THE MECHANISM OF THE STARCH-IODINE REACTION

II. EXPERIMENTS PERFORMED IN ORDER TO CLEAR UP OUR PROBLEMS

By

J. HOLLÓ and J. SZEJTLI

Institute of Agricultural Chemical Technology, Polytechnic University, Budapest

(Received April 25, 1957)

1. Amperometric titration

Our choice of amperometric titration, instead of the usual and generally accepted potentiometric method, was that the former is much less delicate and, while galvanometer readings depend in the former case logarithmically on iodine activity, there is a linear function of it in the latter case. In this way, in the whole range of measurements sensitivity remains unchanged. This advantage is made complete by the fact, that the straight line connecting the measurement points is always easier to be drawn, than a logarithmic curve [10].

a) *The principle of amperometric titration* is the same as dead-stop method. It was first applied by LARSSON and his co-workers [3], and later modified by COTON *et al.* [11]. A voltage of 20—40 mV is applied to thin platinum wires. After polarization of the electrodes, J_2 is added to the system and in proportion to its concentration depolarization occurs; thus, the intensity of the current is proportional to the present concentration of free J_2. During titration the intensity of current is measured by galvanometer and plotted against the ml-s of the added solution. Such a, so-called, amperogram is shown on figure No. 1.

In the dead-stop method the end point is indicated by the deviation of the galvanometer. Just before the end-point there is no free iodine present and consequently no current flows. Carrying out amperometric titration of starch with iodine, a considerable quantity of current also flows before the end-point. In case of 40 mV this is about 2 μA at 25 C°.

Knowing the blank curve, the iodine concentration can be established by the intensity of the current. The horizontal section of the curve has *e. g.* an ordinate of 2,0 μA. In the same system, in the absence of starch, 0,06 ml of 0,01 n J_2 addition gives an intensity of 2,0 μA. The corresponding iodine concentration being (in a volume of 50 ml):

$$\frac{0{,}06 \cdot 0{,}01}{50} = 12 \cdot 10^{-6}\,\mathrm{n} = 12\,\mu\,\mathrm{n}\,.$$

An other striking feature of the amperogram is that the tg α of its steeply rising section is the largest at the blank curve, with amylose it is somewhat smaller, and in the case of starch it becomes still smaller. This is obviously caused by the adsorption occurring.

b) *The apparatus for amperometric titration.* The apparatus applied by us is — apart from insignificant modifications, — substantially identical with the one used by COTON and his co-workers [11]. The electrical circuit consists of a dry Leclanché cell of V 6, a resistance of 8000 ohms, a potentiometer of

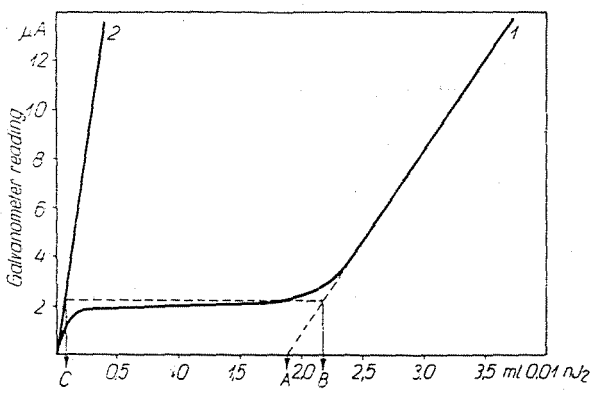

Fig. 1. Amperogram

1. 0,058 g wheat starch titrated in total volume of 55 ml at 25° C at the voltage of 40 mV. Consumption B—C = 2,10 ml. 1 ml of 0,01 n J_2 solution = 1,137 mg J_2. Dry matter content of wheat starch: 85,5%

2. Blank.

Reckoning of the value of J_2 sorption:

$$J_2\,\% = \frac{2{,}10 \cdot 1{,}137}{0{,}058 \cdot 0{,}855} = 4{,}78\,\%.$$

80 ohms, two tin platinum wire electrodes of 3 cm, and a galvanometer sensitivity of $5 \cdot 10^{-8}$ A. The titration cell (of 150 ml volume) with a tightly fitting cover having three ground holes: for a located microburette, an electrode and a stirring rod. The r. p. m. of the stirring rod is 1440/min. The scheme of the device is shown on figure No. 2.

We performed the titration with 0,01 n J_2 solution, at 25 $\pm$ 0,2 C°. For the sake of reproducibility, several factors should be considered:

Temperature should be constant.

The titration cell should be tightly closed, to prevent iodine losses.

Light should be excluded, to prevent any photochemical reaction that might lead to the formation of iodine from iodides.

The revolutions of the mixer should be of constant speed.

The surface of the electrodes should be small, in order to quickly produce a state of equilibrium.

The relative position of the electrode in respect to the mixer should be constant.

The sensitivity and the damping of the galvanometer should be corresponding.

c) *The performance of the measurement:* The first step was the preparation of the solution. This might either be done directly, or by the preparation of a standard solution. When directly, preparing the solution, a quantity correspond-

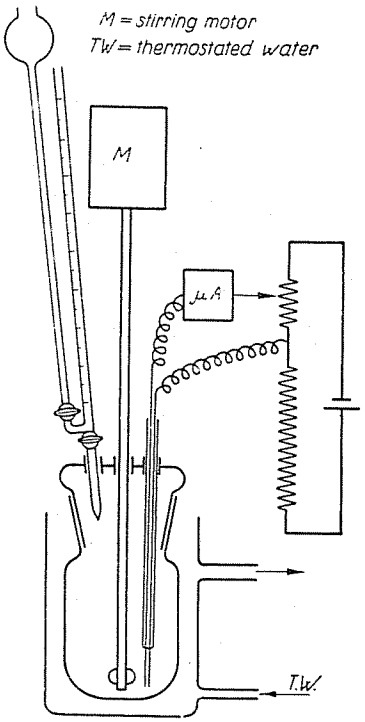

Fig. 2. Scheme of the amperometric titration device

ing to 10—12 mg amylose is weighed with 0,1 mg accuracy. In case of starch this makes about 45—50 mg, in case of flour about 60—65 mg. 20 ml distilled water should be introduced into the titration cell, and the previously weighed material is then poured in. It is essential to have water in the cell when introducing the dry material, otherwise the granules of the sample will stick to the bottom of the cell, local overheating causes the decomposition of amylose, and the results obtained will be lower than the actual ones. About 20 ml boiling water is then poured into the cell and the whole charge is then kept boiling for

fifteen minutes. After sudden cooling 5 ml HCl are added, and the volume of the solution is completed to 50 ml.

The preparation of a standard solution is far more convenient. 200 ml distilled water are introduced into a 250 ml flask and placed into a water bath. The temperature of 95—98 C° being reached, the accurately weighed starch (about 300 mg) is washed into it, by means of a water jet. An additional 15 minutes at the above temperature is kept, then cooled rapidly and then filled up to the mark and thoroughly shaked. It is advisable to titrate 25 ml of this concentrate with the addition of 5 ml n HCl and 20 ml of distilled water.

Titration is performed by connecting the cell containing the solution to be titrated to the cover starting the circulation of the thermostate water and the stirring motor. The temperature of the thermostate being attained, titration begins. 0,2 ml/min (in the horizontal section of titration curve, 0,5 ml/min) measuring solution are added and galvanometer readings are also recorded every minute. Current circuit is closed for only 15 seconds per minute, just before readings are taken. The measuring solution consists of 0,01 n J_2. The amperogram should be drawn by plotting the galvanometer readings in the function of the ml-s of the added measuring solution, directly onto a squared mm paper.

d) *Evaluation of the amperogram.* COTON and his co-workers [11] performed the evaluation of the amperogram by extrapolating on the abscissa. According to their opinion the end-point coincedes with point „A". (See figure No. 1.) In our view, this only stands in that case, in which tg α of the sample's amperogram coincedes with the blank one, *i. e.* in the case of the dead-stop titration, and with some approximation in the case of amylose titration. If this is not the case — and in amperometric titration of starch this is not the case, as adsorption occurs too — the horizontal section of the amperogram should be taken for the abscissa. Consequently, the end-point coincedes — in our view — with the point „B" from which the value of „C" has to be substracted, as such an amount of iodine solutions in free state, *i. e.* in excess, is present in the end-point, and even sooner. Consequently, the numerical value of the consumption is identical with B—C. In spite of all our efforts, the titration curve of the sample showed a certain fluctuation, this fact, however, only affects the result, if „A" is considered to be the end-point.

From this value expressed in ml, the percentage of bound iodine may be calculated in the following way:

$$J_2\,\% = \frac{\text{consumed ml} \cdot \text{equivalent weight of } J_2}{\text{weight of starch mg}} \cdot 100$$

2. The temperature function of iodine concentration in state of equilibrium

It is well-known that the blue colour of the starch-iodine complex disappears on heating. It may be concluded that with rising temperature the quantity of bound iodine decreases, too. In order to test this assertion, aliquot parts of standard starch solution has been amperometrically titrated at different temperatures. Determinations at temperatures above 50 C° have not been performed, first, because titration must be carried out in an acid medium in which hydrolysis already attains at such temperature a considerable intensity, and, on the other hand, because the kinetic current caused by the equilibrium

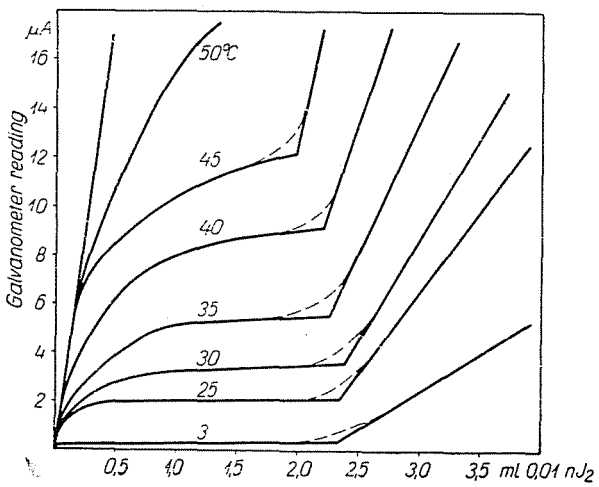

Fig. 3. Configuration of the amperograms in the function of temperature

iodine concentration in the sorptive section increases so rapidly, that the amperogram cannot be reliably evaluated. (See figure No. 3.)

Investigating the temperature function of J_2 sorption of amylose, it was striking that performing titrations at different temperatures, the ordinate value of the first section of the amperogram, *i. e.* the equilibrium iodine concentration substantially increased, while the value of J_2 sorption didn't still decrease. From this fact the following questions have arisen :

a) Is the presence of free iodine at all sure?

b) What kind of mechanism could explain, that the first section of the amperogram is approximately horizontal (*i. e.* the equilibrium iodine concentration is constant)?

c) How does the equilibrium iodine concentration change in the function of temperature?

In order to elucidate these items, the following experiments have been performed.

A) 49,9 ml of distilled water, 5 ml n HCl and 0,1 ml of 0,01 n J_2 solution were introduced into the titration cell. After the amperometric titration device had been put into action, the microburette was replaced by a thermometer, the relay of the ultrathermostate was shut off, and the stirring motor, as well as, the heating device was put on. Consequently, the temperature increased continuously, while the total iodine concentration remained at a constant level. The same procedure has been repeated with 0,3 and 0,5 ml of 0,01 n J_2 solution, too.

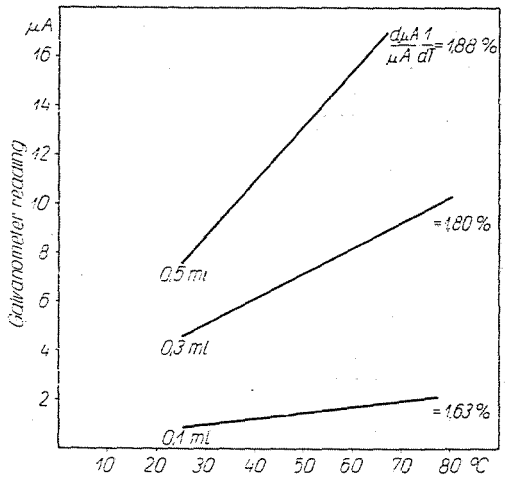

Fig. 4. The blank curve in the function of temperature

Plotting the galvanometer readings as a function of the temperature changes, the interdependences shown on figure No. 4. can be stated. These interdependences represent the temperature function of the blank curve. In the interpretation of these curves it can be stated, that the current of diffusion increases with increasing temperature. In this case, the $\frac{\mathrm{d}\,\mu A}{\mu A} \cdot \frac{1}{\mathrm{d}\,T}$ is around 1,8%. The current inducing effect of a constant iodine concentration actually depends on the temperature.

B) In the device reassembled as for the previous test, to a solution containing 0,0642 g of decomposed wheat-starch in 30 ml, 19 ml of distilled water, 5 ml of n HCl, and eventually 1,00 ml of 0,01 n J_2 solution were added. This corresponds to a saturation of 50%, occurring in the horizontal, *i. e.* in the portion of the amperogram representing amylose. Plotting the interdependence of temperature and the current in the form previously described, the curve shown on figure No. 5. had been obtained. This experiment was also repeated with potato-starch. Our results were very much alike.

The interpretation of the test: The point corresponding to the temperature of 25 C° shows, according to the amperometric blank-curve, the presence of 0,1 ml of 0,01 n J_2 (see the description of the amperometric titration method). Comparing the curve plotted in experiment „B" with the 0,1 ml curve of the experiment „A", it is obvious that the latter much more steeply rises than the first one. Consequently, the concentration of free iodine must have considerably increased.

Knowing the temperature-coefficient of the current of diffusion [12]

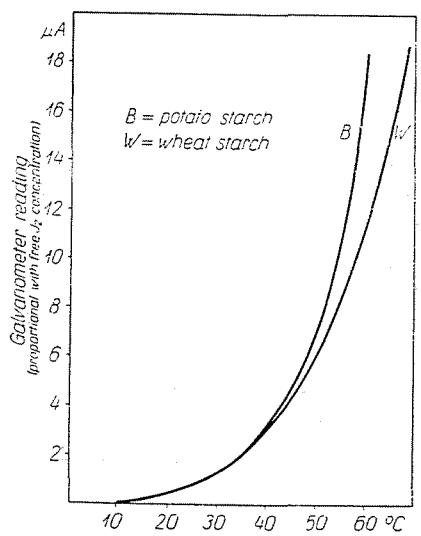

Fig. 5. Change of equilibrium J_2 concentration in the function of temperature
abscisse: temperature in C°
ordinate: galvanometer reading (proportional with free J_2 concentration)

— which is of 1,8% —, it is to be seen, that the former current has a kinetic character, being larger of about 1 magnitude (exactly of 9,8%).

Let us now examine whether the questions can be given an answer to.

Let us first consider the answer to question *a)* — the time being — as positive. As to question *b)*, we illustrate it only with MEYER—BERNFELD's equation, that no equation describing a similar equilibrium can express the nearly horizontal section of the amperogram. According to this equation, equilibrium can be expressed by the following formula [9]:

$$K = \frac{(\text{starch})^n \cdot (J_2)^m}{(J_2 - \text{starch})}$$

where both n and $m > 2$.

The J_2 concentration of the amperogram's horizontal section being at a constant level, there is no exponent that could keep the interdependence between starch and iodine starch on a constant level.

To solve this problem, let us imagine the performance of the following test: let us suppose that we introduce into a solution containing adsorbent „A" enough iodine to saturate the adsorbent. Thus, any further amount of iodine would remain in excess. The state of equilibrium is represented on the coordinata system of figure No. 6, by point No. 1. The abscissa is plotted in units of normality of equilibrium iodine concentration and the ordinate in

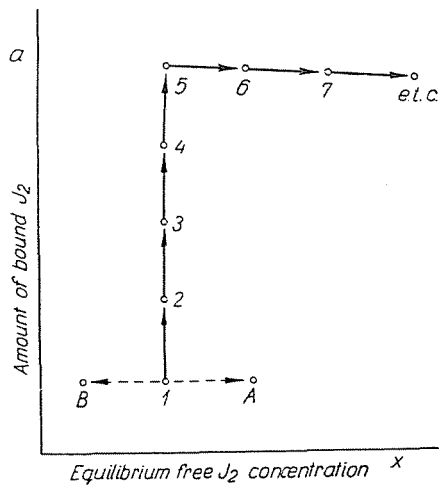

Fig. 6. Imaginary test for elucidation the J_2 sorption of amylose

units of measurement (*e. g.* in g) of bound iodine. (Thus not related, as usually, to 1 g of adsorbent.) Adding more iodine to the system at this state of equilibrium, we arrive at the point marked by „A" (see figure). Adding only adsorbent and no iodine, we reach point „B". Adding both in such proportions that the adsorbent is just saturated with iodine, we reach to point No. 2. While going further with these additions, supplementary points 3, 4, 5, etc. can be reached. Let us now suppose that reaching point No. 5 our supply of adsorbent is completely exhausted so that further iodine can be only added. This way, we arrive to points 6, 7, etc.

Though this imaginative test seems rather abstract on first sight, it helps to give us a good pattern of the horizontal section of the amperogram. As it has been pointed out by RUNDLE [7] and experimentally checked by ourselves, the saturation of amylose helices is *not* a simultaneous process. If the saturation of one helix has begun, the saturation of a next doesn't begin until the saturation of the first one is completed. Thus, it has nothing to do with equilibrium. Actually, the process runs as follows: continuously adding to

the amylose containing solution, iodine somewhere, such a concentration is reached, at which the first helix is completely saturated. The other helices are not concerned with the equilibrium, just as if they weren't present at all. (Explanation will be found when discussing the mechanism of forming helices.) We emphasize, this is proved by experimental facts! Surpassing the equilibrium iodine concentration mentioned above, the next amylose helix comes into the foreground (just as if it would have been introduced into the system), together with iodine, and adsorbs iodine in exceeding equilibrium. This goes on until all the same size amylose molecules are saturated with iodine. This corresponds to the horizontal section of the amperogram. When the large helices are saturated, and the saturation of smaller ones begins, the horizontal section starts to rise „stepwise", the equilibrium iodine concentration being higher when they are saturated. After complete saturation the free iodine concentration should increase at the rate in which iodine is added, if there would not interfere a further — though smaller — possibility of adsorption by iodine-amylose, mainly however by amylopectin. Thus, question *b)* can be explained, and even question *a)* could be proved.

The explanation of question *c)* now becomes obvious: with increasing temperature, free iodine concentration keeping equilibrium at the same level of saturation, increases. The mechanism of this will become perfectly evident when discussing the structure of amylose helices. Calculating the values $\frac{d\mu A}{\mu A} \cdot \frac{1}{d\Gamma}$ from curve μA against C°, when — apart from the last section in which the quantity of iodine loss caused by elapsing becomes considerable — a coefficient of 9,8% is obtained, doubtlessly caused by a current of kinetic character [12]. In this system, kinetic current can be exclusively produced by the increase of equilibrium concentration of free iodine. So the presence of free iodine is incontestably proved.

Plotting the interrelation of $\log \mu n$ against $1/T$ a straight line has been obtained. This straight line may be expressed by the following equation:

$$\log \mu n = -m \cdot 1/T + A,$$

respectively,

$$\mu n = e^{-m\frac{1}{T}} + A$$

respectively,

$$\mu n = e^{-1{,}63 \cdot \frac{10^3}{T} + 5{,}85}.$$

By means of this equation, the equilibrium iodine concentration can be figured out for any temperature, for a given type of starch.

The complex forming reaction heat can be directly calculated from the μn—C° interdependence with CLAUSIUS—CLAPEYRON's equation.

$$\ln \frac{P_1}{P_2} = \frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

P_1 and P_2 should be substituted with the corresponding equilibrium concentration values.

The values of reaction heat calculated in this way are the following (27). Between 30 and 35 C° :

$$\ln \frac{18{,}8}{11{,}6} = \frac{\Delta H}{1{,}987}\left(\frac{1}{303} - \frac{1}{308}\right)$$

$\Delta H = 16{,}9$ Kcal/mol.

Between 35 and 40 C° :

$$\ln \frac{30{,}4}{18{,}8} = \frac{\Delta H}{1{,}987}\left(\frac{1}{308} - \frac{1}{313}\right)$$

$\Delta H = 16{,}9$ Kcal/mol.

A more reliable value has been obtained from the $\mathrm{tg}\,\alpha$ of the whole straight line, as in this case the error of individual measuring points are compensated.

$$-\frac{\Delta H}{4{,}576} = \mathrm{tg}\,\alpha = 3{,}76$$

$\Delta H = -17{,}2$ Kcal/mol.

The values thus obtained check very well with the results of direct measurements known from literature : 11,2 Kcal/mol according to GILBERT and MARRIOT [13], and 19,6 Kcal/mol according to DUBE [14].

3. The effect of hydrolysis on the equilibrium concentration of iodine

It is well known that with the decrease of the length of the chain free equilibrium concentration increases. In order to thoroughly investigate this fact, the following experiments have been performed.

0,6400 g of potato-starch after decomposition has been completed to 740 ml in a 1000 ml flask provided with a reflux cooler, a thermometer, a sampling hole and KPG mixer. The flask was heated to 60 C° and 10 ml 10% HCl were added. Keeping the solution exactly at 60 C°, from time to time samples were taken. The samples were immediately cooled and amperometrically titrated. The amperograms are shown on figure No. 7. Having consumed about half of the total quantity to be used, if 1,00 ml are supposed to be added, plotting

the μA values in the function of the time of the hydrolysis the results are shown on figure No. 8.

Interpretation of the test: During the hydrolysis, lengths of the chains at first quickly differentiate. Consequently, the curve starting horizontally always

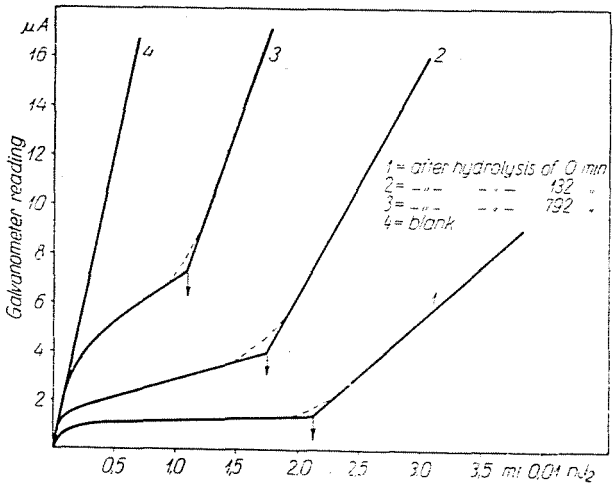

Fig. 7. Effect of hydrolysis on the configuration of the amperogram

becomes steeper. Simultaneously more and more helices are reduced to members less than 35, which is the lower limit of the blue colouration [13]. Thus, the absolute length of the horizontal section, *i. e.* the consumption is constantly decreasing.

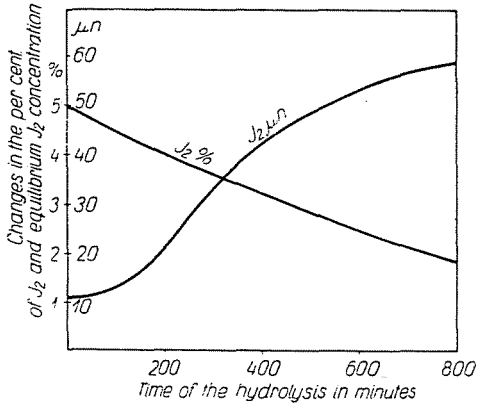

Fig. 8. Changes in the amount of J_2 that may be absorbed by amylose and the free equilibrium concentration

By means of these methods one can conclude as to the degree of polymerization of starch hydrolysates, dextrins and even as to the dispersion of decomposition products.

4. The influence of alcohol on the J_2 adsorption of starch

Alcohol substantially reduces the amount of iodine that can be bound by starch. Exceeding a concentration for each type of alcohol, which is characteristic, the blue complex loses its colour.

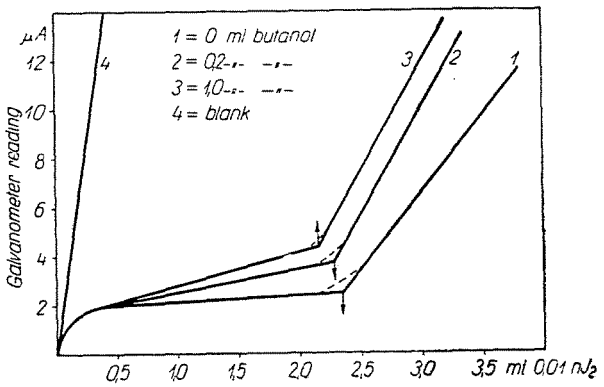

Fig. 9. Effect of alcohol on the amount of J_2 that may be bound by starch

In order to explain this phenomenon, the following experiment has been performed : starch solutions have been titrated in the presence of different amounts of alcohol and the amperograms thus produced were confronted with an amperogram taken without alcohol. These amperograms are shown on figure No. 9.

Interpretation of the test : On one hand, it can be stated, that J_2 liable to be bound is decreasing and, on the other hand, that the amount of free iodine in equilibrium with the bound iodine is increasing. The fact that the total amount of iodine liable to be bound decreases, gives evidence that alcohol occupies a part of the points usually filled by iodine. As it is an incontested fact, that alcohol molecules intrude into helices during the alcoholic precipitation of amylose, the situation here is much the same. It is however, striking, that the original amperogram deforms at the effect of alcohol, just the same as during the hydrolysis. This means that the section that has been originally approximately horizontal, not only shortens, but also rises. It is well-known that a higher equilibrium iodine concentration corresponds to a lower level of polymerization. Alcohol can by no means promote hydrolysis. Why is the chain notwithstanding this

shorter? — It is known from the experiments of SOZABURO ONO and his co-workers [15] that the length of the chain does not in such cases mean the degree of polymerization of amylose, but the degree of polymerization of the poly-iodine chain developing within the amylose helix. Only the upper limit of the length of the poly-iodine chain is determined by the length of the amylose chain. As a matter of fact, in a considerable length of amylose helices a plurality of shorter poly-iodine chains might be contained, if the single poly-iodine chains are interrupted by iodide ions. In this respect, according to the tests of said authors, the effect of alcohols is much the same as the one's iodide ions.

From the curves it can also be seen that while alcohol molecules have not filled up but a small percentage of the helices, free iodine concentration has already substantially increased, *i. e.* the length of the poly-iodine chain has strongly been reduced. Hence, it can be concluded that the alcohol molecules intrude till the middle of the helices, and do not get fixed on the ends of them. The length of a poly-iodine chain of a long amylose helix can be reduced to half of its original size in two ways : the alcohol molecules start to fill up the helix from one end and are followed by other alcohol molecules as long as the helix becomes filled till its middle. In this case, the length of the originally horizontal section is liable to strongly decrease. As such does not happen however, only the second mechanism can be taken into consideration, according to which a single alcohol molecule is sufficient to divide the chain into approximately equal portions, inserting itself into the middle of the helix. In this way, the equilibrium of free iodine concentration might substantially increase with a small decrease of the ability of binding iodine.

5. Viscosimetric investigation of the mechanism of iodine-sorption

The purpose of these tests has been to establish how the viscosity, *i. e.* how the structure of a molecule changes during the iodine-sorption of an amylose solution.

A freshly prepared amylose solution has been filtrated through glass cotton. In an amount of 3,00 ml of solution the amount of iodine which can be taken up by amylose has been amperometrically established. This value has been found to be 1,68 mg. The remaining portion of the solution has been used for viscosimetric examinations. Into 10 testing tubes $10 \times 3{,}00$ ml of amylose solution was introduced, and 0,01 n J_2 solution added in increasing amounts. Each tube has been completed with distilled water up to a level of 5,5 ml. From each tube 5 ml was withdrawn and viscosity at 25 C° was measured using a capillary viscosimeter. The amylose content of the various samples were therefore constant, and only the iodine concentration varied. The results are shown on drawing No. 10.

The abscissa of the break-point is 100% (see figure) which therefore exactly corresponds to the 1,68 mg of iodine amperometrically stated. This method can be applied to state the iodine sorption of amylose, too. 12 hours after the experiment the viscosity of the solutions on this side of the break-point was not changed, while the solutions beyond the break had become rigid, tixotropical gels.

Interpretation of the experiment: During the iodine sorption of amylose no change of viscosity of the solution can be observed. Hence, the form of the

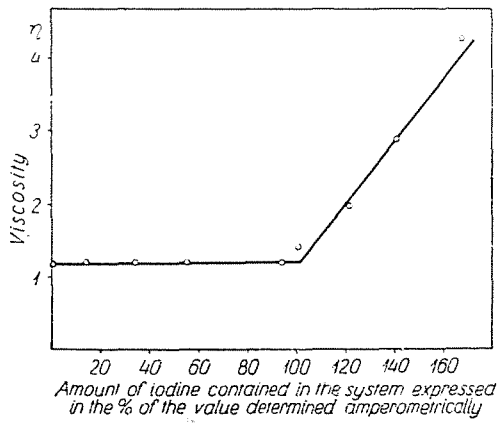

Fig. 10. Changes of the viscosity of iodine-starch solution in the function of J_2-concentration

molecules does not substantially change, the iodine is thus taken up by the inferior of the helical amylose molecules. Once the interior of the amylose helices is filled up, the external parts form bridges between the single amylose helices, and the viscosity of the solution increases with rapidly increasing iodine concentration.

We shall revert to a more detailed interpretation on the occasion of the examination of the structure of dissolved amylose molecules.

6. The sorption isotherm of starch

The iodine-sorption of starch should be divided into two distinct parts. First, Ss. W. NEDSWEZKI [16] pointed, on the basis of viscosimetric tests, to the fact that iodine sorption occurs in two distinct steps. In view of the development of starch chemistry of his epoch, he was however not able to elucidate the mechanism of such a phenomenon. Notwithstanding, for a considerable time a unique starch-iodine complex had been spoken of, and various empirical formulae had been given as to the alleged composition of it [9].

In order to clear up this question, the sorption isotherm of various starch samples has been established. According to the nature of the isotherm this has been done in two sections : the vertically rising first section has been established by means of amperometric titration, and the second section titrating the free iodine, after separating the formed complex on reaching the equilibrium state of the adsorption with thiosulphate.

a) Plotting of the first section : from the samples to be tested, solutions of known starch content have been prepared, and portions of it have been amperometrically titrated. From the amperograms thus prepared the equilibrium concentration has been figured out with known methods be means of the

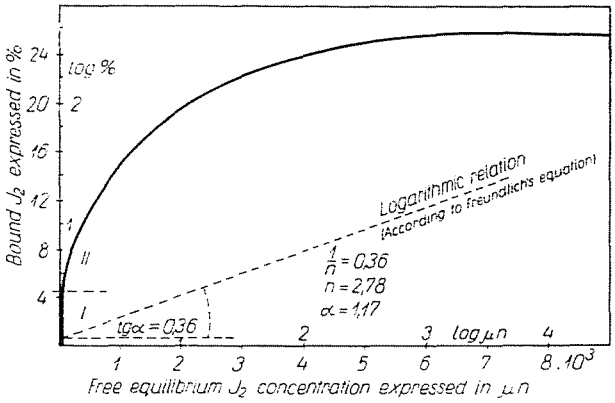

Fig. 11. Total isotherm

blank curve. Substracting the value of equilibrium concentration from the concentration figured from the total of added iodine and converted into weight per cent (related to the amount of starch), the bound iodine has been expressed in per cents.

b) The plotting of the second section : 20 ml of the remaining portion of the above standard solution have been withdrawn by pipette, hydrochloric acid and 0,01 n J_2 solution has been added in increasing amounts, and finally as much distilled water as to have in each case 50 ml in each centrifugal tubes provided with ground stoppers. The purpose of hydrochloric acid is to hasten the precipitation of iodine-starch. Thermostating at a given temperature, quickly centrifuging and thermostating again, 25 ml of the clear solution above the precipitated iodine-starch are pipetted out, and free J_2 in equilibrium contained in it is titrated with a freshly prepared 0,005 n thiosulphate solution.

The results obtained in such a way are represented in the $a-x$ diagram shown on figure No. 11. Representing the same results on a log a — log x diagram, the curve can be straightened out to a line corresponding to Freundlich's isotherm, the characteristics of which can be seen from the figure.

Interpretation of the experiment: The amperometrically plotted first section, respectively, the vertically rising portion of it corresponds to that very state in which iodine is taken up by the interior of the helices. The height of the vertical section numerically gives the value of the iodine sorption of amylose, the evaluation of which might be directly made from the amperogram.

The second section characterized by Freundlichs' equation refers to the iodine-sorption of the exterior of the helices and of the amylopectin molecule.

It is striking that the second section joins the first one just at the break-point, where the isotherm figured from the amperogram starts, so as to be more flat and linear. The reason for this fact has to be sought in the vivid and energetic stirring while titrating. The very fact that beyond the vertically rising section (which corresponds on the amperogram to the horizontal one) the free iodine concentration rises more quickly with the rising iodine excess than in the state of rest, brings us to the conclusion, that no substantial equilibrium can be attained here. The fact that this section is linear is of no importance; first, because exceeding the break-point with about 0,8 ml, linearity is lost and the curve becomes more and more steep, coing near to the angle of the blank curve, and, on the other hand, because the initial section of an adsorption isotherm is nearly always straight.

*

References will be published in our next communication.

Summary

Present paper, representing the second part of our article, deals with experiments carried out to clear up the mechanism of starch-iodine reaction.

The summarizing interpretation of these experiments will be published in the third part of our article in the following issue.

Prof. Dr. J. HOLLÓ,
J. SZEJTLI
Budapest, XI., Gellért tér 4. Hungary