X-RAY STUDIES REGARDING THE STRUCTURE AND BEHAVIOR OF NATIVE CELLULOSE MEMBRANES[1]

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[1] Presented at the Symposium on X-ray Studies of Substances of High Molecular Weight, held at the Ninety-eighth Meeting of the American Chemical Society in Boston, Massachusetts, September, 1939, under the auspices of the Divisions of Physical and Inorganic Chemistry, Colloid Chemistry, Organic Chemistry, Paint and Varnish Chemistry, and Rubber Chemistry of the American Chemical Society.

I. INTRODUCTION

X-ray diffraction analysis, as a research tool, has two closely related fields of application. The first is concerned with the form, properties, and three-dimensional arrangement of atoms and molecules within a single crystal; the second is concerned with the form, arrangement, and properties of crystalline aggregates in a polycrystalline material.

Since the x-ray diffraction diagram of a native cellulose fiber consists principally of definite diffraction rings, one is forced to conclude that the major portion of the fiber consists of crystalline cellulose. The first field of x-ray analysis, therefore, as applied to cellulosic materials, is the interpretation of the stereochemistry of the cellulose molecule within the crystal lattice. This structure, which may be referred to as "cellulose structure," has been discussed by Mark (29) in the preceding paper of this symposium.

From the fact that cellulose fibers give continuous diffraction rings (i.e., Debye–Scherrer diagrams), a second important deduction may be made: namely, that the crystallinity of the fiber is discontinuous. In other words, a cellulose fiber is not a single crystal; it is a crystalline aggregate. This is definitely proven by the fact that even a single fiber, when photographed by a micro method (7, 37), gives smooth rings instead of Laue spots. These small crystals of cellulose which build up the cell wall of a fiber will be referred to as "cellulose crystallites," and the material between these crystalline areas as "intercrystalline material." The second field of x-ray analysis, therefore, as applied to cellulosic materials, is the interpretation of the form, arrangement, and properties of the cellulose crystallite and its relation to the intercrystalline material within the plant cell wall. This dual structure built up of crystalline and intercrystalline material, which is discussed in the present paper, will be referred to as "membrane structure."

The x-ray data used in the interpretation of cellulose membrane structure are of two types: (1) certain characteristics of the x-ray diagram of the untreated fiber, and (2) the changes produced in these characteristics by the action of various physical and chemical treatments of the fiber.

II. CHARACTERISTICS OF CELLULOSE DIFFRACTION PATTERNS

X-ray diagrams may be described and differentiated one from the other in terms of the following characteristics: (A) Number of diffraction rings; (B) diameter of each ring; (C) relative intensity of each ring; (D) concentration of rings into arcs,—orientation; (E) width or diffuseness of each ring; and (F) general scattering,—amorphous pattern.

The number (A), diameter (B), and relative intensity (C) of the diffrac-

tion rings appear to be constant for all native cellulose fibers. Since these characteristics are associated with crystalline structure, it may be concluded that the crystalline structure of cellulose is the same for each fiber. The arcing (D) and width (E) of each diffraction ring, and the general scattering (F), however, are not the same for each fiber, and since these characteristics are associated in part with the membrane structure, it may be concluded that this structure varies from fiber to fiber. Any concept of cellulose membrane structure, therefore, must take into account these latter characteristics of the x-ray diagram and their variation from fiber to fiber.

A. Orientation

In most cellulose fibers such as cotton, ramie, and flax, the x-ray diffraction rings are concentrated into arcs to give a fiber pattern. This characteristic is directly related to the orientation or alignment of the cellulose crystallites (b-axes of unit cell) parallel to the fiber axis (48). There is also present in some membranes, such as *Valonia ventricosa* (2, 35, 49, 50), a further selective orienting tendency of the *101* plane parallel to the membrane surface, which causes the 101 line (innermost line in cellulose diagram) to be absent when the x-ray beam is perpendicular to the surface (38, 40).

B. Width of diffraction ring

For a given sample and slit system the x-ray diffraction lines should have a definite width. In most cellulose patterns this line breadth is greater than that theoretically expected. Furthermore, in many of the fibers which show orientation, the diffraction lines arising from planes parallel to the b-axis (equatorial lines) have a greater width than the lines arising from planes perpendicular to the b-axis (meridian lines) (19). The width of the equatorial lines also varies from fiber to fiber. In some of the bast or lignified fibers, such as ramie or wood, the lines are very broad; in cotton they have a medium width, while in *Valonia* they are very sharp (49).

C. Amorphous pattern

The presence of a certain amount of amorphous material in most fibers is indicated by a general fogging in the x-ray diagram. The nature of this fogging varies from fiber to fiber (47). In some fibers it approaches a broad amorphous band similar to that of a homogeneous liquid. In other fibers, such as wood, it takes the form of a disk extending to the central beam, which is typical of a heterogeneous amorphous material. The amount of fogging also varies from fiber to fiber. For example, in

cotton it is very faint, while in some of the woody or lignified tissues it may almost completely mask the crystalline cellulose pattern.

III. EFFECT OF VARIOUS TREATMENTS ON THE X-RAY DIAGRAM

Aside from the characteristics of the diffraction patterns themselves, other important information regarding cellulose membrane structure may also be obtained by observing how these characteristics are affected by various physical and chemical treatments of the membrane.

A. Purification

When fibers such as young cotton or wood, which give amorphous scattering, are subjected to the usual purification treatments, a large portion of the scattering is often removed without affecting the crystallinity or orientation of the cellulose (41, 42). In some cases there is also a sharpening of the diffraction lines (47).

B. Degradation

When cotton fibers, which give an oriented cellulose pattern, are treated with hydrochloric acid (15), they lose most of their original physical properties and may be ground to a powder. This powder gives the same crystalline x-ray diagram with slightly sharper lines, but the orientation is now random.

C. Swelling

On the basis of the change in the x-ray diagram, Katz (23) has classified swelling as either intermicellar or intramicellar. In the first case (intermicellar), such as produced by water, or weak acids and alkalies, there is no change in the cellulose pattern; an amorphous liquid pattern becomes superimposed upon the pattern of the original cellulose. In the second case (intramicellar), such as produced by strong alkalies or acids, there is a change in the crystalline cellulose pattern. This change may consist of the formation of an entirely new crystalline pattern, corresponding to the formation of a swelling compound between the cellulose and the reagent (e.g., strong sodium hydroxide), or it may consist of a complete disappearance of the cellulose pattern (e.g., strong sulfuric acid). In most cases where the swelling agent produces a new crystalline diagram, this diagram reverts to that of hydrate (mercerized) cellulose upon removal of the swelling agent.

D. Deformation

If a stress is applied to a swollen fiber a certain amount of viscous flow takes place and the fiber is extended. The only effect produced upon the x-ray diagram by this process of extension is to change the intensity dis-

tribution around the diffraction ring, corresponding to a change in the orientation of the crystalline cellulose material (28, 47).

E. Dispersion

Many of the swelling processes, such as cuprammonium and viscose, which produce a new x-ray diagram are also able to swell further and disperse the fiber. If the dispersed cellulose is later coagulated in the form of fibers, a definite crystalline x-ray pattern (hydrate) is obtained. Furthermore, when the fiber is extended there is again the unmistakable evidence of cellulose crystallites which move as a unit (28).

It is possible to cite many other processes which indicate a discontinuity of cellulose crystalline structure, but the above examples will suffice to illustrate the general nature of the x-ray data which need to be explained.

IV. THEORIES OF CRYSTALLITE STRUCTURE

In discussing the structure of a discontinuous cellulose membrane built up of crystalline and amorphous areas which will satisfy the previously outlined x-ray data, mention will be made of only three concepts. These will be referred to as the micellar theory, the continuous structure theory, and the cellulose particle theory. It is not the purpose of the present paper to review the literature or discuss in detail the relative merits of these concepts, but rather to outline briefly how they serve to explain the x-ray data. Special emphasis will be placed on the presentation of unpublished observations correlating the x-ray data with the microscopic behavior of the cellulose particle (12, 47).

A. Micellar theory

The micellar theory was first postulated by Nägeli (34) in 1858. His concept of submicroscopic crystalline particles was based upon polarized light and swelling studies. Later on, after 1920, when x-ray workers found cellulose to be definitely crystalline, the concept was again revived to describe the cellulose crystallite (33). According to Meyer and Mark (30, 32), these micelles are submicroscopic in size, are much longer than they are thick, and are arranged with their long axes roughly parallel or spiral with respect to the fiber axis. Primary valence forces hold the glucose units in the form of a chain; secondary valence forces hold the chains along side each other to form the micelle; and tertiary forces, or amorphous cementing material between the micelles, hold them together.

The estimated size of the micelle (over 500 Å. long and 50 Å. thick (19); see later discussion) would account for the abnormal line breadth of cellulose diffraction lines, while the arrangement of the micelles would account for the orientation effects obtained in the various cellulose fibers. The

presence of an intermicellar material, which was not present in Nägeli's original concept, would account for the amorphous portion of the x-ray diagrams. A hydrolyzing or oxidizing agent would tend to attack first the forces or material between the micelles, and thus account for the fact that these reagents may disintegrate the fiber without disintegrating the crystallite. When a fiber is treated with a swelling agent, the reagent may enter either between the micelles without affecting the crystalline cellulose (intermicellar swelling), or it may enter into the micelle, penetrate the spaces between the cellulose chains, and produce a new diffraction pattern (intramicellar swelling) (22, 23). If the fiber is stretched while in the swollen condition the micelles rotate or move as a unit to produce the improved orientation indicated in the x-ray diagram (28). If the fiber is treated with a dispersing agent, the solvating process begins with a swelling and subsequent dissolving of the intermicellar material, and if the conditions are right the micelles are dispersed without essentially altering their size.

B. Continuous structure theory

Since 1930 considerable emphasis has been placed on "long-chain" or "giant" molecules. Ultracentrifugal determinations (24, 52, 56), viscosity measurements (53, 54, 55), and related physicochemical methods (25) indicate the molecular cellulose chain to be more than ten times longer than the estimated size of the micelle. As a result there has evolved a new concept of the micelle, which will be referred to as the "continuous structure" theory (17, 26, 27, 36, 51, 54).

Although the x-ray data imply a discontinuous crystalline structure for cellulose, there is, however, no proof that the discontinuity consists of discrete crystalline particles or micelles as originally postulated by the micellar theory. The chains need not be broken lengthwise or separated sidewise to form individual crystals in order to explain the x-ray data. If it is assumed that the crystalline regularity of the cellulose chains is interrupted by regions where the chains are not sufficiently close or regular to form a crystal lattice, then these regions would produce in the x-ray diagram the same effect as though they were amorphous material separating well-defined crystallites. In the cell wall of a fiber those regions which possess a definite crystalline regularity of cellulose chains may be considered as "crystallites"; at other places, where the chains have an irregular arrangement, these areas may be considered as "amorphous" or "intercrystalline" cellulose material.

The various characteristics of the x-ray diagram may be explained upon this assumption in very much the same manner as with the original micellar theory. The irregular areas would account for the amorphous

portion of the diagram, while the size and arrangement of the crystalline areas would account for the line breadth and orientation of the crystalline pattern. When the fiber is swollen or dispersed the liquid would enter the meshwork of regular and irregular regions and separate the material into minute particles of cellulose. These particles, as they behave toward the x-rays and toward swelling and deformation, or as they exist in the dispersed or in the regenerated state, may be considered as micelles.

C. Cellulose particle theory

The original work of Farr and Eckerson (13, 14) and subsequent work by Farr (8, 9, 10, 11), showing the formation of cellulose membranes from microscopic particles of uniform size in linear arrangement, has led to the suggestion that the cellulose particle may be substituted for the micelle in the current interpretation of x-ray diffraction data (15, 39). These particles, which are ellipsoidal in shape (1.1 μ thick and 1.5 μ long), exhibit all the properties of crystalline cellulose and are covered with a coat of non-crystalline substance. The assumption that these particles are fundamental building units is based upon the fact that they may be observed in the living cytoplasm of young cotton fibers (13). During fiber growth the particles unite end to end to form fibrils, which are deposited in a spiral arrangement to build up the mature cell wall. Confirmation of their continued existence in the mature fiber comes from microscopic studies which show that the membrane may be disintegrated into fibrils and these, in turn, into particles by means of suitable solvents (14).

With these observations in mind, we turn now to a consideration of how this concept of membrane structure may serve as a basis for explaining the various characteristics of the x-ray diagram.

V. EXPLANATION OF CHARACTERISTICS OF CELLULOSE DIFFRACTION PATTERNS ON THE BASIS OF THE CELLULOSE PARTICLE

A. Orientation

In orientation studies it is desirable to work with single plant cells, just as single crystals are desirable in crystal structure determinations. One of the cells most satisfactory for orientation studies is the marine alga *Valonia ventricosa*, which often grows to a diameter of over 3 cm. This large size enables one to cut out small sections of the cell wall which may be mounted for x-ray examination (35, 38).

Microscopic studies (11) show that cellulose particles unite end to end at the inner surface of the growing cell to form fibrils. The mature membrane is built up of two sets of fibrils which lie in opposite directions, crossing each other at angles of approximately 80°. X-ray diagrams of the same

sample with the x-ray beam perpendicular to the membrane show the usual equatorial diffraction lines concentrated into four arcs, with two sets at approximately 80° to each other. Thus, by comparison of x-ray diagrams and photomicrographs it may be shown that the *b*-axes of the cellulose unit cells are oriented parallel to the axes of the fibrils, and hence to the long axis of the cellulose particle.

Further confirmation of this conclusion comes from another similar single-cell marine alga, *Halicystis*. The x-ray diagrams taken perpendicular to this membrane show random orientation (45). Microscopic studies show that the cellulose particles in *Halicystis* do not form fibrils as they do in *Valonia*, but exist separately in random arrangement (11). *Halicystis* also differs from *Valonia* in that the cellulose exists in the mercerized or hydrate form rather than in the usual native form (45).

The x-ray diagrams show a selective orientation for both *Valonia* and *Halicystis*. With the x-ray beam perpendicular, the 101 crystallographic line is missing, but with the beam parallel the 101 line now exists as two arcs. This means that the 101 crystallographic plane is oriented parallel to the membrane surface in addition to the orientation shown in the perpendicular diagram. Thus, *Valonia* may be described as having a double biaxial orientation, and *Halicystis* as a selective uniplanar orientation (40). This higher orientation cannot be detected in the microscope because of the ellipsoidal shape of the particle, but the microscope does not belie its existence, since cross sections show a laminated structure for both *Valonia* and *Halicystis* (11).

From comparative x-ray and microscopic studies on a membrane such as *Valonia*, which possesses a definite biaxial orientation, it is possible to draw certain conclusions regarding the structure of the cellulose particle (47). First, the cellulose chains (*b*-axis of the unit cell) run parallel to the long axis of the particle. Whether a single chain runs the entire length (1.5 μ) of the particle, or only part of the way, is not known. Second, the various crystallographic planes of the unit cell extend continuously in the same direction throughout the particle. In other words, the glucose units which build up the cellulose particle are arranged within the particle to form a crystalline structure which approaches that of a single crystal. From the intrinsic nature of the x-ray data it is impossible to say definitely that the cellulose particle does not contain still smaller crystalline units, but if such is the case the present data impose the condition that these smaller units have a perfect three-dimensional orientation within the particle.

By assuming the cellulose particle to be the cellulose crystallite, it has been possible in every membrane so far examined in our laboratory to account completely for the orientation observed in the x-ray diagram

on the basis of the cellulose particle orientation observed in the microscope (12, 47). For example, the high degree of fibering in the x-ray diagram of ramie fibers (38), and the rather wide deviation from a parallel orientation in cotton (42) may be directly correlated with the fibril orientation observed in the cell wall (43, 47). An interesting case is that of the *Avena* coleoptile, where bands of cellulose lie perpendicular to the long axis of the epidermal cells (16). X-ray diagrams of this material indicate that the cellulose should have a preferred orientation parallel to the long axis of the cell. Detailed microscopic studies show that these bands are made up of cellulose particles, united not end to end as they are in fibrils, but side by side with their long axes oriented in the direction indicated by the x-ray diagram.

B. Width of diffraction ring

The abnormal equatorial line breadth of cellulose diffraction patterns may be explained in several ways; it may be due to crystal size, strain, impurities, imperfectly formed crystals, or to a combination of any of these. From calculations based upon a theoretical relationship between crystal size and line breadth, Hengstenberg and Mark (19) have estimated the size of the micelle in ramie to be approximately 50 Å. in diameter and over 500 Å. long. The method has been employed with success in estimating the particle size of many colloidal materials, but the method is only valid provided other factors are absent (19). With cellulose fibers it is difficult to be sure that other factors are absent. For example, it is well known that a condition of strain within a crystal will produce a broadening of the diffraction lines (3), and the effect of a small amount of foreign atoms included in the crystal lattice in producing a broadening of the lines has been clearly demonstrated in the case of metals (6).

Since many non-cellulosic materials are so closely associated with cellulose during its formation in the cytoplasm, it is possible that there may be a sort of mixed crystallization of the cellulose with non-cellulosic materials at the surface of the particle. This is suggested by comparative x-ray and microscopic studies (12, 47) of a number of cellulose membranes which indicate that whenever a large amount of non-doubly refractive material may be observed on the surface of the cellulose particle, the equatorial diffraction lines are always broad and unresolved. If the surface of the cellulose particle, on the other hand, is observed to be comparatively free from non-doubly refractive material, then the diffracting lines are sharp and more clearly resolved. One would not expect the surface of the cellulose particle, molecularly speaking, to be as smooth as the surface of crystals which are built up of small molecules held together by secondary valences. It is not unreasonable to assume that the long primary-valence

cellulose chains would protrude at the surface and especially at the end of the particle to give a fringe structure. Such a structure would not only greatly increase the effective particle surface, but also permit a more permanent end-to-end union of the particles to form fibrils, and allow the polar hydroxyl groups of the protruding chains to become closely associated with other hydrophilic cytoplasmic constituents during particle formation. The outer portion of the particle would thus vary from crystalline cellulose to an amorphous mixture of cellulose and non-cellulosic materials at the outer surface. This outer portion would try to crystallize as best it could, producing a lattice strain and distortion which would extend throughout the particle.

If the broadening of the diffraction lines is due to impurities or strain, the question may arise as to why the equator and meridian lines are not equally affected. It will be remembered in this connection that the substitution of hydroxyl by other groups often affects only the crystallographic planes parallel to the cellulose chains, the meridian lines remaining constant (31).

C. Amorphous pattern

Comparative x-ray and microscopic studies (12, 47) indicate that the crystalline pattern of cellulose arises from the cellulose particle, which shows double refraction in polarized light. Furthermore, the size of the particle (1.1 x 1.5 μ) is small enough to give the Debye–Scherrer patterns observed. It is unnecessary to assume crystalline units smaller than the particle, since powder patterns are obtained whenever the crystals of the diffraction sample become smaller than about 5 μ.

There is also reason to believe that the amorphous pattern present in the x-ray diagram of cellulose fibers may be partly accounted for by the non-doubly refractive material which may be observed on the surface of the particles. This assumption is based largely upon purification studies. For example, the x-ray diffraction diagram of a young cotton fiber is very complex, showing the presence of both amorphous and crystalline non-cellulosic materials (41). This x-ray result is confirmed by microscopic examination (13). Extraction of these young fibers with organic solvents removes a fraction which gives an x-ray pattern characteristic of a waxy material; extraction with ammonium oxalate, a fraction which gives a pattern characteristic of a pectic material; and extraction with hot dilute alkali, a fraction which gives an amorphous pattern. After these extractions the residue gives only the crystalline diffraction pattern of cellulose, upon which there is superimposed a weak amorphous pattern. Microscopic examination shows this residue to contain cellulose particles covered with a thin coat of non-doubly refractive material, the other non-cellulosic materials originally present in the young fiber having been removed by

the purification process (41). In order to reduce further the intensity of the amorphous pattern it is necessary to give the residue such drastic treatment as to destroy the property of the cellulose particles to cement themselves together as a coherent membrane upon drying. These preliminary studies, therefore, would indicate that the amorphous portion of a cellulose membrane diffraction diagram may arise from two more or less overlapping sources. One source is that of the non-cellulosic materials which often may be removed by the usual purification processes without destroying the membrane structure. The other is that of an as yet unidentified material which is more intimately associated with the crystalline cellulose, and which apparently plays the rôle of a cementing material which holds the particles together.

VI. EXPLANATION OF THE EFFECT OF VARIOUS TREATMENTS ON THE BASIS OF THE CELLULOSE PARTICLE

A. Purification

Comparative x-ray and microscopic studies show that the amorphous pattern gets weaker and the cellulose lines sharper as the non-doubly refractive material, which may be observed on the surface of the particle, is removed by purification treatments (12, 47). It is difficult to picture this increased sharpness of the diffraction lines as being due to an increase in micellar size, a conclusion which must follow if the line breadth is attributed to the size of the micelle. It would seem more logical to conclude that the amorphous material exists as a separate phase, which is closely associated with the crystallinity of the cellulose.

B. Degradation

Since the cotton fiber may be disintegrated without destroying the crystalline x-ray diagram (15), this would indicate that the major portion of the cellulose exists in the form of crystallites which are less subject to attack than the intercrystalline material or forces which bind them together. Microscopic studies show that hydrochloric acid preferentially attacks the interparticle phase, with a resulting disintegration of the membrane into fibrils and these in turn into particles (15). The lack of change in the crystalline pattern does not necessarily mean that the chemical behavior of the cellulose chains has not been affected, but it does mean that the crystalline arrangement of the chains within the particle has not been disturbed.

C. Swelling

Comparative x-ray and microscopic studies on the same material (12, 47) indicate that in the case of intermicellar swelling, such as is produced by water or weak acids or alkalies, all of the swelling takes place in the

amorphous phase between the particles. The particle itself is not changed. This swelling or taking up of the liquid by the interparticle phase apparently accounts for the appearance in the x-ray diagram of the amorphous pattern which is superimposed upon the unchanged crystalline cellulose pattern.

With intramicellar swelling, such as produced by ethylenediamine (57), where there is the appearance of a new crystalline pattern corresponding to the formation of a swelling compound, the cellulose particle may be observed to increase in diameter. This increase in particle diameter is of the same order as the lateral increase in the unit cell dimensions calculated from the x-ray diagram (12, 47). The formation of a swelling compound does not destroy the double refraction of the cellulose particle, and after swelling has once taken place there is no further swelling of the particle or change in x-ray diagram with further application of the swelling agent. Intramicellar swelling is also produced by strong alkalies, but here it is accompanied by excessive fiber swelling and the appearance of a pronounced liquid pattern superimposed upon the crystalline pattern of the new swelling compound. In this case the liquid pattern and most of the fiber swelling may be accounted for by simultaneous swelling of the interparticle material (46).

In the second type of intramicellar swelling, such as produced by strong sulfuric acid, where the crystalline pattern disappears completely, microscopic examination shows the particle to swell first in diameter and later in all directions with the disappearance of double refraction (10). In this type the swelling is progressive with further addition of reagent until the particle is disrupted.

From the preliminary x-ray and microscopic results now available it would appear that the terms "inter- and intra-particle" swelling may be used synonymously with the terms "inter- and intra-micellar" swelling.

D. Deformation

Since the crystalline cellulose pattern changes only in orientation when a swollen fiber is stretched (28, 47), this would indicate that the crystallites themselves are not deformed, but that they move as a unit during the fiber deformation process. This is in keeping with comparative microscopic studies which indicate that the interparticle material, softened as a result of the swelling reagent, permits the fibrils and particles to glide past each other and move as a unit during deformation. All changes in orientation observed in the x-ray diagram may be accounted for by changes in orientation of cellulose particles (12, 47).

E. Dispersion

Since "regenerated" cellulose gives the same type of x-ray diagram (mercerized or hydrate) as cellulose which has been subjected to intra-

micellar swelling and shows the same evidence of crystallites which move as a unit when the fiber is extended, this would indicate that the crystallites resulting from these two processes are the same. This is in agreement with slit ultramicroscopic (5, 44) and dark-field microscopic studies (10), which indicate the presence of cellulose particles in Brownian movement in both cuprammonium and xanthate dispersions of cotton fibers. These reagents apparently first produce a swelling of the fiber (both inter- and intra-particle swelling) followed by a dispersion of the fiber to give cellulose particles in colloidal suspension (10, 44). In the presence of a coagulating bath the particles are flocculated and deswollen to give a product in which cellulose particles may still be observed. This mechanism of "solution" and "regeneration" would account for the fact that the x-ray diagrams of "regenerated" and "mercerized" cellulose are the same.

VII. DISCUSSION AND SUMMARY

The essential attribute of the micellar theory is the existence of discrete rod-like submicroscopic crystalline particles, which are oriented with respect to the fiber axis and are separated one from another by intermicellar material which coheres and yet allows the micelles to move as a unit during intermicellar swelling and plastic flow and also to be dispersed as a unit during the early stages of the solution process. The essential attribute of the continuous structure theory is the existence of long cellulose chains, which have crystallized out as best they can in the cell membrane in such a way that the crystalline regularity in the membrane is intercepted or warped by irregular regions which behave essentially as amorphous material toward x-rays and toward the penetration of swelling and dispersing liquids. The essential attribute of the cellulose particle theory is the existence of ellipsoidal microscopic crystalline cellulose particles, which are oriented with respect to the fiber axis and separated one from another by amorphous materials which cement the particles together and yet allow them to behave as a unit during swelling and plastic flow and also to be dispersed as a unit by many reagents.

With the exception of the size and shape of the particles, the essential features of the micellar and particle theory are identical. Furthermore, the interpretation of x-ray diffraction data on the basis of the two concepts is essentially the same. The interpretation differs, however, in that the identification of the cellulose crystallite with the micelle is founded upon the existence of a hypothetical building unit, while the cellulose particle is a unit whose existence may be demonstrated by direct experimental evidence,—microscopic observation. In identifying the cellulose crystallite with the particle, the only assumption necessary is one which will account for the width of the x-ray diffraction lines. If it is assumed that the particle has a continuous but imperfect crystalline

structure so as to account for the width of diffraction lines and the porosity of the particle to chemical reagents, then the major x-ray arguments for the existence of submicroscopic micelles in natural fibers cease to exist. The present preliminary data would indicate that the existence of crystalline cellulose particles separated by an amorphous interparticle material is adequate for explaining that portion of the x-ray data pertaining to cellulose membrane structure. This interpretation enables one to make a more direct correlation between x-ray and microscopic data without contradicting other physical and chemical data which point to the existence of a dual structure.

All of the chemical data which point to the preëxistence of well-defined micelles in native fibers rest upon acts of disruption and are therefore open to suspicion (1). The methods of viscosity (53, 54, 55), the ultracentrifuge (24, 25, 52, 56), diffusion coefficients (21), osmotic pressure (4), total surface (20), and methylation (18) are useful for estimating the average size of the "micelle" or "molecule" as it exists in solution, but unless one is certain concerning what happens during the solution process, it is difficult to extrapolate the results to untreated native cellulose membranes. The conclusion that it is unnecessary to assume a crystalline unit smaller than the cellulose particle in order to explain the x-ray data, however, in no way discredits the important rôle which cellulose chain molecules or a further secondary structure of the particle may play in the interpretation of many chemical and physical data. It merely emphasizes the fact that both microscopic and submicroscopic structures may play an important and often interrelated part in the behavior of native cellulose membranes.

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