AN X-RAY STUDY ON THE MICELLAR AND INTERMICELLAR ZONES OF SOME CELLULOSE FIBRES

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On account of manifold uses of fibres in everyday life, the importance of the investigations of fibres, in general, is felt universally. It is accepted that fibres are long chain molecules. The natural fibres are usually polysaccharides or proteins and cellulose is the main constituent of polysaccharides. Published information concerning the physical and chemical properties of cellulose fibres are voluminous and in that connection the work of Haworth, Astbury, Sission, Clerk, Hermans, Meyer, Mark, etc., may be specially mentioned. The X-ray study on cellulose reveals that the unit cell is monoclinic with $a = 8{\cdot}35$ Å, $b = 10{\cdot}3$ Å, $c = 7{\cdot}9$ Å and $\beta = 84°$ and the space group is P_{2_1}. Usually the internal structure is built up of small crystallites separated by amorphous or intercrystalline area and the entire crystal area is built up by repetition of such unit cells. In the present investigations our study is confined to four varieties of cellulose fibres, namely, (1) Sida, (2) Mesta, (3) Chukai and (4) Alissima.

Fibres have been studied very extensively by X-ray diffraction. In India investigations on jute fibres and some other vegetable fibres have been carried out in different laboratories and on that line valuable informations have been presented in the papers of Banerjee (K.) and Roy (1941), Sarkar, Rudra and Saha (1944), Banerjee (N. G.), Basak and Sen (1945), Bose and Ahmed (1946) and Banerjee (B. K.) (1946). All these papers deal with the general X-ray fibre diagrams of different varieties of jute. Average sizes of the crystalline region and changes in the fibre diagrams due to stretching, and chemical treatment are also discussed in these papers.

The present X-ray investigations on different varieties are primarily intended to compare in detail the order of orientations of cellulose crystallites with respect to the fibre axis for different varieties of jute as well as to ascertain the size and nature of the intermicellar spaces.

A special camera of 3 cms. radius was constructed for this purpose and X-rays from a Philips sealed tube (Cu-rays) was used and run at voltage of 45 kV with a tube current of 15 mA. The rays were usually incident on a bundle of fibres about 1 mm. in diameter normal to the length of the fibre. Usually exposures of $6\frac{1}{2}$ hrs. were given.

The glancing angles were calculated from the following relation, $\cos\theta \cos\mu = \cos 2\theta_m$ where θ and μ, the angular co-ordinates, were obtained in the usual way. The glancing angles are compared with the Bragg angles of various planes and comparison of these yield the identification of the spots.

Details of the indices, intensity and character of each variety of the fibres are given in Tables I to IV. The X-ray pictures are shown in plate I (figs 1 to 4).

TABLE I

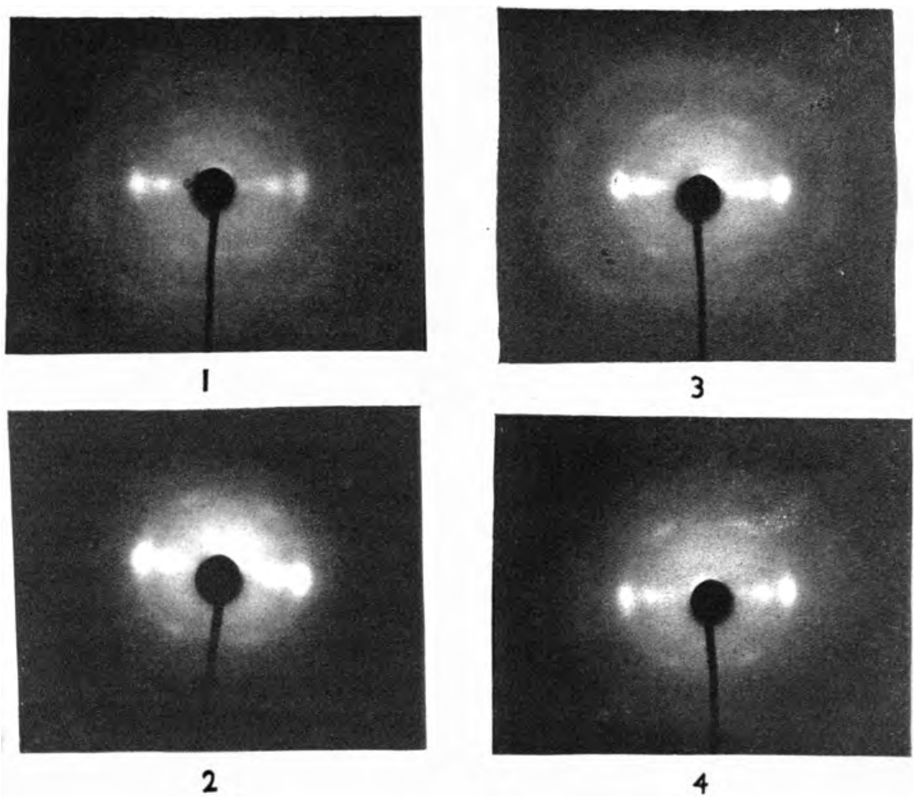
Sida Fibres

Indices	Intensity	Character
101	s.	Sharp and well resolved.
002	v.s.	Sharp and distinct.
004	w.	Extended along the radial direction.
310	m.	Extended in radial direction well resolved.
120 } 221 }	m.s.	Slightly broad.
130 } 032 }	m.w.	Diffuse.
131	m.w.	Extended into arc and diffuse.
042	w.	Extended into arc.

TABLE II

Chukai Fibres

Indices	Intensity	Character
101	s.	Sharp and well resolved.
002	v.s.	Sharp and bent into arc.
004	w.	Extended along the radial direction.
310	m.w.	Extended in radial direction and well resolved.
221 } 120 }	m.s.	Slightly broad.
130	w.	Diffuse.
032	m.w.	Diffuse and extended into arc.
040	w.	Diffuse.
042	w.	Extended into arc.



X-ray diffraction patterns of

1. CHUKAI. 3. ALISSIMA.
2. SIDA. 4. MESTA.

TABLE III

Mesta Fibres

Indices	Intensity	Character
(101)	s.	Sharp and well resolved.
002	v.s.	Sharp and bent along the arc of the circle on which the spot lie.
310	v.w.	Extended into arc.
120 } 221 }	m.	Well resolved.
032 } 130 }	m.w.	Bent along the circumference of a circle on which spots lie.
040	v.w.	Diffuse.

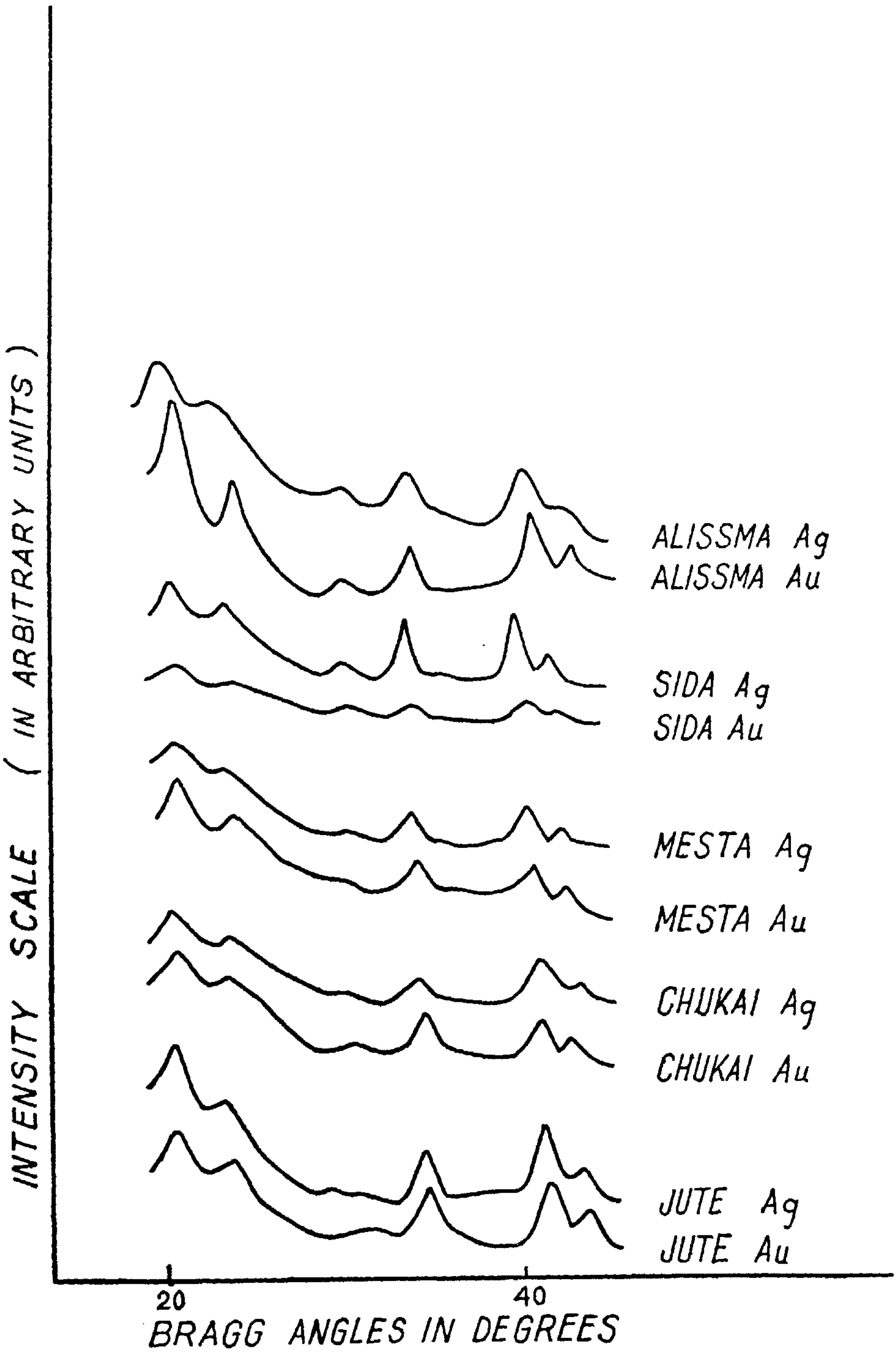
TABLE IV

Alissima Fibres

Indices	Intensity	Character
101	s.	Sharp and well resolved.
002	v.s.	Sharp and bent along the arc of the circle on which the spots lie.
004	v.v.w.	Extended into arc. Diffuse.
310	w.	Extended into arc.
221 } 021 }	m.s.	Well resolved.
130	m.w.	Diffuse.
032 } 131 }	m.w.	Extended into arc.
040	w.	Diffuse.
042	w.	Extended into arc.

It is observed that the orientation of '*b*' axis of Chukai, Alissima and Mesta is much more parallel to the fibre axis than that of the Sida fibre. The spots on the equator are clearly broader than those in other layer lines and therefore the dimension of the crystallites in the perpendicular direction is much smaller than in the direction of fibre axis.

Apart from the preferential oriented crystalline domains of the cellulose crystallites, there are regions known as narrow intermicellar spaces. With a view to obtain some informations for this space, following Frey-Wyssling (1937) we introduced such foreign substances as would reveal the dimensions of the intermicellar



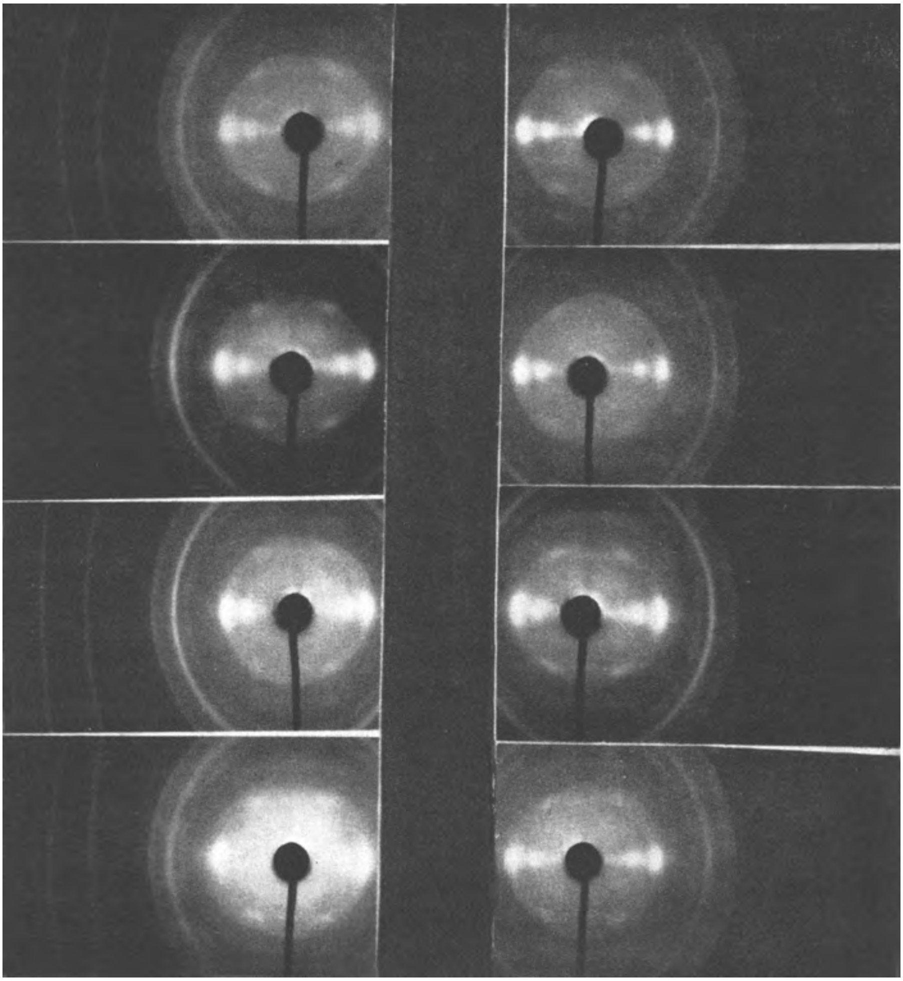
Note.—Read ALISSIMA for ALISSMA.

A E

B F

C G

D H



X-ray diffraction patterns of

A. Chukai (with silver lines).
B. Chukai (with gold lines).
C. Sida (with silver lines).
D. Sida (with gold lines).
E. Alissima (with silver lines).
F. Alissima (with gold lines).
G. Mesta (with silver lines).
H. Mesta (with gold lines).

spaces. For this purpose gold and silver, in the form of colloidal gold and colloidal silver are dispersed following the procedure adopted by Ambronn. To disperse colloidal silver in the lattice fresh fibres are usually soaked in freshly prepared 7·5% silver nitrate solution and then finally treated in hydrazine hydrate. The treated fibre is then dried and mounted in the usual way in a fibre camera and X-ray pictures are taken. In addition to the fibre diagrams the lines due to crystalline silver also come in the X-ray pictures. The same procedure is repeated to disperse gold particles in which case the fibre is first treated in 7·5% auric chloride solution and then in hydrazine hydrate. Finally X-ray pictures are taken. The gold and silver lines of each varieties of fibres are then photometered in Moll's type of microphotometer and the breadths at half maximum are measured from the photometric curves and finally the particle size is calculated from Scherrre's equations. The particle sizes of each variety are given in Table V and the photometric curves given in the Figure. The X-ray pictures are shown in Plate II.

TABLE V

Fibres of different varieties	Particle size calculated from gold lines	Particle size calculated from silver lines
(1) Chukai	77 Å	77 Å
(2) Alissima ..	97 Å	96 Å
(3) Mesta	94 Å	96 Å
(4) Sida	103 Å	103 Å
(5) Jute (low variety) ..	80 Å	84 Å

It is evident from the preceding table that the size of two different dispersoids in the case of same fibre comes to a similar value and the measurement of particle sizes of gold and silver lines incrusted within the fibre framework varies from 77 A.U. to 103 A.U. width for different fibres obtained from calculations. Similar observations were also made by Frey-Wyssling in the case of ramie fibres where he found the intermicellar spaces as 84 Å-85 Å width by the same method as above but with lower concentration of gold and silver solutions. In his case the lines due to gold and silver were weaker apparently due to the total intermicellar space in ramie being less than the fibres studied by us. The results of measurements given in the present communication can, we think, represent the nearest approach to the correct value of the dimensions of the intermicellar spaces in the fibre framework. Our works support the view expressed by Frey-Wyssling on fibres (Frey-Wyssling, Sub-microscopic morphology of Protoplasms and its derivatives).

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ABSTRACT

In this communication, X-ray pictures of cellulose fibres of different varieties, namely, Alissima, Sida, Mesta and Chukai are studied in detail. The orientation of cellulose crystallites with respect to the fibre axis has been discussed and further, in order to get an insight of the structure of intermicellar zones, in each of these varieties gold and silver are incrusted in the form of colloidal gold and colloidal silver wherein it is observed that the particle size of the colloidal dispersoid values from 77 Å to 103 Å (depending on the type of fibres) which gives an insight into the intermicellar regions of the above-mentioned fibres.

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