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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Wolf, Rainer and Schulz, Rolf C.(1968) 'Optical Rotatory Dispersion of the Starch Iodine Complex. Part 2', *Journal of Macromolecular Science, Part A*, 2: 4, 821 – 832

To link to this Article: DOI: 10.1080/10601326808051443

URL: <http://dx.doi.org/10.1080/10601326808051443>

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Optical Rotatory Dispersion of the Starch Iodine Complex. Part 2*

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SUMMARY

The deep blue aqueous solutions of starch iodine show an abnormal rotatory dispersion with a peak near the absorption maximum. This induced Cotton effect is discussed on the basis of the known structure of the channel compound of iodine and amylose helix. The optical rotation of starch iodine solutions and also of amylose iodine solutions is very much increased with time, whereas absorption remains constant. Addition of salts or solvents to starch iodine solutions causes a shift for both the absorption maximum and the Cotton peak. Conditions that will destroy the helix or the iodine chromophore in the inner space of the helix (for example, heating, addition of urea, or detergents) cause disappearance of the induced Cotton effect.

INTRODUCTION

It is well known that addition of an aqueous iodine solution to an aqueous solution of starch results in a deep blue color. There are many investigations of this striking color reaction in the literature [1], but only since 1940 have detailed conceptions existed about the structure of this complex.

Freudenberg et al. [2] suggested a channel complex, and later this was proved and confirmed by several groups of authors [3-5]. Helices are built up by the amylose macromolecules with 6-8 glucose units

*Part 1: R. Wolf and R. C. Schulz, *Tetrahedron Letters*, 1967, 1799;
Part 3: R. C. Schulz, R. Wolf, and H. Mayerhöfer, *Kolloid-Z.*, in press.

forming one turn of the helix. The iodine atoms are located within the tube-like space of these helices, and they build up chains by overlapping of their electron orbitals. Every two iodine atoms are enclosed by one turn of the helix, or by 6-8 glucose units. It was possible under certain conditions to prepare iodine amylose complexes in the solid state, and X-ray measurements have been made on these samples. The structure, derived from these measurements, is figured in a somewhat simplified model in Fig. 1.

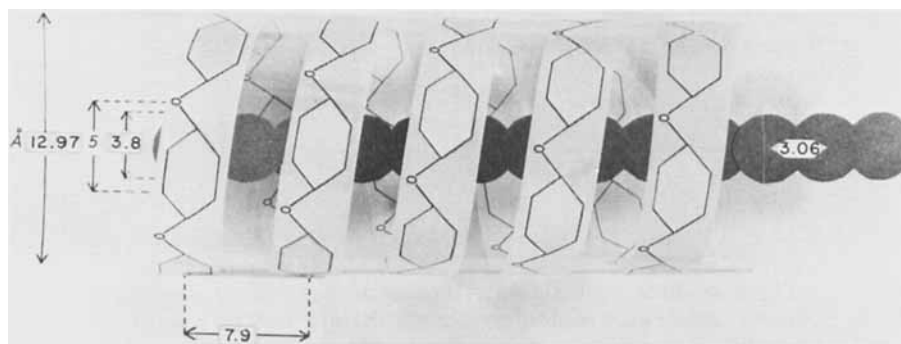


Fig. 1. Simplified model of the iodine amylose complex. The distances are taken from X-ray data.

The length of the helix depends on the degree of polymerization of the amylose sample. Increasing the length of the amylose channel also increases the length of the iodine chain, and this shifts the absorption maximum of the complex in the direction of longer wavelengths. Therefore, different samples of amylose iodine complexes have their absorption maxima at different positions. Usually, maxima will be found located between 490 and 645 $m\mu$ [6]. On the other hand, absorption maxima can be calculated for different lengths of the iodine chains, using the electron gas theory. According to these calculations, an iodine chain consisting of 14 iodine atoms will exhibit an absorption maximum at 625 $m\mu$ [4].

Although many physical properties of the amylose iodine complex have been investigated [1], in solution as well as in the solid state, nothing was known about its optical activity.

The linear chain of iodine atoms is not optically active, but is located within a strong disymmetrical environment. The amylose contains asymmetrical carbon atoms in its recurring units and furthermore the helix itself is a chiral structure. Although the iodine atoms are not chemically bonded to the amylose helix, their electron transitions can be expected to be asymmetrically induced by this environment. Therefore a so-called induced Cotton effect

should appear, and the extremum of rotation is expected to be found near $600\text{ m}\mu$. Induced Cotton effects are already known in the case of certain helical polypeptides [7]. These peptides exhibit an absorption maximum and ORD Cotton effects due to peptide bonds in the $220\text{-m}\mu$ region. Addition of an optically inactive dye shifts the peak of the optical rotation curve toward the absorption maximum of the dye. This induced Cotton effect will disappear if the helical structure is destroyed. In these cases the dyes are ionically bonded to the acid or basic groups of the proteins and the dye molecules are located on the external surface of the protein helix. In relation to their chemical structure, the kind of bonding to the chromophore, and the location of the chromophore, there are fundamental differences between the protein dye adducts and the amylose iodine channel complexes.

RESULTS AND DISCUSSION

In Fig. 2 extinctions and specific rotations are plotted against wavelengths. A pure solution of starch in water does not absorb at wavelengths greater than $250\text{ m}\mu$. A solution of iodine in potassium iodide solution has a characteristic spectra with two peaks at 350 and $290\text{ m}\mu$. The iodine starch complex has a strong peak at $565\text{ m}\mu$. As mentioned above, the position of this peak depends on the origin of the starch sample and on the preparation of the solution. In the lower part of this figure, the optical rotation dispersion (ORD) for the same solutions of starch and the iodine complex is shown. The starch exhibits a plain curve [8], but for the channel complex the expected induced Cotton effect appears with a peak at $585\text{ m}\mu$. Optical rotation in this region is about four times as high as that of a pure starch solution.

Starch is known to be a mixture consisting of different polysaccharides. The main components are amylose and amylopectin, which are both able to form iodine complexes. According to their different chemical structure, the amylose and amylopectin iodine complexes have different colors [9]. The absorption spectra and rotatory dispersion curve of both types of iodine complexes are shown in Fig. 3.

The amylose iodine complex has an absorption peak at $600\text{ m}\mu$. Indeed, in this case the induced Cotton effect has a peak at $610\text{ m}\mu$. On the other hand, the absorption of the amylopectin iodine complex is much weaker and shifted to a shorter wavelength. There is also a Cotton effect in this case, but the peak is weaker and appears at $560\text{ m}\mu$.

Amylose of high purity and definite degree of polymerization is difficult to prepare. Besides this, the Cotton effect of the iodine complexes for polysaccharides of higher molecular weights are expected

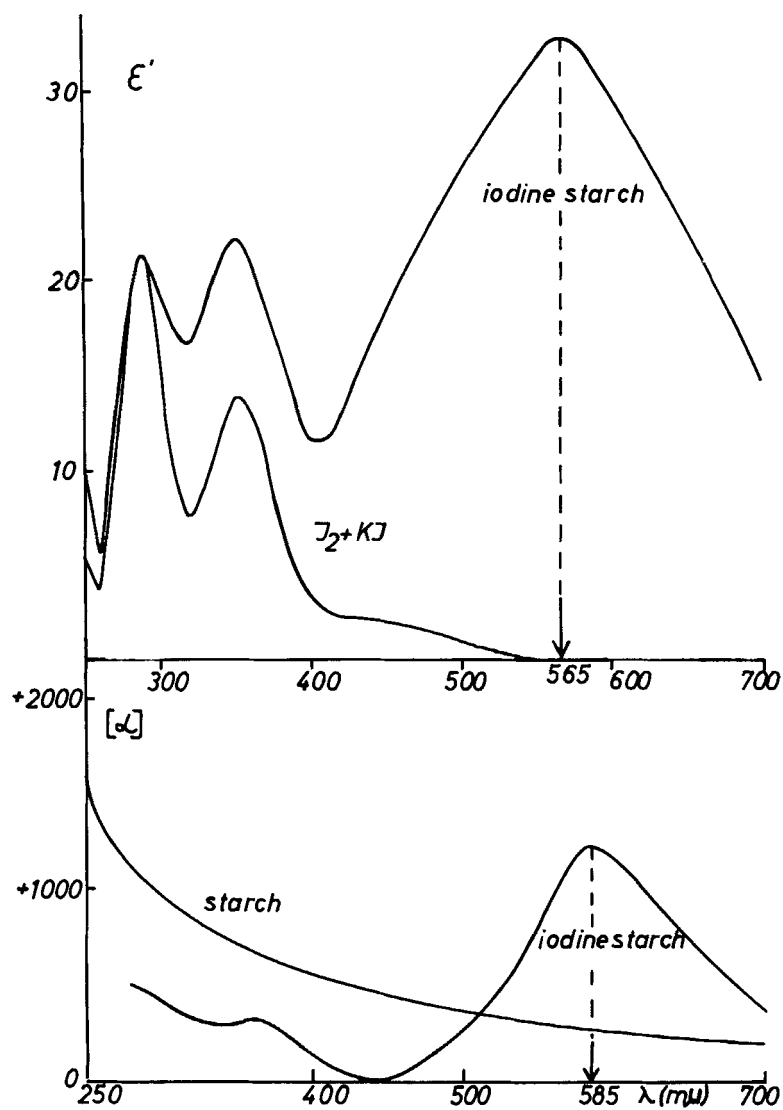


Fig. 2. Absorption spectra (above) and ORD (below) of iodine starch and iodine-iodide solution in water (0.25 g/liter of soluble starch (Merck); 0.06 g/liter of J_2 ; 0.06 g/liter of KJ) ϵ' related to g of J_2 /liter; $[\alpha]$ related to g of starch/100 ml.

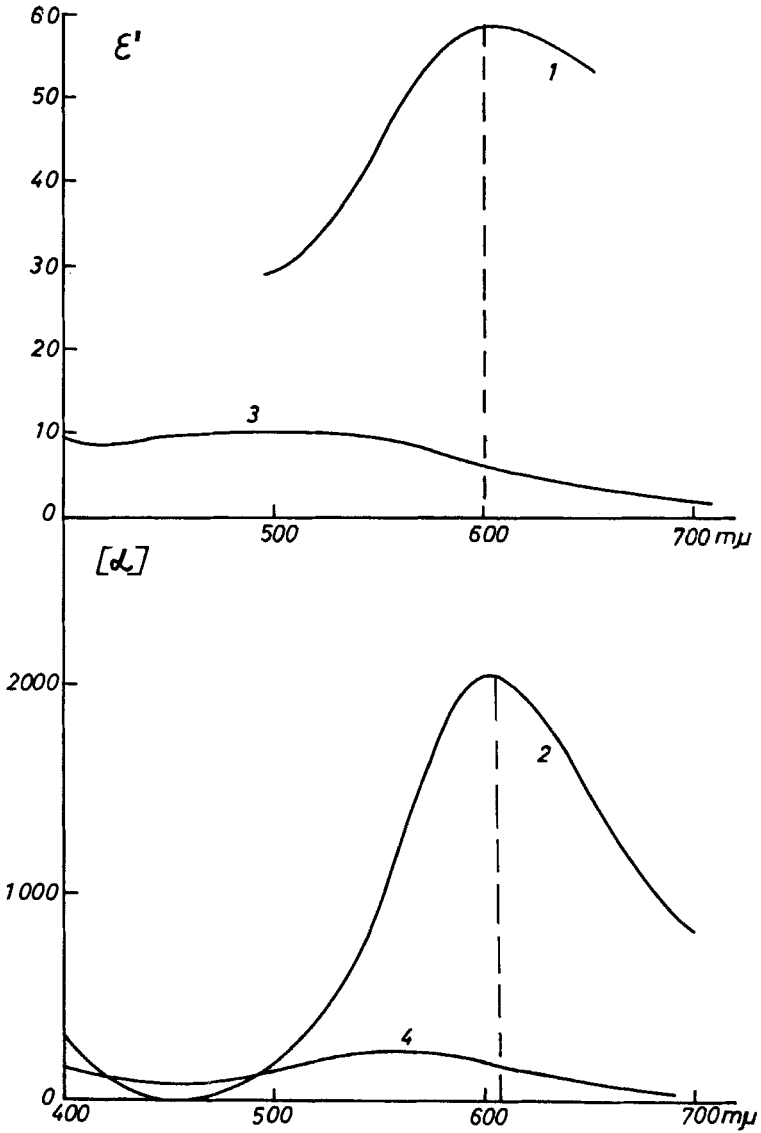


Fig. 3. Absorption spectra (above) and ORD (below) for iodine amylose (1, 2) and iodine amylopectine (3, 4).

to appear in a region of the spectra that is not as easy to measure with our instruments. Therefore, the investigations are continued with water-soluble starch.

It is well known that the absorption of the iodine complexes depends not only on the origin of the polysaccharides but also on the pH of the solution, the presence of electrolytes, salts etc. Therefore, the influence of the amount of iodine to the optical rotation was examined.

Figure 4 shows that with an increasing iodine to glucose unit ratio rotation starts to increase linearly and becomes constant at a ratio of approximately 1:6. This is nearly the same ratio between iodine and glucose units that was obtained for these complexes from X-ray measurements, potentiometric titrations, and spectroscopic measurements [11] under similar conditions [10]. It may be concluded that only the amount of iodine that is included in the amylose channel contributes to the optical activity. Again, this confirms our previous assumption.

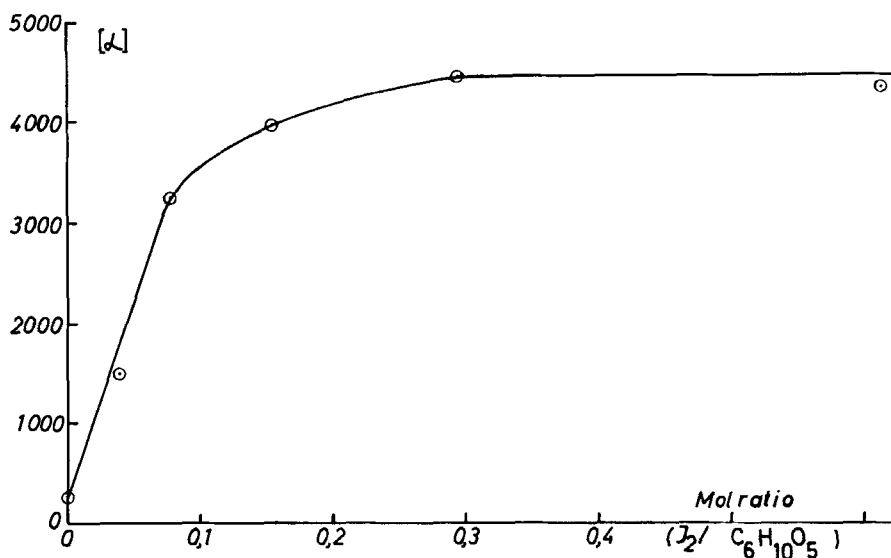


Fig. 4. Rotatory power in the Cotton peak of iodine starch versus iodine to base unit ratio (0.25 g/liter of starch, 5 g/liter of KJ).

A very unexpected observation was the time dependence of the ORD. The blue color of starch iodine complexes suddenly appears after mixing these compounds, and the reaction rate must be very high. The absorption spectra of the complex is unchanged for a couple of days. However, in contrast to this, the optical rotation of

these complexes increased during this time. For example, there is an increase from about 800 to about 2000° within 40 hr (see Fig. 5). The dashed line in Fig. 5 shows the extinction which remains constant during this time.

This change of rotatory power with time certainly is not based on the formation of new covalent bonds, because it is completely reversible. On heating the starch iodine solution to about 70°C, the color disappears, as a result of destruction of the amylose helix. The induced Cotton effect also disappears. On cooling to 25°C, the blue color suddenly appears again, and the solution is again optically active, but the optical rotation will reach its original value only after several hours.

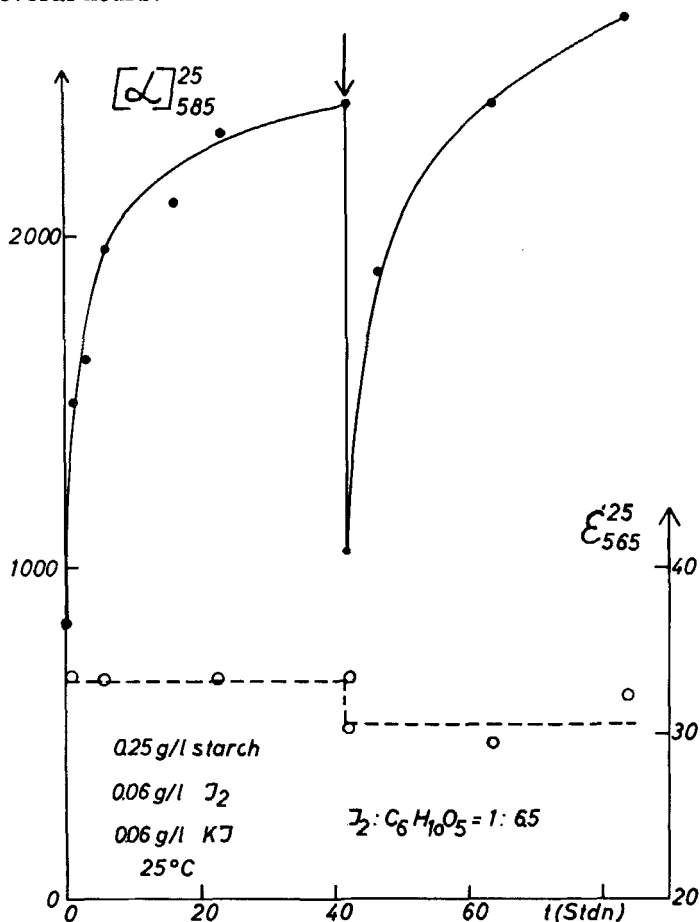


Fig. 5. Time dependence of $[\alpha]$ and ϵ' of iodine starch at 25°C. After 40 hr (\downarrow) the solution was heated above 70°C for 2 min.

The extinction is nearly the same before and after heating and remains constant over long time. This time-dependent increase in optical rotation can be observed with starch iodine and some amylose iodine solutions. In the case of amylopectin iodine solutions, optical rotation increases very little with time.

The effect probably has its origin in the helical structure of the complex, but we still have no explanation. Furthermore, it is known that addition of salts or solvents influence the absorption maximum of a starch iodine solution and also its extinction. It was proved if there is a correspondent change in the induced Cotton effect. Previously the solutions contained 0.06 g/liter of iodine (2.36×10^{-4} mole/liter) and 0.06 g/liter of potassium iodide (3.61×10^{-4} mole/liter). Increasing the concentration of potassium iodide resulted in an increase in the absorption and the optical rotation. There is no shift in the wavelength of the absorption or in the optical rotatory dispersion (see Fig. 6).

With very high concentrations of potassium iodide, the absorption maximum is decreased and shifted to shorter wavelengths. The maximum of the Cotton effect is also shifted the same amount in the same direction. At high iodide concentrations, the iodide ions can be assumed to be incorporated into the helix channel, causing an interruption in the electron cloud surrounding the iodine chain. The result is a hypsochromic shift in absorption. There is no destruction of the helix structure, and the induced Cotton effect is still present.

Very similar results were obtained by addition of sodium chloride, methanol, or dimethyl sulfoxide. The absorption peaks were always shifted to shorter wavelengths, and the Cotton effects that were still present were shifted the same amount in this direction.

As mentioned above, the Cotton effect will disappear if the helix is destroyed by heating the solution. We therefore added some compounds to the starch iodine solutions which can be assumed to partially or totally destroy the helix even at room temperature.

Figure 7, shows the influence of urea on the starch iodine reaction. Both maximum of absorption and Cotton peak are shifted to longer wavelengths, even at low urea concentrations. But there is a very marked decrease in optical rotation. With increasing concentrations of urea, the shifts are enlarged and the amplitudes are decreased. At an urea concentration of 500 g/liter (8 moles/liter), the solution shows a green-yellow color and has a nearly normal rotatory dispersion, similar to an aqueous solution of starch. These results can be discussed in the following manner. In the solutions, iodine-filled helices with different lengths are present. On addition of urea, the short helices are destroyed first. This increases the proportion of longer iodine chains, and the absorption maximum is shifted to longer wavelengths. The Cotton peak is shifted in the same direction, but, with the decrease in helix concentration, there

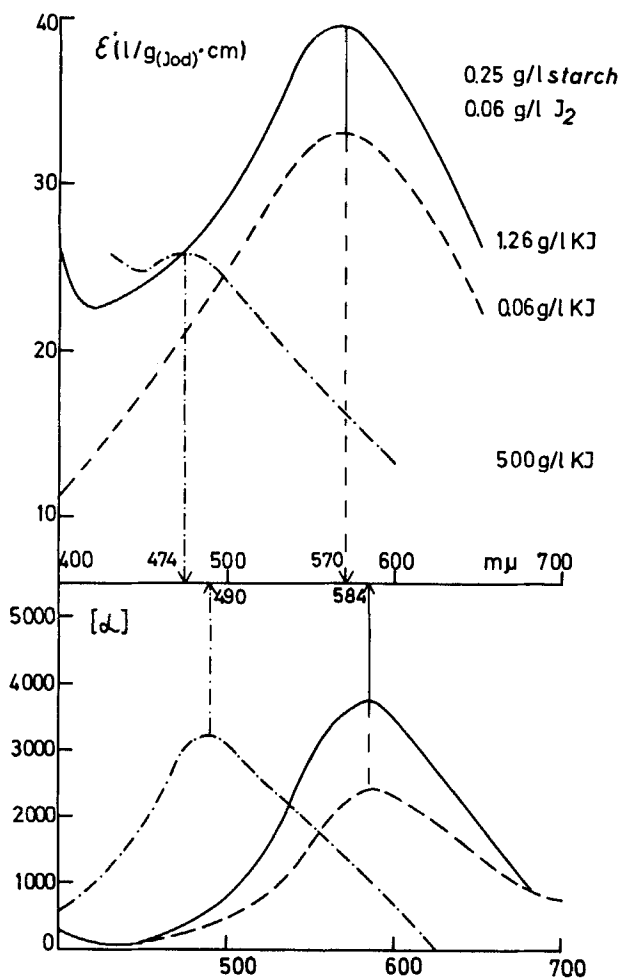


Fig. 6. Absorption spectra (above) and ORD (below) of iodine starch under the influence of added potassium iodide.

is also a decrease in optical rotation. At a certain concentration of urea, no amylose iodine complexes are present, only a mixture of iodine and amylose which does not exhibit an induced Cotton effect.

The influence of a neutral detergent (Triton X, 100 octylphenoldecyl-ethylene glycol ether) on the absorption and the ORD of starch iodine solution are shown in Fig. 8.

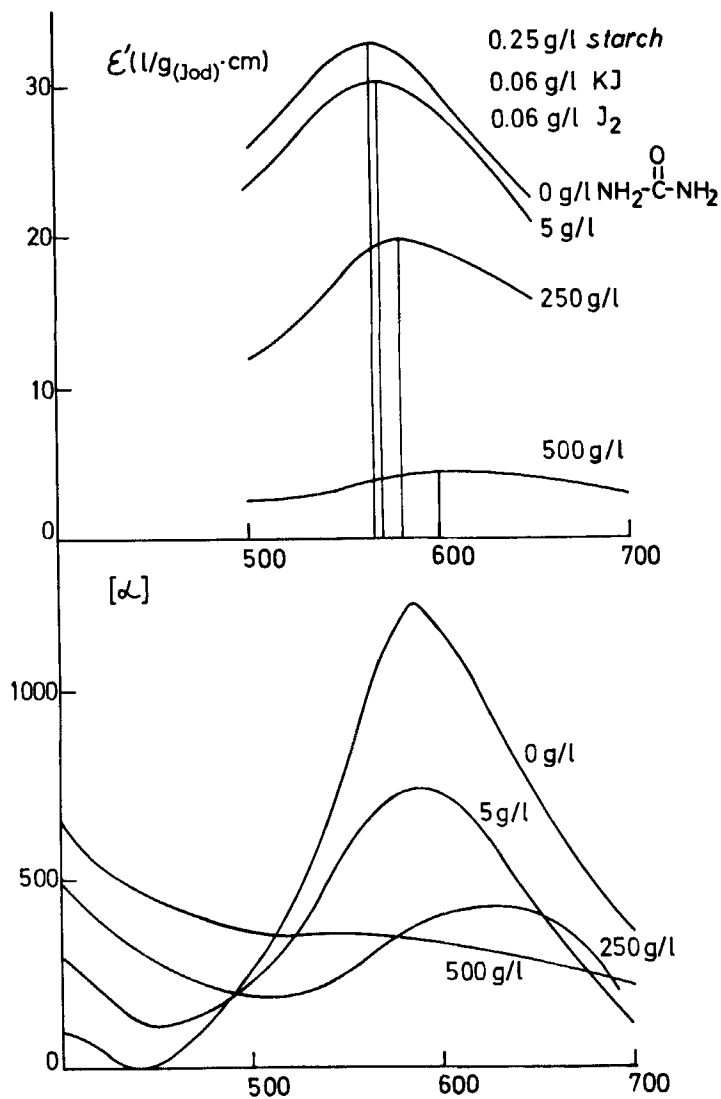


Fig. 7. Absorption spectra (above) and ORD (below) of iodine starch under the influence of added urea.

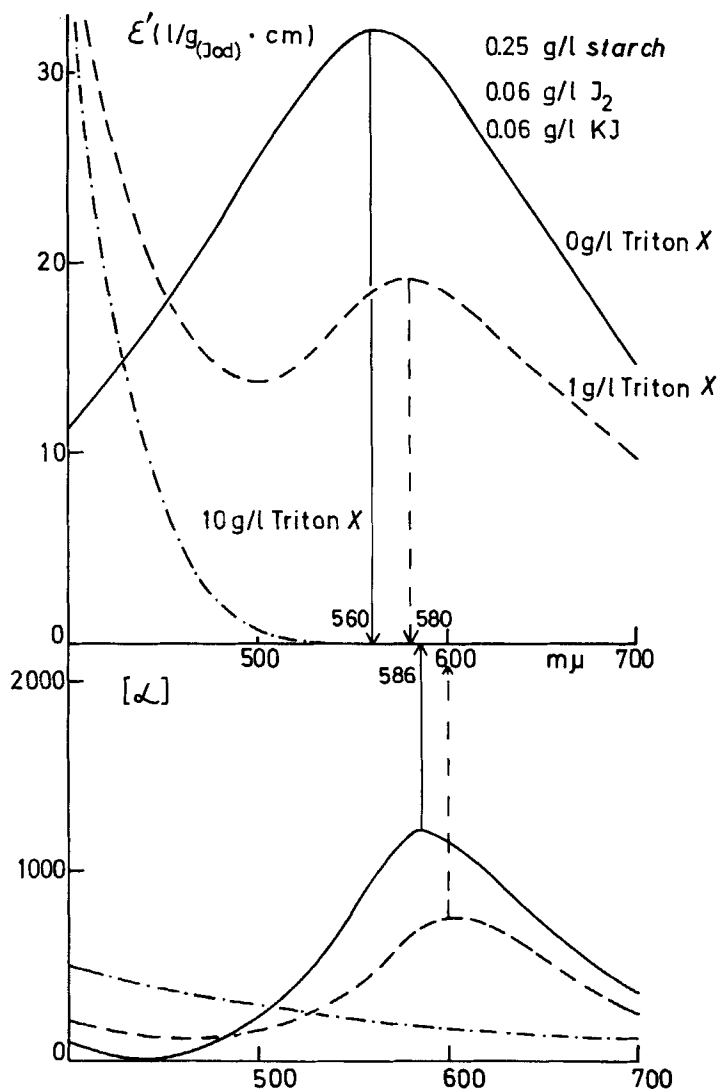


Fig. 8. Absorption spectra (above) and ORD (below) of iodine starch under the influence of added detergent (Triton X 100, octylphenyl-decaethylene glycol ether).

Very low concentrations of about 0.2 to 2 g/liter are sufficient to destroy the induced Cotton effect. Presumably in this case the helix is not destroyed, but the iodine chain in the channel is displaced by glycoether chains, and therefore the necessary chromophore is absent.

Further investigations are in progress.

ACKNOWLEDGMENTS

R. Wolf wishes to express his sincere gratitude for a Liebig-Stipendium of "Fonds der Chemischen Industrie." Our thanks are also due to Deutsche Forschungsgemeinschaft and Stiftung Volkswagenwerk for financial support of this study.

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Accepted by editor February 15, 1968

Received for publication February 26, 1968