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SPECTROPHOTOMETRIC STUDY OF AQUEOUS SOLUTIONS OF IODINE-STARCH AND IODINE-AMYLOSE

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The iodine-starch reaction was discovered in 1814 by Colin and Gaultier de Claubry (1) and, in the same year, independently of them by Stromeyer (2). Over the past century and a half, an enormous number of works have been devoted to the study of the reaction of iodine with starch and amylose. However, up to the present time it has not been possible to establish the nature of the bond between iodine and these high polymers.

Many investigators of this problem regarded iodine-starch as a chemical compound, assigning to it one or another chemical formula (3–8). With the development of colloid chemistry, the view of iodine-starch as an adsorption compound became widespread (9–14). Hypotheses that considered iodine-starch as a solid solution or as a solution of highly dispersed iodine stabilized by a colloid had less success (15–18). Nadzwiecki (19) in 1934 studied the change in viscosity of solutions of iodine-starch and iodine-amylose, as well as the process of coagulation of the complex. The author suggested that the addition reaction of iodine to these polymers proceeds in two phases. In the first phase, addition of iodine occurs according to the type of ordinary chemical reactions, and this phase ends when 1 g of soluble starch has added 38.4 mg of iodine, and 1 g of amylose 53.4 mg of iodine. Thereafter, in the second phase, adsorption combination takes place.

In 1939, Freudenberg (2) used, to explain the structure of iodine-starch, the helical (screw-like) model proposed in 1937 by Hanes (21) to explain the α-amylase degradation of starch. Along the central axis of the channel of this model, iodine molecules are arranged in the form of a polyiodide chain, forming an inclusion compound. Subsequently Rundle and co-workers (22–26) and other investigators confirmed Freudenberg' s concept. However, this spatial model also does not reveal the nature of the bond between iodine and the polymer molecule.

The inconsistency of the experimental data presented in the literature on this question is explained by two main reasons. First, complexes were studied that contained different, often even completely undefined, amounts of iodine per one

Figure 1

Figure 1: Figure 1

part by weight of polymer. Second, investigation of the course of the reaction was carried out in arbitrarily chosen and, as a rule, very narrow ranges of values of the components of the complex. An exception is the work of Nadzwiecki (^{19}), who was the first to succeed in clearly noting the dual character of iodine addition.

At present we do not possess reliable experimental data on the nature of the bond of iodine with molecules of starch or amylose. The literature data on the quantitative ratios of the components in the process of iodine addition to the high-polymer molecule are also contradictory and require clarification ($^{15-27}$).

The study of the iodine-starch reaction has not only theoretical but also great practical significance. Solutions of iodine-starch and iodine-amylose possess sharply pronounced antimicrobial properties with a broad—

spectrum of (action) (^{28}), nontoxicity, and a positive effect in the treatment of a number of diseases (^{29}).

These circumstances prompted us, for the study of this reaction, to investigate the absorption spectra of solutions of iodinated starch and iodamylose in the range 220-800 mμ.

Experimental Part

0.1-1.0% solutions of iodinated starch were prepared from soluble starch of the grade "Reagent OST 27, GOPKh 1866" in twice-distilled water by the action of a calculated amount of iodine in a solution of potassium iodide or in ethanol. The iodine preparation of "chemically pure" grade was subjected to double sublimation. Amylose was obtained by the diffusion method of Gusemann and Bartl (^{3}) from potato starch. Spectrophotometric studies were carried out at room temperature on an SF-4 spectrophotometer. Colorimetric measurements were carried out on an FEK-M photoelectric colorimeter.

Fig. 1. Absorption curves of aqueous solutions of iodamylose at a layer thickness of 0.1 cm:
a—C_{amylose} 0.1 wt.%; C_{J_2} 0.03%. Iodine introduced into the solution together with ethyl alcohol.
b—C_{amylose} 0.1%; C_{J_2} 0.01%. Iodine introduced into the solution together with ethyl alcohol.
c—C_{amylose}—0.04%; C_{J_2}—0.017%. Iodine introduced in a mixture with KJ.

The electronic absorption spectra of aqueous solutions of iodinated starch and iodamylose in the range 220-800 mμ are characterized by four absorption bands with maxima at 226, 288-290, 344-360, and 585-620 mμ. The first two maxima

Figure 2

Figure 2: Figure 2

Fig. 3. Dependence of the optical density of solutions of iodized starch at constant starch concentration and varying iodine concentration for $\lambda = 600$ mμ. Thickness of the solution layer 0.011 cm

Figure 3: Fig. 3. Dependence of the optical density of solutions of iodized starch at constant starch concentration and varying iodine concentration for $\lambda = 600$ mμ. Thickness of the solution layer 0.011 cm

are not constant for blue solutions of these iodinated high polymers. The maximum at 226 mμ is observed only when iodine is introduced into the solution together with a metal iodide, for example in the presence of potassium iodide. Therefore it is absent from the spectra of solutions of iodinated high polymers obtained by the action on the polymers of iodine solution in ethanol (Fig. 1 a, b). The maximum at 288-290 mμ occurs at relatively high iodine concentrations; as is seen in Fig. 1, this maximum is observed, for example, at a ratio of 0.3-0.42 g I/1 g amylose (Fig. 1 a, c) and is absent at 0.1 g I/1 g amylose (Fig. 1 b). The absorption bands at 344-360 mμ and 585-620 mμ are constant in the absorption spectra of all the iodine solutions investigated by us in the presence of high polymers. As is known, an absorption band with a maximum at 344-360 mμ is present in the absorption spectra of aqueous and alcoholic iodine solutions; consequently, this absorption band is not associated with the presence of the high polymer. At the same time, in the spectra of all aqueous solutions of iodinated high polymers this absorption band occurs.

Fig. 2. Dependence of the molar absorption coefficient χ_{600} of iodine for $\lambda = 600$ mμ on the ratio of the iodine and high-polymer contents in the solution: *a*—ratio of iodine and starch; *b*—ratio of iodine and amylose.

The values of the absorption coefficient χ_λ were determined by us at $\lambda = 600$ mμ and starch concentrations of 0.1; 0.25; 0.5 and 1.0 per 100 ml of water. For the system H_2O—J_2—KJ–starch, as well as H_2O—J_2–starch, the maximum value of χ_{600} was obtained at a J_2/starch ratio equal to 40 mg J_2/1 g starch. For the system H_2O—J_2—KJ–amylose, χ_{600} reaches its maximum value at a J_2/amylose ratio equal to 53.3 mg J_2/1 g amylose. As can be seen in Fig. 2, the values of χ_λ below this boundary fall rapidly. The maximum values of χ_λ obtained by us agree very well with the data of Niedzwicki ([19]) cited above, and also with the results of Gollo and Szeitli ([31]), obtained by amperometric titration.

The sorption isotherm of iodine by starch obtained by us (Fig. 3) reveals the dual character of this process: in the interval 0.01-0.04 g J_2/1 g starch it is a linear function; subsequently (0.04-0.5 g J_2/1 g starch) it takes the form of an adsorption isotherm.

Fig. 3. Dependence of the optical density of solutions (D) of iodized starch at constant starch concentration and varying iodine concentration for $\lambda = 600$ mμ. Thickness of the solution layer 0.011 cm.

However, in our opinion this does not give grounds to suppose that in the first segment of the optical-density isotherm the addition of iodine proceeds by the principal valences, i.e., according to the type of ordinary chemical reactions. We can only assert that in the first phase of the reaction (on the first segment of the optical-density isotherm) the addition of iodine is accompanied by complete subordination of the solution to the Bouguer—Beer law, whereas in the second phase of the reaction the optical-density curve assumes the form of a Freundlich adsorption isotherm. Together with this undoubted distinction, an important element of similarity between the two reaction phases must also be noted: as the increase in optical density at $\lambda_{\max}$600 mμ shows, in the second segment of the isotherm the concentration of absorption centers or color centers, i.e., the color intensity of the solution, apparently continues to increase up to the moment of saturation of the amylose.

The frequently encountered disregard in the literature for the dual character of the iodine-starch reaction results from an incorrect choice of concentrations of iodine interacting with the polymer. This leads to a one-sided interpretation of the mechanism of iodine addition and to an incorrect generalization of results obtained in narrow intervals, on small segments of the optical-density isotherm.

As an example one may cite the paper of Meyer and Bernfeld (^{27}), who limited themselves to a very narrow interval within the first segment of our isotherm. It was found that when the concentration of one of the components was doubled, the intensity of the coloration, proportional, in the authors' opinion, to the concentration of the blue addition product, increased by approximately 3.3–4 times. This is expressed by the equation: $[K \cdot \text{starch} \cdot \text{J}_2] = [\text{starch}]^n[\text{J}_2]^m$, where n and $m \approx 2$, K is a constant. Although this equation is refuted by our spectrophotometric data, we decided to repeat the experiments of Meyer and Bernfeld with the aid of a photoelectric colorimeter. We used two light filters: $\lambda_{\max}$410 mμ (blue) and $\lambda_{\max}$595 mμ (yellow). When the iodine concentration was increased in the ratio 1:2 and the starch concentration, taken in large excess, was kept constant, we obtained the following ratios of optical densities: with the blue light filter—1) 1:1.99, 2) 1:2.08, 3) 1:2.02 (mean value 1:2.03; in (^{27}) 1:4), with the yellow light filter—1) 1:1.79, 2) 1:1.93 and 3) 1:1.85 (mean value 1:1.86; in (^{27}) 1:3.3). In repeating the experiments of Meyer and Bernfeld with amylose (the iodine complex was obtained by the action on an amylose solution of an aqueous solution of ···

iodine) were obtained with a yellow light filter ($\lambda_{\max} = 595$ mμ): 1) 1 : 1.76; 2) 1 : 1.72 (mean value 1 : 1.74; in (^{27}) 1 : 4). Thus, the colorimetric data obtained by us do not confirm the conclusions of Meyer and Bernfeld and are in complete agreement with the results of our spectrophotometric investigations.

The dual (two-phase) character of the iodine–starch reaction has been established by studying changes in the viscosity of solutions of iodine high polymers and the process of coagulation of the complex (19), by the method of amperometric titration (29), and by spectrophotometric investigation of the systems: 1) H_2O—J_2—KJ—starch, 2) H_2O—J_2—starch, and 3) H_2O—J_2—KJ—amylose.

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