A STUDY OF THE ORDERED ADSORPTION OF METAL IONS ON THE SURFACE OF CELLULOSE MICROFIBRILS

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SUMMARY

Following observations already made on copper impregnated wood, a detailed study is made of the adsorption by a variety of celluloses of a number of cations from salt solutions. The uptake/concentration curve follows a LANGMUIR adsorption isotherm so that a surface phenomenon is certainly involved. The uptake is accompanied by a fall in pH of the solution, so that cations appear to be exchanged for hydrogen ions, and is initially rapid.

The resultant metal–cellulose complex gives characteristic electron diffraction diagrams of which two types only have been found (together with "hybrids" between them). These diagrams are identically the same whatever the source of the cellulose and for any metallic cation. They can be interpreted on the basis of two-dimensional arrays of copper ions whose parameters are: I: $p = 6.15$ Å, $q = 7.05$ Å, $\Theta = 90°$; II: $p = 7.32$ Å, $q = 5.68$ Å, $\Theta = 87°$–$90°$ (variable). It is concluded that the copper is adsorbed as a monolayer on the outer surface of the microfibrils and this is taken to imply order in the disposition of the chain-molecules at this surface. The parameters bear no relation to the accepted parameters of the (three-dimensional) unit cell of cellulose and suggest further, therefore, that the order at the surface is in some way different from that inside the microfibrils.

The impact of the above findings on methods of determining the –COOH content of cellulose is briefly discussed.

INTRODUCTION

When samples of wood or wood cellulose treated with aqueous salt solutions are examined in the electron microscope by means of limited area electron diffraction, characteristic diagrams are observed. These have been interpreted as evidence for the existence in these samples of a metal–cellulose complex[1]. The diffraction diagrams were found to be associated with, and oriented with respect to, the corresponding cellulose microfibrils and it was evident that a further study of this complex would be likely to yield new information on the structure of the microfibrils[2]. It was decided to extend the investigation to other types of cellulose, and to combine quantitative

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chemical methods with a crystallographic analysis of the electron diffraction diagrams. The present paper describes the results of this extension.

METHODS AND RESULTS

Preliminary study

α celluloses were chemically isolated from the following sources:

Valonia ventricosa vesicles
Cotton (*Gossypium hirsutum*) hairs
Beech (*Fagus* sp.) wood
Douglas Fir (*Pseudotsuga taxifolia*) wood
Rhodymenia palmata fronds,

using the fractionation technique of JERMYN AND ISHERWOOD[3] as modified by CRONSHAW, MYERS AND PRESTON[4]. Each of the celluloses was analysed by hydrolysis and paper chromatographic identification of the resultant sugars, and their constitution is presented in Table I. The isolated celluloses were treated with a range of dilute aqueous salt solutions and after washing in distilled water were blended, dried, shadowed with aluminium and examined in the electron microscope. Electron diffraction patterns implying well oriented complexes were obtained from such diverse specimens as cellulose from *Rhodymenia palmata* containing 50% xylose, and from cotton containing only 1.5% xylose, treated with for example gold, silver or copper salts. Interplanar spacings corresponding to the arcs of the diffraction diagrams were calculated using as calibration the aluminium reflections superimposed on each individual diagram.

TABLE I

THE SUGAR CONTENT (BY WEIGHT) OF THE HYDROLYSATE OF VARIOUS α CELLULOSES

Source of α cellulose	*Glucose* %	*Xylose* %	*Mannose* %
Rhodymenia	50.0	50.0	—
Beech	85.0	15.0	—
Cotton	98.5	1.5	—
Valonia	100.0	—	—
Douglas Fir	94.5	—	5.5

In the case of X-ray diffraction diagrams interplanar spacings can be calculated using the well known Bragg equation

$$n\lambda = 2d \sin \theta,$$

where λ is the wavelength of the X-rays and θ is the glancing angle which can be calculated from $r/D = \tan 2\theta$, r being the radial distance of the diffraction arc to the centre of the diagram and D the specimen-film distance. In the case of electron diffraction, however, since the wavelength of the electron beam (λ) is small compared with the interplanar spacing (d), $\sin \theta$ is approximately equal to θ; therefore we may write:

$$d = \frac{n\lambda D}{r} \qquad (1)$$

In the electron microscope this simple geometrical relationship between r and D

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no longer holds, since there is a projection lens between the specimen and film so that the radial distance between the arcs on the diagram can be varied by means of the controls. Thus equation (1) becomes

$$d = \frac{n\lambda F}{r},$$

where F is the focal length of the projection lens. Thus for a given setting of the controls

$$d = K/r$$

where K is a constant. Since it is impracticable always to work at the same setting, and since the high-potential supply to the electron gun is subject to small fluctuations causing small variations in the wavelength (λ) of the electron beam, the unknown interplanar spacings of the diffraction arcs were calculated from the known interplanar spacings of the superimposed aluminium diagram. For a given diagram

$$d_x = \frac{d_{Al}\, r_{Al}}{r_x},$$

where d_{Al} is the interplanar spacing of the inner ring of the aluminium ring pattern (2.33 Å), r_{Al} is the radius of the inner ring of the aluminium pattern, d_x is the interplanar spacing of an arc of the oriented pattern, and r_x is the radial distance of the diffraction arc of the oriented pattern from the centre of the diagram.

All of the patterns obtained may be identified with one or other of two types which are superficially similar but differ in their individual spacings (Fig. 1a and 1b), or with hybrids between the two (Fig. 1c). Although no patterns have so far been recorded for *Valonia* cellulose pretreated with metal salts, there is chemical evidence for complexing (to be discussed in the following section) and the lack of diffraction diagrams may be due to difficulties encountered in specimen preparation.

The evidence suggests, therefore, that the type of complexing under investigation is of general occurrence throughout a wide range of cellulosic material.

Chemical estimations

If this uptake from salts is of the cation only, then it could be expected that the immersion of cellulose in a dilute salt solution would be accompanied by a fall in the pH of the solution. This was tested experimentally by the addition of a small sample of cellulose to a dilute copper sulphate solution, when a considerable fall in pH was observed. A similar fall in pH, as judged by both the use of indicators and pH-meter, was observed using other salt solutions such as potassium chloride and silver nitrate.

After treatment with copper salts, cellulose retains sufficient copper to give a green colouration which remains even after prolonged washing with distilled water, and it was decided to use this metal to obtain quantitative data on the course of the uptake. Such a determination could be made either by measurement of the decrease in concentration of the experimental solution or by release and subsequent estimation of the "bound" copper in the cellulose. The latter method was chosen as being the more accurate, particularly for the measurement of a relatively small uptake from a concentrated solution. Although the complex is stable in distilled water and in dilute alkali, it is instantly decomposed by dilute acid, and from this was developed a method of analysis. The experimental procedure was as follows:

0.20 g of cellulose was added to 25 ml of the solution of a copper salt of known

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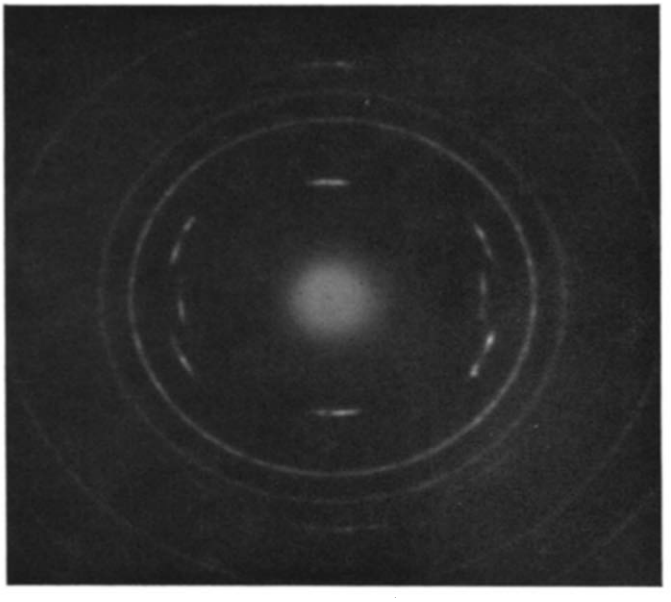

Fig. 1a.

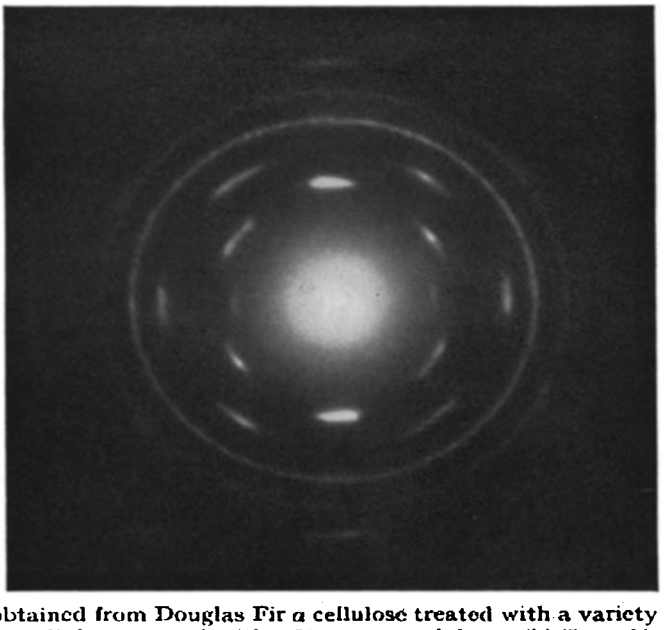

Fig. 1b.

Fig. 1. Electron diffraction diagrams obtained from Douglas Fir α cellulose treated with a variety of metallic-salt solutions. (a) Type I. α cellulose treated with 4% copper sulphate. (b) Type II. α cellulose treated with 4% copper sulphate. (c) Hybrid. α cellulose treated with 4% cobalt sulphate.

concentration, in a stoppered flask, and agitated for 15 min (a period adopted for reasons which will be given below). The cellulose was then recovered by filtration in a sintered glass funnel and washed in several changes of glass-distilled water. Tests showed that further prolonged washing over a period of 4 h did not remove any of the "bound" copper. After removing all traces of the copper-salt solution, the "bound"

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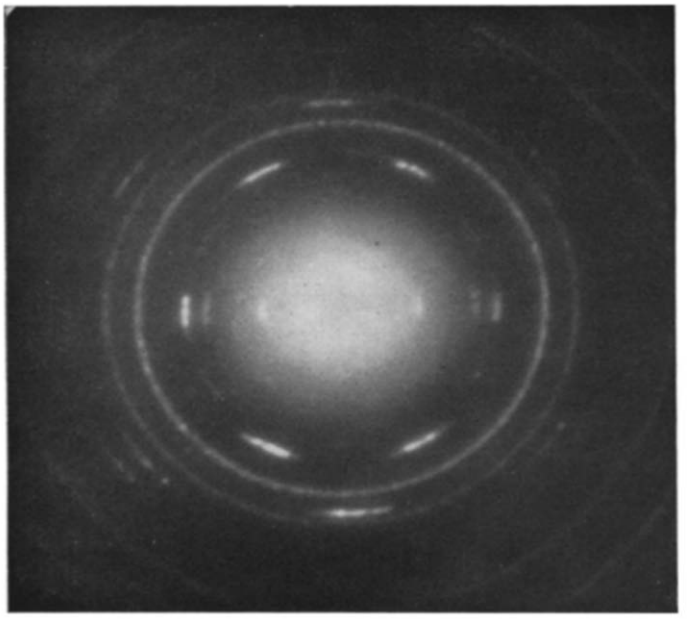

Fig. 1c.

copper was released by adding 15 ml of 10% (by volume) acetic acid and the cellulose was removed by filtration. The last traces of acid were washed into the flask with a further 20 ml of glass-distilled water. The filtrate, containing the copper released from the cellulose, was transferred to an Erlenmeyer flask and 15 ml of 6% potassium iodide solution was added. The solution was titrated against standard sodium thiosulphate using a 2% starch solution as indicator. This experimental procedure was found to give consistent results.

Copper uptake by cellulose was first examined as a function of time, using Beech α cellulose with a 0.03 N solution of copper acetate, and the results are illustrated graphically in Fig. 2. The uptake was extremely rapid, reaching an approximate maximum in less than 10 min. It was in fact found that the weight of copper complexed per 100 g of cellulose increased by only 0.03% after treatment for a further 24 h beyond the period represented in the graph. In all subsequent

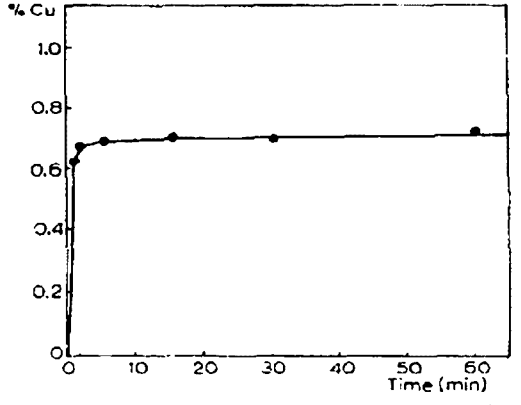

Fig. 2. The uptake of copper from 0.03 N copper acetate solutions by Beech α cellulose.

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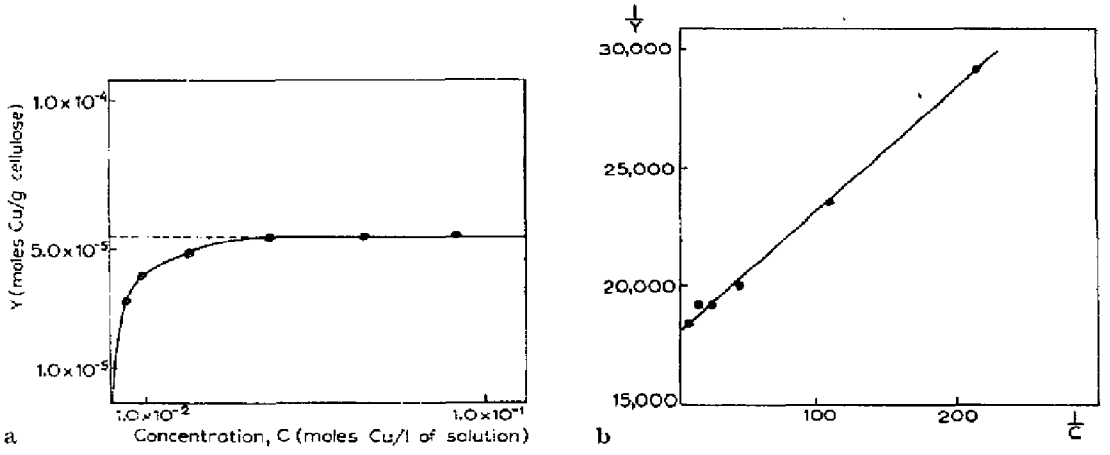

Figs. 3a and 3b. The uptake of copper from copper sulphate solutions by Beech *a* cellulose.

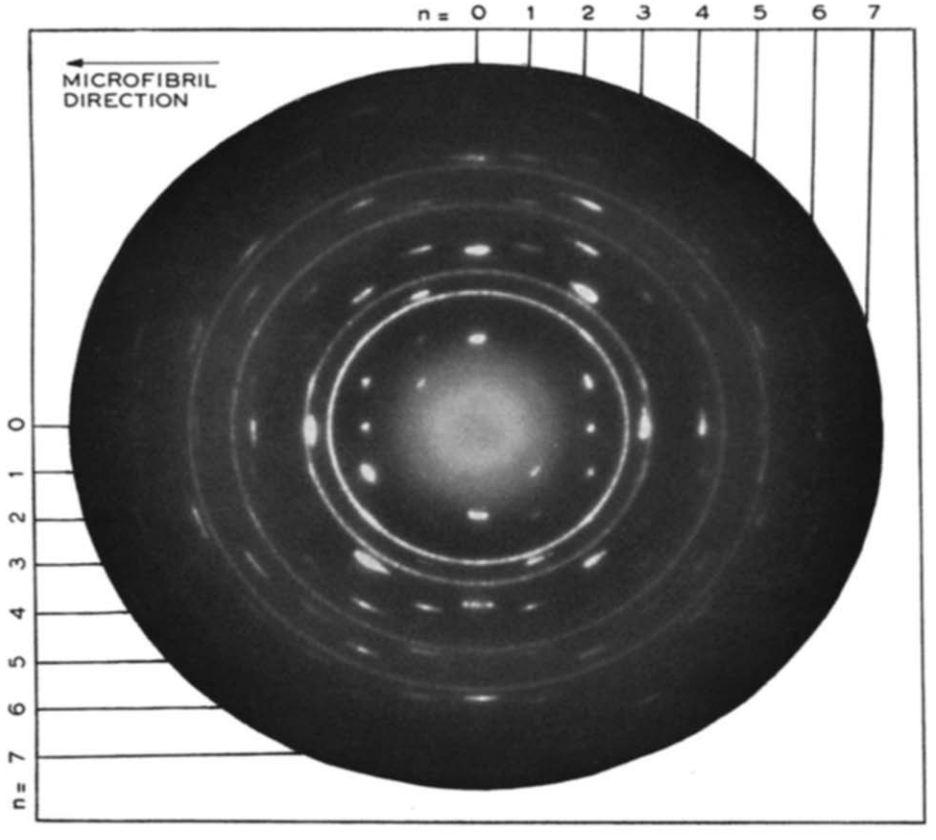

Fig. 4. An electron diffraction diagram obtained from microfibrils of *Pseudotsuga* (Douglas Fir) *a* cellulose treated with an aqueous 1 % ferric sulphate solution. The two sets of intersecting layer lines are indicated diagrammatically.

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determinations, therefore, the celluiose was treated with the copper salt solution for 15 min only.

Copper uptake was then examined as a function of the concentration of the copper-salt solution. Beech α cellulose was again used with a range of both copper acetate and copper sulphate solutions. The results are presented graphically for copper sulphate solutions in Fig. 3a, the uptake being expressed as moles of copper per gram of cellulose and the concentration of the test solution as moles of copper per l. From this graph, the reciprocal of the uptake was plotted against the reciprocal of the concentration and a straight line graph was obtained as shown in Fig. 3b. This clearly indicates that the uptake of copper is an adsorption phenomenon in accordance with the isotherm of LANGMUIR. The maximum uptake of copper was significantly higher in the copper acetate solution.

Finally each of the whole range of isolated α celluloses was in turn treated for 15 min in a 0.01075 *N* copper acetate solution, and the uptake recorded in each case. The results are given in Table II.

TABLE II

THE COPPER UPTAKE, FROM 0.1075 *N* COPPER ACETATE SOLUTION, OF A NUMBER OF ISOLATED CELLULOSES

Source of α cellulose	*g Cu per 100 g cellulose*
Rhodymenia	0.845
Beech	0.780
Cotton	0.004
Valonia	0.200
Douglas Fir	0.970

Interpretation of the diffraction diagram

The adsorption curves thus obtained suggest that the complexing must be largely limited to adsorption at the outer surfaces of the cellulose microfibrils. The arrangement of these adsorbed atoms must naturally be dependent upon the configuration of the surface layer of the cellulose microfibrils. An adsorbed layer of metal atoms arranged on the surface of a microfibril in a regular two dimensional array could act as a diffraction grating to a beam of electrons, and could therefore be responsible for the electron diffraction diagrams obtained. It has proved possible fully to interpret all these diagrams on the basis of this concept.

A particularly good example of a Type I pattern is illustrated in Fig. 4. The pattern may be regarded as consisting of two sets of layer-lines, reflexions occurring at their intersections, as required by such a two-dimensional lattice. The parameters p (along the microfibril length) and q are given by the spacings corresponding to the first-order reflexions along the meridian and equator respectively, the angle Ø between them being 90°. From the dimensions of this unit cell theoretical values may be calculated for the position of the other reflexions. This may be carried out with regard both to the interplanar spacing (d) and to the angle (θ) between the meridian and the line joining the arc to the centre of the diagram. The results of such an analysis are tabulated in Table III, and it can be seen that the calculated values are in good agreement with the measured values obtained from the diagram.

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The unit cells for the two types of pattern obtained may be defined provisionally as follows:

Type I [illegible]

Type II [illegible]

TABLE III

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

In addition, in the Type II diagram, reflexions are occasionally noted along the equator corresponding to a *c* parameter of [illegible] Å. It should be noted that each diagram is given by an aggregation of microfibrils, so that the length of the arcs in the diagram is a measure of the dispersion of the microfibrils about a common direction. From specimens containing randomly arranged microfibrils, *e.g.* *Rhodymenia* cellulose, diagrams showing a single orientation were seldom observed. In the case of the oriented diagrams, "hybrids" were occasionally noted consisting of various combinations of patterns of Types I and II. All of the celluloses so far examined, irrespective of their source and pre-treatment, gave the same types of patterns with arcs corresponding to the same spacings. With regard to pre-treatment, samples of cellulose of *Pseudotsuga* (Douglas Fir) when examined in this way gave the same types of patterns before and after mercerisation.

DISCUSSION

It has been demonstrated that the oriented electron diffraction diagrams, first observed in an examination of timber treated with a water-soluble preservative, are of general occurrence in a wide range of cellulosic materials treated with aqueous salt solutions. The patterns were always either of one of two types or of "hybrids" between them, and thus appear to be independent of the chemical composition of the cellulose and of the particular metal atoms adsorbed.

The drop in pH recorded in aqueous test solutions of various salts on the addition of a sample of cellulose suggests that complexing involves the replacement of hydrogen by metal atoms. This view is reinforced by the observation that, under acid conditions, the reverse of the above process occurs resulting in the release of the complexed metal atoms. It appears probable, therefore, that complexing is governed by the Law of

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Mass Action and is dependent upon the pH of the test solution. This would account for the higher copper uptake in copper acetate solutions than in copper sulphate solutions, the former having a significantly higher pH in aqueous solution. It is not possible at this stage to go further into the precise mechanism of complexing, but it is hoped that future work, including infra-red spectrographic analysis and an examination of the magnetic resonance properties of complexed cellulose, will reveal the precise nature both of the site and of the type of bonding between the metal atoms and the substrate.

The rapid uptake of copper from an aqueous copper acetate solution (Fig. 2) and the typical LANGMUIR adsorption isotherms obtained in uptake-concentration experiments (Fig. 3b) indicate that complexing is an adsorption phenomenon and therefore limited to surfaces. In this connection some confusion may arise, since it is well known that cellulose microfibrils, in addition to their external surface, possess internal surfaces in those amorphous or para-crystalline regions where the cellulose molecules are largely arranged in a parallel manner but are not evenly spaced[17]. Within these regions water can penetrate and adsorption reactions might conceivably take place. The effective internal surface is considerably increased if the cellulose is treated with a swelling agent, such as sodium hydroxide solution, which reduces the lattice order of the crystalline cellulose. NORMANN[5] first observed the addition compound, sodium cupricellulose, which forms when cellulose is treated with sodium hydroxide and copper hydroxide. This copper–cellulose–alkali complex has since been called the NORMANN-compound and it has been found on analysis to contain one atom of copper per glucose residue. It has further been shown that the X-ray diffraction diagram has changed after complexing[6], the characteristic interplanar spacings for cellulose being considerably modified.

The mechanism of this reaction has recently been the subject of an investigation[7] and it has been shown that there is a gradual uptake of copper, from copper alkali solutions, over a period of 8 h. ROSCHIER has also demonstrated that under these conditions the uptake of copper conforms to LANGMUIR's adsorption isotherm. The results presented by ROSCHIER do not include any determinations of copper uptake during the first 2 h, but it seems certain that a rapid initial uptake takes place, as demonstrated in this investigation, followed by a gradual uptake as the swelling of the cellulose by the sodium hydroxide increases the effective surface area.

The extremely rapid uptake obtained using aqueous salt solutions, quickly reaching a maximum of the order of 1% with no significant further increase, together with the observations that (a) the X-ray diffraction diagram of our complexed cellulose remains unchanged and (b) the electron diffraction diagram can be interpreted in terms of a two-dimensional array, leads us to suppose that the complexing in this case is limited to the *outer* surface of the cellulose microfibrils.

This demonstration of the adsorption of metal ions onto cellulose microfibrils has direct bearing on the validity of current methods of determination of carboxyl groups in cellulose. It has been noted in the past that this determination is complicated by the number of techniques available and the general disagreement on results[8]. The principal methods in use at the present time include uranyl cation adsorption[9], methylene blue adsorption[10], the silver *o*-nitrophenolate method[11], the calcium acetate method[12], and the sodium chloride method[13]. The most recent review of the literature is that of ANT-WUORINEN[14], who has proposed a technique for

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carboxyl group estimation based on the pH drop induced when a sample of cellulose is added to a sodium chloride solution. These methods are all based on the cation-exchange action of the carboxyl groups of cellulose and may be concerned with the phenomenon described in this investigation. They may be criticised in that they are pH-dependent and therefore yield different values of the number of carboxyl groups if the pH of the experimental solution is varied, and also in that the result varies with the concentration and type of salt solution used. Although to date evidence concerning the precise nature of the complexing described here is inconclusive, there are indications that simple salt formation involving carboxyl groups located at the surface of the microfibrils is unlikely. For example, it is inconceivable that the outer surface of the cellulose microfibrils contains localised high density regions of acidic groups in such an array as demanded by the two-dimensional lattice which alone seems to explain the diffraction diagram presented here. More probable sites for adsorption are the hydroxyl groups, and in this respect it is relevant to note the views of VAN DER WYK AND STUDER[15], who contended that the acidic properties of cellulose are due to the hydroxyl groups.

From the interplanar spacings of these unit cells derivable from the electron diffraction diagrams the maximum % copper by weight in a given cellulose may be calculated assuming the total outer surface of all of the microfibrils to be fully complexed.

The volume occupied by 100 g cellulose is 100/1.59 cm^3 (assuming density = 1.59 g/cm^3) or $6.3 \cdot 10^{25} Å^3$. The total length of microfibrils (l) in 100 g *Valonia* cellulose is therefore given by

$$6.3 \cdot 10^{25} = \pi \, 10{,}000 \, l$$

assuming the microfibrils to be circular cylinders of diameter 200 Å.

$$\therefore \qquad l = 2 \cdot 10^{21} \text{ Å}$$

The total surface area (a) of microfibrils in 100 g *Valonia* cellulose is therefore

$$a = 2 \times \pi \cdot 100 \cdot 2.0 \cdot 10^{21}$$
$$= 12.6 \cdot 10^{23} Å^2$$

Now, assuming the spacings of Type I unit cell (*i.e.* a = 6.15 Å, b = 7.05 Å), the number of Cu atoms per 10,000 $Å^2$ of surface is:

$$\frac{100}{6.15} \cdot \frac{100}{7.05} = 230$$

The maximum number of Cu atoms which can be adsorbed in this way by 100 g *Valonia* cellulose is therefore

$$12.6 \cdot 10^{23} \cdot 0.023 = 2.9 \cdot 10^{22}$$

This amounts to a Cu uptake of 3.05% (by weight).

Similarly with *Rhodymenia* cellulose, in which the microfibrils are narrower (diameter 150 Å) the maximum uptake is 4.4%. These may be compared with the results obtained experimentally, presented in Table II. It appears that in the case of cellulose treated with an aqueous copper acetate solution, the surface of the

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cellulose microfibrils is not fully saturated with copper atoms. This is to be expected and the precise amount of copper adsorbed is undoubtedly dependent on the pH of the solution. It can further be seen that the amount adsorbed under a given set of conditions by different celluloses can perhaps be related to the total surface area of microfibrils. This is to be expected from the results of the above calculation in the case of *Valonia* cellulose and *Rhodymenia* cellulose, and has been confirmed experimentally as shown in Table II, the larger *Valonia* cellulose microfibrils having a relatively lower copper uptake than the smaller microfibrils of *Rhodymenia* cellulose. The calculation is based on approximations of both the density and the diameter of the microfibrils in each case but does at least serve to illustrate that the distribution of copper atoms on the surface of the microfibrils arrived at by crystallographic analysis is compatible with the quantitative data obtained in the chemical study of copper uptake.

The arrangement of metal atoms thus envisaged must imply a high degree of order of molecules at the surface of the cellulose microfibrils, and; since identical patterns are obtained from celluloses treated with a variety of metal salts, it must be concluded that the spacings of the unit cell of the complex relate to the outer layer of the cellulose substrate. This conclusion is completely unexpected, for all current theories of microfibril structure postulate an outer layer of para-crystalline cellulose.

The interplanar spacings of the unit cells of the two-dimensional arrangement of metal atoms do not correspond to any of the spacings of the well known three-dimensional unit cell of cellulose after MEYER AND MISCH[15] as determined by X-ray diffraction analysis, but can probably be accounted for by the differing intermolecular forces operating at the surface. This may perhaps indicate that, at the surface, the molecular configuration differs from that of the body of the cellulose microfibril. Such a modified surface layer would not be detectable using normal X-ray or electron diffraction techniques. A study of adsorbed metal atoms on the surfaces of cellulose microfibrils, therefore, constitutes a new method of investigation, a method which we hope may be applicable to other fibrillar substances.

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