complete absence in the spectrum also of the band with λ_{max} 460 mμ, i.e. the disappearance of J_2 from the solution. At the same time, curves 2 and 3 reveal a gradual increase in the optical density of the absorption bands at λ 350—360 and 600 mμ, which indicates an increase in the concentration of JO^- and of the iodine-starch complex in connection with the increase in starch concentration. The rise of the ordinates at λ 280—290 and λ 460 mμ with increasing concentration

starch in solution occurs through the growth of broad absorption bands upon formation of the anion JO^- and of the iodine-starch complex, which extend into these ordinates. This is also confirmed by the chemistry of the reaction: the increase in ordinates at λ350 and λ600 m at a strictly constant iodine concentration can occur exclusively through absorption by J_3^- (corresponding to 280—290 m) and J_2 (corresponding to 460 m).

As is known, when iodine dissolves in water a reversible reaction takes place:

$$J_2 + H_2O \rightleftarrows HJ + HJO,$$

the equilibrium of which is strongly shifted to the left.

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In this case the formation of the complex anion J_3^- is observed through attraction of the J_2 molecule to J^-, in the same way as the latter attracts water molecules. The J_3^- ion is in equilibrium with the products of its dissociation:

Fig. 3. Effect of starch on an aqueous iodine solution subjected to dialysis: 1 —absorption curve of the aqueous iodine solution; 2 —the same after addition of starch. Initial concentration of J_2 solution 0.002 N. Layer thickness 0.4—5.005 cm

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$$J_3^- \rightleftarrows J^- + J_2 \quad (^{11}).$$

When starch is added to an iodine solution, interaction of the latter with the J_3^- anion begins, with formation of the iodine-starch complex. This leads to disturbance of the equilibrium, further splitting of J_2, and an increase in the concentration of JO^-. What has been said is in full agreement with the spectrophotometric data obtained by us.

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We also demonstrated the formation of the iodine-starch complex by inclusion of the J_3^- anion with the aid of dialysis. An aqueous 0.002 N J_2 solution was subjected to dialysis through a cellophane membrane 40 μ thick. Nine hours after the start of dialysis, only an absorption band with λ_{max}280 m was observed in the absorption spectrum of the solution (Fig. 3, 1). After starch was added to this solution, λ_{max}570 m was found in the absorption spectrum, while λ_{max}280 m disappeared (Fig. 3, 2). These changes in the absorption spectra are direct proof of the formation

iodine-starch complex by direct interaction of starch with the anion J_3^-.

Comparison of our spectrophotometric data with the chemistry of aqueous iodine solutions makes it possible to represent the mechanism of the iodine-starch reaction in the form:

$$J_2 + H_2O \rightarrow 2H^+ + J^- + JO^-, \tag{1}$$

$$J_2 + J^- \rightarrow J_3^-, \tag{2}$$

$$J_3^- + \text{starch} \rightarrow \text{iodine-starch}. \tag{3}$$

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