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Fig. 1. Absorption spectra of the system J_2—KJ—PVA—H_2O at KJ concentrations: 1.3% (I), 1.5% (II), 1.65% (III), 1.8% (IV), 2.0% (V), 2.6% (VI) ($C_{PVA} = 0.02\%, C_{J_2} = 1.0\%$)

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Abstract

Full Text

Chemistry

L. G. Gebelev, N. A. Silkina

On the Influence of Potassium Iodide on the Iodine-Polyvinyl Alcohol Color Reaction

(Presented by Academician I. I. Chernyaev, 9 X 1964)

The question of whether, in the interaction of iodine with starch, iodide is merely a component that promotes an increase in the content in solution of complex-forming species (iodine molecules, triiodide ions), or whether J^- ions are necessary, along with the others, for the formation of the "blue" complex, still remains controversial ([1,2]). The nature of the participation of potassium iodide in the interaction of iodine with polyvinyl alcohol (PVA) has not been studied at all. It seems to us that a certain contribution to the resolution of this problem may be made by studying the features of the absorption spectra at different concentrations.

Fig. 1. Absorption spectra of the system J_2—KJ—PVA—H_2O at KJ concentrations: 1.3% *(I)*, 1.5% *(II)*, 1.65% *(III)*, 1.8% *(IV)*, 2.0% *(V)*, 2.6% *(VI)* ($C_{PVA} = 0.02\%,\ C_{J_2} = 1.0\%$)

The materials used in the study were: chemically pure potassium iodide, chemically pure iodine, twice sublimed, and an industrial sample of PVA ($\bar{M} = 38 \cdot 10^3$; content of acetate groups 1.3%; ash content 0.7%). The optical densities of iodine–iodide–PVA solutions were measured on an SF-4 spectrophotometer relative to standard iodine–iodide solutions.

We obtained absorption spectra in the visible region for iodine–iodide–PVA solutions that differ in their potassium iodide content (Fig. 1). As is evident from the spectrogram, even a considerable iodine content (relative to the polymer) (for example, one-percent iodine in one-and-a-half-percent iodide (curve *II*)) is not a sufficient condition for the formation of the "blue" iodine–PVA complex. This follows from the fact that at some, evidently insufficient, J^- concentrations (curves *I*, *II*) the 600 mμ band characteristic of this complex is

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

absent. Meanwhile, in the 490 mμ region, at the same low J^- concentrations, an absorption band is distinctly observed, apparently due to the formation of yet another, hitherto unknown complex compound of iodine with PVA, which, in contrast to the "blue," "long-wavelength" complex (600 mμ), we shall call "short-wavelength" (490 mμ). The presence of an intersection node of the curves (in the region of 530 mμ) indicates that the two forms of colored centers corresponding to the 490 and 600 mμ bands are in equilibrium, one of the factors of which is the iodide concentration.

With an increase in the iodide concentration (at the same iodine and PVA concentrations), the equilibrium, as is seen from Fig. 2, shifts toward an increase in the concentration of the "blue" complex at the expense of a decrease in the concentration of the "short-wavelength" one.

On the basis of the data presented, it may be assumed that free iodine is substantially necessary in the formation of the "short-wavelength" complex responsible for the appearance of the 490 mμ band, whereas the appearance of the 600 mμ band is due to the formation of the "blue" complex, whose composition must necessarily include triiodide ions, because the latter band appears only with an excess of potassium iodide, i.e., under conditions of practically complete binding of iodine into triiodide ions.

Fig. 2. Effect of iodide concentration on the intensity of the absorption bands at 490 (I) and 600 mμ (II)
($C_{\text{PVA}} = 0.02\%,\ C_{\text{J2}} = 1.0\%$)

Fig. 3. Dependence of composition on optical density.
I —optical densities reduced to a layer thickness of 1 cm for $\lambda = 490$ mμ; II — the same for $\lambda = 600$ mμ
($C_{\text{PVA}} = 0.2\%,\ C_{\text{J2}} + C_{\text{KJ}} = 0.09 + 0.11\%$)

A similar effect of J^- ions on the spectra of iodine-amylose solutions was observed by J. A. Thoma and D. French ([1]), who consider the compound formed when there is a deficiency of J^- ions to be a complex of the type J_2-amylose. Consequently, the participation of iodide in the blue iodine-polyvinyl alcohol reaction is not distinctive, as V. O. Mokhnach and I. L. Zueva ([2,3]) suppose, but is analogous to the participation of J^- ions in the blue iodine-starch reaction.

Using (similarly to how J. A. Thoma and D. French did this for determining the composition of the iodine-cyclohexaamylose complex ([4])) the method of continuous variations (Fig. 3), we determined the equivalent ratios for the "blue" and "short-wavelength" complexes. It turned out that the number of J_2 molecules/number of CH_2CHOH groups is 1/3.2 for the "short-wavelength" complex and 1/5.5 in the case of the "blue" one; i.e., under these conditions

the "short-wavelength" complex binds almost twice as much iodine as the "blue" one.

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