The Visible and Ultraviolet Absorption Spectra of Cellulose- and Amylose-Iodine Complexes

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The structure of the amylose-iodine complex has been established, by Rundle and his co-workers[1], as a helical α-amylose chain in which the iodine molecules are arranged in a linear array, parallel to the helical axis. On the other hand, it has been described in a few books[2,3] that cellulose, structurally related to amylose, also gives a blue color on treatment with iodine. So, an attempt has been made, in the present work, to compare the cellulose-iodine complex with the amylose complex by means of their absorption spectra.

A solution of cellulose was obtained by dissolving a filter paper (the Toyo filter paper, No. 1 with a diameter of 12.5 cm.) into about 100 ml. of aqueous solution of commercial guaranteed zinc chloride. By adding a drop of solution of iodine and potassium iodide into this cellulose solution a deep blue color yields at once and numerous blue fibers precipitate. This blue color disappears at about 80°C by warming and re-appears by cooling.

1) R. E. Rundle and D. French, *J. Am. Chem. Soc.*, **65**, 1707 (1943); **69**, 1769 (1947).
2) Y. Kondo, "Experiments in Microchemistry of Cellulose Fibers", Bosekizashi, Osaka (1939), p. 5.
3) Y. Tsuzuki, "Simple Experiments in Organic Chemistry" Shokabo, Tokyo (1949), p. 58.

The visible absorption band of amylose-iodine complex has been found to shift toward the shorter wavelengths with increasing iodide concentration[4]. Thus, in the present measurement, a saturated iodine water was used to avoid an effect of iodide. The solution of cellulose-iodine complex to be measured was obtained after removing the blue fibers from the solution by a centrifuge.

α-Amylose was fractionated from an alkaline solution of potato starch as a complex with n-butanol[5]. The complex was crystallized three times from butanol. After washing it with ethanol it was dried by a vacuum pump for four hours and α-amylose was obtained. By adding a little iodine water into a solution of amylose and zinc chloride the sample of amylose-iodine complex was prepared. The absorption measurement was carried out with Hitachi Quartz Spectrophotometer Model EPU-2 at room temperature.

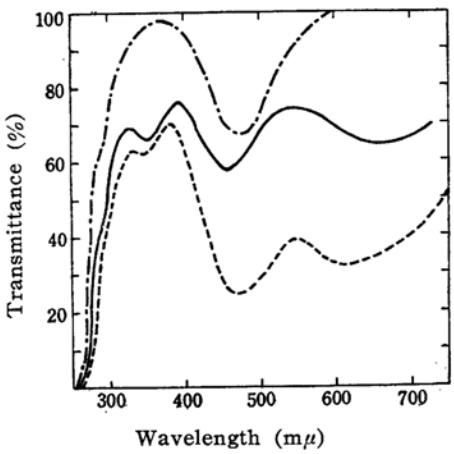

Fig. 1. Absorption spectra of cellulose-iodine complex (——), amylose-iodine complex (- - - -), and iodine in zinc chloride solution (—·—·).

The results in Fig. 1 show that the absorption spectrum of cellulose-iodine complex in solution of zinc chloride is closely analogous to that of amylose-iodine. The absorption band at about 470 mμ seems to be attributed to iodine, because the spectrum of iodine in aqueous zinc chloride is observed at the same region. It is well known that a blue color of starch-iodine is decolorized by warming and is regenerated by cooling. As described above, the color of cellulose-iodine is found to behave like starch-iodine towards change in temperature. In the present experiments the cellulose-iodine complex is, thus, analogous to amylose-iodine. This fact leads to the suggestion that the cellulose-iodine complex is able to yield the blue color by the same mechanism as that by which the amylose-iodine does; in other words the iodine molecules may be arranged in the helical cellulose chain.

If a little of the iodine iodide solution is droped on a filter paper immersed in a solution of sodium hydroxide (of a concentration above several per cent.) for half an hour at room temperature and the paper is washed with water, a blue color can be seen distinctly on it. It has been found that the β-amylose is transformed to the helical α-amylose on treatment with a solution of sodium hydroxide[6]. It seems, therefore, possible that by sodium hydroxide cellulose is also transformed to a helical state giving a blue color with iodine.

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4) S. Ono, S. Tsuchihashi and T. Kuge, *J. Am. Chem. Soc.*, **75**, 3600 (1953).
5) H. Azumi and T. Nakajima, *Sci. Rep. Tohoku Univ.*, 1, **36**, 282 (1952).
6) J. R. Katz and J. C. Derkson, *Z. phys. Chem.*, **A150**, 81 (1930).