Change of Lattice Constants of Fibroin by Perfect Drying

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Abstract.

Textile fibres were examined by means of X-rays and by measuring their net densities. Fibre and powder photographs were taken when textile fibres were in the ordinary state containing some moisture, and when they were kept perfectly dry in a vacuum camera. It was observed that the lattice of the crystal of silk fibres was somewhat modified by perfect drying, and returned to its original state by regaining the moisture.

The results of measuring the net densities of the fibres in the primary normal alcohols and in water agree very well with those obtained by the X-ray examination.

Introduction

According to Katz[1], textile fibres give exactly the same X-ray photographs whether the fibres are dry or wet. This means that the absorbed water does not penetrate into the interior of the crystal: that is, it causes only intermicellar swelling.

Recently I. Sakurada and K. Hutino[2] examined ramie fibre from which alkali in the mercerised ramie cellulose had been carefully removed by washing; and they observed that the water penetrated into the interior of the crystal lattice, by transforming it into hydrate cellulose. On the other hand K. Sobue[3], who had investigated the hysterisis of an elongation of various kinds of fibres at various humidities, concluded that the swelling phenomena would occur more or less in both intermicellar and intramicellar ways, and that the degree of intramicellar swelling differed in different fibres: natural cellulose fibres showing the smallest, artificial fibres greater, and animal fibres treated by alkali the greatest. An interesting experiment on the hydration and denaturation of the proteins was also carried out by W. T. Astbury and R. Lomax[4]. In their investigation they dried the specimens over phosphorus pentoxide.

1. J. R. Katz: Ergebnis d. exak. Naturwiss., **3**, 374 (1924).
2. I. Sakurada & K. Hutino: Bull. Inst. Phys. Chem. Research (Tokyo) **14**, 171 (1935), and **15**, 973 (1936).
3. K. Sobue: Soc. Chem. Industry Japan, **37**, 1670 (1934).
4. W. T. Astbury & R. Lomax: Jour. Chem. Soc., **54**, 846 (1935).

The apparatus used in the present experiment for drying the specimen was a vacuum camera such as B. Takei[1] employed in examining the starches of rice and potato by means of X-ray. In his experiment Takei observed that the lattices of starch crystals of rice and potato were somewhat modified by perfect drying, and that the lattices thus modified by drying returned to their original state by absorbing moisture. In the present experiment a Cenco Hyvac pump and a mercury diffusion pump were used in evacuating the vacuum camera, in which the specimen was fixed just behind the slit.

Silk fibre is composed of two parts: the sericin in its outer part and the fibroin in its inner part. It had been previously observed by the writer[2] that the lattice of fibroin is changed by perfect drying.

In the present investigation the writer determined the lattice constants of fibroin in the perfectly dry state and in the wet state by means of X-rays; and he measured the net density of the specimens in primary normal alcohols and in water by the evacuation method proposed by U. Yoshida and B. Takei[3], which is especially suited for obtaining the net densities of porous and powdery substances.

X-ray Experiment

1) *Bombyx mori.* First, fibres of silk or *Bombyx mori*, which were stretched to some extent (the same result was obtained with unstretched fibres) and had been soaked in water for two days, were attached behind a pin-hole slit (1.0 m.m. in diameter) of the X-ray camera. To keep them from drying, a cup of water was placed in the camera. In this manner X-ray photographs were taken with the K radiation of Cu or Fe as shown in Fig. 1, Plate I. Table I gives the mean values of the results obtained with many photographic plates and films placed at various distances, 28.5 m.m. or 48.5 m.m. from the specimen.

From the lattice constants of silk fibre obtained by O. Kratky and S. Kuriyama[4] the following quadratic equation is obtained:

$$\frac{4\sin^2\theta}{\lambda^2}=0.0144h^2+0.0204k^2+0.0137l^2-0.0061hl,$$

where λ is the wave length of the X-rays employed which is ex-

1. B. Takei: Jap. Phys., **8**, 25 (1933).
2. Y. Matsunaga: Die Naturwiss., **24**, 446 (1936).
3. U. Yoshida & B. Takei: These Memoirs, **15**, 1 (1932).
4. O. Kratky & S. Kuriyama: Zeit. phys. Chemie, B, **11**, 363 (1931).

Table I

Spots	Kratky & Kuriyama[1]	Trogus & Hess[2]	ordinary state	100% wet state
	d (A.U.)	d (A.U.)	d (A.U.)	d (A.U.)
A_1	9.17	9.45	8.94	8.80
A_2	4.50	4.81	4.76	4.76
A_3	4.33	4.29	4.21	4.31
A_4	3.07	2.99	2.98	3.04
A_5	2.38	2.35	—	2.31
I_1	5.62	5.53	5.51	5.51
I_2	3.91	3.64	3.81	3.89
I_3	3.62	—	3.63	3.63
I_4	2.25	2.22	—	—
II_0	—	3.45	3.43	3.45
II_1	3.29	3.26	—	—
II_2	2.77	2.74	2.79	2.76
II_3	2.33	2.22	—	—
III_1	2.24	2.27	2.27	2.29
III_2	2.06	2.06	2.06	2.06

pressed by the unit of A. U. and h, k, l are the indices of the atomic planes. The dimension of a unit cell of the fibroin which is used in deducing the above formula is

$a=9.68$ A. U., $b=7.00$ A. U., $c=8.80$ A. U., $\beta=75^\circ 50'$.

The values of $\frac{4\sin^2\theta}{\lambda^2}$ for various spots which were calculated and observed by O. Kratky and S. Kuriyama, were corroborated by the writer in ordinary and 100% wet states; and they are tabulated in Table II. The variation between calculated and observed values in ordinary and 100% wet states does not exceed a reasonable limit of experimental errors. Thus it may be concluded that the lattice constants of silk fibre in an ordinary state containing some water are equal to those in the fully wet state of 100% humidity.

Next, the camera, in which the specimen and the photographic plate or film were set at the same distance as before, was evacuated for many hours by a Cenco Hyvac pump and mercury diffusion pump. After confirming the completed evacuation of the hygroscopic water

1. O. Kratky & S. Kuriyama: loc. cit.
2. C. Trogus & K. Hess: Biochem. Zeit., **230**, 376 (1933).

Table II

Spots	Indices	$\frac{4}{\lambda^2}\sin^2\theta$			Intensity
		Calc.	Observed by Kratky etc.	Observed by the writer in 100% wet	
A_1	100	0.0114	0.0119	0.0124	S
A_2	200	0.0456	0.0481	0.0441	VS
A_3	002	0.0548	0.0533	0.0539	VS
A_4	300	0.1026	0.1062	0.1082	W
A_5	400	0.1824	0.1767	0.1876	VW
I_1	110	0.0318	0.0317	0.0329	W
I_2	210	0.0660	0.0654	0.0660	VW
I_3	012	0.0752	0.0763	0.0759	S
I_4	313	0.1914	0.1976		W
II_0	020	0.0816		0.0840	W
II_1	021	0.0953	0.0924		
II_2	120	0.0930			
II_3	220	0.1227	0.1304	0.1314	W
II_4	022	0.1364			
II_5	320	0.1842	0.1842		
III_0	030	0.1834	0.1842		W
III_1	130	0.1950	0.1992	0.1908	W
III_2	031	0.1973			
III_3	032	0.2384	0.2358	0.2358	W
III_4	230	0.2292			

in the fibres by the Geissler discharge, the X-ray exposure was made by evacuating the camera continuously; and the patterns, differing slightly from those of wet fibroin, as shown in Fig. 2, Plate I, was obtained; as has already been reported by the writer[1]. Generally the diffraction spots diverged a little by perfect drying, and this tendency was especially predominant with the sports III_1 and III_2.

To determine the lattice constants in the perfectly dry state, several X-ray photographs were taken by employing the K radiation of Cu and Fe; and the mean values of the results obtained with many photographic plates and films are given in Table III. The calculated values of $\frac{4\sin^2\theta}{\lambda^2}$ in the table are obtained by the following quadratic equation:

1. Y. Matsunaga: loc. cit.

Table III

Spots	Indices	$\frac{4}{\lambda^2}\sin^2\theta$		Intensity
		Calc.	Observed by the writer	
A_1	100	0.0124	0.0125	S
A_2	200	0.0496	0.0492	VS
A_3	002	0.0576	0.0570	VS
A_4	300	0.1116	0.1126	W
A_5	400	0.1984	0.1941	VW
I_1	110	0.0356	0.0357	W
I_2	011	0.0376		
I_3	210	0.0724	0.0724	VW
I_4	012	0.0808	0.0813	S
I_5	313	0.2096	0.2050	W
II_0	020	0.0928	0.0934	W
II_1	021	0.1072		
II_2	120	0.1052		
II_3	220	0.1422	0.1385	W
II_4	022	0.1504		
II_5	320	0.2034	0.2053	W
III_0	030	0.2088	0.2075	
III_1	130	0.2212		
III_2	031	0.2232	0.2260	W
III_3	230	0.2584	0.2640	W
III_4	032	0.2664		

$$\frac{4\sin^2\theta}{\lambda^2}=0.0124h^2+0.0232k^2+0.0144l^2-0.0062hl,$$

where λ is the wave length of the X-rays which is expressed by the unit of A. U., and h, k, l are the indices of the atomic planes; the above quadratic expression was obtained by taking the dimension of a unit cell of perfectly dry fibroin as

$a=9.19$ A. U., $b=6.63$ A. U., $c=8.56$ A. U., $\beta=76°43'$,

which is different from that of wet fibroin. As seen in Table III the variation of $\frac{4\sin^2\theta}{\lambda^2}$ between the values calculated and observed is negligible. Consequently it may be concluded that the volume of the unit cell of wet fibroin is greater than that of perfectly dry fibroin, and consequently that the silk fibre manifests intramicellar swelling by absorbing water.

After the diffraction photographs with X-rays were taken by keeping the silk fibres in vacuum camera, air was let into the camera, and diffraction photographs were taken again with the same sample; it was confirmed that the interference spots returned to those of the wet fibroin by absorbing the moisture in the air.

Next some cocoons were boiled in a digester at 155°C for 5 hours. The loss in boiling-off was 40.38% and the net density after boiling was 1.427. With this degree of boiling the sericin may be considered to be almost perfeclty boiled off. The fibroin thus separated from sericin was powdered in a mortar. The powder photographs of perfectly dry and perfectly wet fibroin powder were taken in the manner stated before; they are reproduced in Figs. 3 and 4 in Plate I. The difference between the dry and wet fibroin is clearly perceptible in this case too.

2) Wild Silk. *Altheraca pernyi* and *Antheraca Yamamay* were also examined in the ordinary and the perfecly dry states; and the same difference as in the case of *Bombyx mori* was observed.

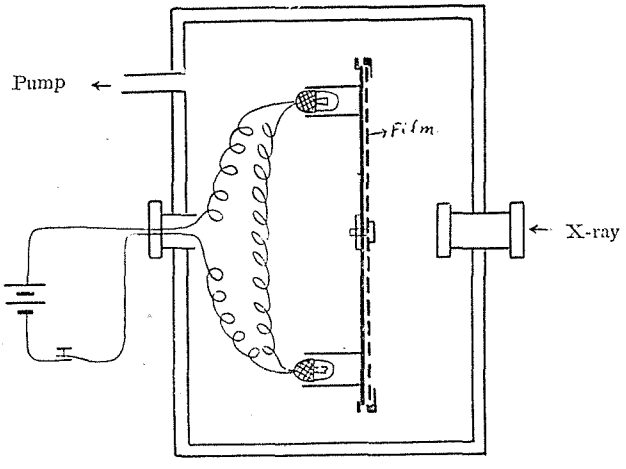
3) Ramie and Artificial Silk. Several experiments on the intramicellar swelling of hydrate cellulose had recently been carried out by I. Sakurada and K. Hutino[1]. The writer also observed the intramicellar swelling of hydrate cellulose. Moreover he observed that ramie also manifested intramicellar swelling. For artificial silk fibre i. e. viscose rayon, Bemberg silk and Nitrocellulose fibre, the swelling was observed to be merely intermicellar.

Measurement of the Contraction of Photographic Film by Evacuation

Now in a vacuum camera the film is dried as well as the sample. Thus the writer attempted to measure the contraction of the photographic film by evacuation. Fig. 1 shows the principle of the apparatus. The film, inserted in the frame of brass, was fixed at its centre with a small brass bolt and a nut. Two small electric lamps were attached, separated sufficiently on the other side of the brass plate at the positions just opposite to the two pin-holes having the diameter of about 0.1 m.m. By these two electric lamps photographic images of the two pin-holes were impressed on the film just below the brass plate. Thus by taking two such photographs, one in the ordinary air and the other in perfectly evacuated and consequently dried state, the

1. I. Sakurada and K. Hutino: loc. cit.

Fig. 1



contraction of the photographic film by evacuation was obtained by measuring and comparing the distances between the images of the two pin-holes on the photographic films. The contraction was found to be about 0.94~0.84% which was very much smaller than the displacement of the diffraction spots by perfect drying observed with fibroin and ramie. Moreover the absence of displacement of the diffraction spots by perfect drying with rayon fibres seems to confirm the view that the displacement of the diffraction spots caused by perfect drying, as was detected with fibroin and ramie, is due really to the change of the size of the unit cell of the crystals.

Consideration from the Net Density

The net densities of silk, ramie and viscose rayon were measured in water and in the primary normal alcohols from methyl alcohol to amyl by the evacuation method devised by U. Yoshida and B. Takei[1]. The results are tabulated in Table IV. As will be seen in the table, points to be noticed are that the net densities of silk fibroin, viscose rayon and ramie decrease with the size of the molecules of various kinds of alcohols, and that the densities of silk fibroin and ramie cellulose which are

Table IV

	Silk (fibroin)	Viscose rayon	Ramie
Water	1.426	1.614	1.614
Methyl alco.	1.483	1.614	1.629
Ethyl alco.	1.445	1.580	1.591
n Propyl alco.	1.382	1.585	1.575
n Butyl alco.	1.380	1.563	1.584
n Amyl alco.	1.382	1.550	1.580

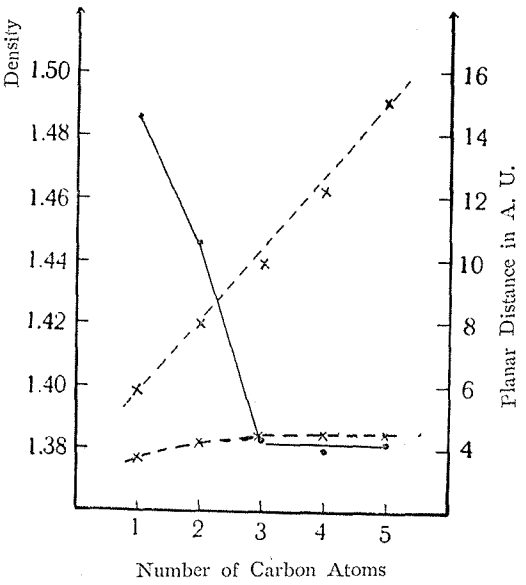
1. U. Yoshida & B. Takei : loc. cit.

measured in water are smaller than those measured in methyl alcohol. This latter fact seems to accord with the view that the intramicellar swelling takes place with silk fibroin and ramie cellulose in water. In the case of viscose rayon, where intramicellar swelling was not detected, the density measured in water is the same as that measured in methyl alcohol.

Next the lattice of perfectly dried silk fibroin soaked with methyl alcohol, was examined by means of the X-ray diffraction. A small glass tube which contained some silk fibroin, was evacuated for hours and then sealed. The silk fibroin thus dried perfectly was soaked with methyl alcohol by breaking the sealed glass tube in methyl alcohol, and then it was sealed in a small thin glass tube. The X-ray examination made on such perfectly dried silk fibroin soaked with methyl alcohol indicated that the crystal lattice was entirely the same as that revealed in the vacuum camera. This fact indicates that the swelling of perfectly dried silk fibroin in methyl alcohol, and probably also in other kinds of primary normal alcohols, is only a intermicellar one.

An investigation on the size of the molecules of primary normal alcohols from methyl to lauryl, has been already carried out by G. W. Stewart and R. M. Morrow[1] Their results are here represented by the broken lines in Fig. 2, by taking the planar distance of ordinates and the number of carbon atoms as absissae. The lower broken line represents the thickness of the molecules, and the upper broken line gives the chain length of the molecules.

Fig. 2



To get a general idea of the relation between the net densities of silk fibroin, which was measured in the alcohols, and the number of the carbon atoms

1. G. W. Stewart & R. M. Morrow: Phys. Rev., **30**, 232 (1927).

of the alcohols, the results of the measurement of the net densities are plotted in Fig. 2, by taking the net densities of perfectly dried silk fibroin as ordinates and the number of carbon atoms of the alcohols in which the density was measured as abscissae. As is evident from the curve thus plotted, the net density of perfectly dried silk fibroin decreases at first as the number of the carbon atoms of the alcohols increases, and then becomes constant when the number of the carbon atoms is more than three, i. e. from propyl alcohol to amyl alcohol.

The reason why the density of perfectly dried silk fibroin decreases with the length of the molecular chain of the alcohols seems to be the increasing difficulty of penetrating into the narrow intermicellar space of the silk with a longer molecular chain.

Discussion

From the experiments above discribed it seems to be certain that the lattice constants of silk fibroin in ordinary air which contains some moisture, or in water, are greater than those in the perfectly dried state. From the following considerations it seems very probable that one molecule of water penetrates into a unit cell of fibroin by intramicellar swelling.

Let ρ_v be the theoretical density of fibroin in a perfectly dry state, then it may be easily calculated by the X-ray data and molecular weight of fibroin.

$$\rho_v=\frac{4\times 128\times 1.649\times 10^{-24}}{507\times 10^{-24}}=1.665. \qquad (1)$$

Next, when the penetration of the water molecules by intramicellar swelling into the unit cell is neglected, the theoretical density ρ of fibroin in ordinary wet state, can be calculated from the X-ray data as

$$\rho=\frac{4\times 128\times 1.649\times 10^{-24}}{578\times 10^{-24}}=1.461. \qquad (2)$$

If one molecule of water penetrates into a unit cell of perfectly dried fibroin by intramicellar swelling the theoretical density becomes

$$1.461\times\frac{530}{512}=1.512. \qquad (3)$$

And the water content is

$$\frac{18}{512}=3.5\%. \qquad (4)$$

The determination of the water contents of degummed silk, ramie and viscose rayon under ordinary atmospheric conditions in Japan,

namely a relative humidity of 70%—80% was made according to the following methods:

(1) The weight of the specimen in a weighing bottle was measured first, and repeated while drying in a drying oven at 105°C for one hour until constant weight was secured.

(2) A glass bottle containing the specimen was evacuated with a Cenco Hyvac pump at room temperature.

(3) A glass bottle containing the specimen was evacuated with a Cenco Hyvac pump by heating the glass bottle with boiling water.

Results obtained with the alove three methods are tabulated in Table V.

As seen in Table V, the three methods give nearly the same water content at ordinary wet state. As to the volatile matter the writer

Table V

	Ordinary method 105°C 1 hour drying	Vacuum drying at room temperature	Vacuum drying heating with boiling water
Ramie	9.51%	10.35%	10.70%
Silk	10.10	12.56	13.91
Viscose rayon	11.52	13.10	14.98

repeated the drying and moistening several times with the same specimen, and it was found to be negligible as compared with the water contents given in Table V.

As is stated before, the density of the silk fibroin, measured in various kinds of primary normal alcohol, decreases at first with the size of the molecules of the alcohols, and then remains the same with the molecules greater than that of propyl alcohol. This seems to indicate that the intrusion of the alcoholic molecules into the intermicellar space becomes more difficult with increasing molecular size, so that it is almost arrested with alcoholic molecules greater than propyl alcohol. Thus the density of silk fibroin measured in the alcohols whose molecules are greater than propyl alcohol may be used in estimating the porosity due to the existence of the narrow intermicellar space in silk fibroin.

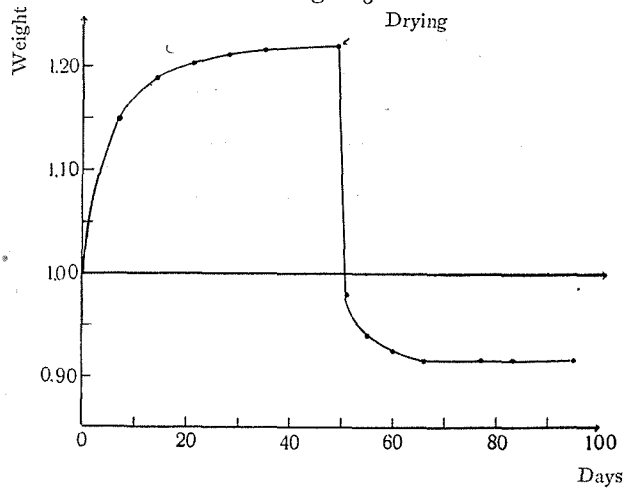
From the theoretical density of perfectly dried fibroin and the apparent density of fibroin measured in normal alcohols, whose molecules are greater than propyl alcohol, the porosity of silk fibroin becomes

$$\frac{1.665-1.380}{1.665}=17.1\%. \qquad (5)$$

Next the writer measured the water content of the silk fibroin

when it was fully wet. About one gram of silk fibroin contained in a weighing bottle was put into a desiccator saturated with water vapour for 49 days, and then it was dried in the desiccator with P_2O_5 for 46 days. By weighing at these two stages the water content of the fibroin at the fully wet state was found to be 30% of the original weight as seen in Fig. 3. This result agrees with that observed by T. Kujirai and his colleagues[1] who observed the water content of silk up to the relative humidity of 95%. As the value of the water content of 30% is that referred to the normal state of the silk fibroin containing the water of about 10%, it becomes 33% when calculated in reference to the perfectly dried state. When silk fibre is fully wet, some water must of course be deposited on the outer surface of the fibre. But if we consider the fact that the silk fibre expands by swelling with water, the absorbing power of silk fibroin for water ought to be considered to be very much stronger in its intermicellar space than on its outer surface. Consequently the amount of water deposited on the outer surface of the fibre is ignored in the following deduction of the amount required for intra- and intermicellar swelling.

Fig. 3



Subtracting the amount of water of 3.5%, which is supposed to have penetrated into the crystal lattice, from the water content of 33% of fully wet fibroin, the quantity of water which intruded into intermicellar space and caused swelling becomes i. e.

29.5%. (6)

Now let us suppose that the silk fibroin is fully wet, then both the intermicellar and the intramicellar swelling are completed. In this

1. T. Kujirai & etc: Bull. Inst. Phys. Chem. Research (Tokyo) **2**, 105 (1924).

case we shall take the net density D of the fibroin micell as $D=1.512$ as stated before. Then the net volume V_1 of the fibroin occupied by its mass M is given by

$$M=V_1D=1.512V_1 \qquad (7)$$

Next let V_2'' be the volume of the intermicellar space occupied by the water swollen perfectly, then from the volume of 29.5% as the weight percentage of the mass of water intruded into the intermicellar space in the fully wet state, we get

$$\frac{V_2''}{1.512V_1}=0.295, \quad \text{or} \quad \frac{V_2''}{V_1}=0.446 \qquad (8)$$

and from (8) we obtain

$$\frac{V_2''}{V_1+V_2''}=\frac{V_2''}{V_1+0.446V_1}=\frac{V_2''}{V_1}\cdot\frac{1}{1.446}=0.309 \qquad (9)$$

This equation means that, when the silk fibroin is fully wet, the volume of the water which has penetrated into the intermicellar space is 31% of the total volume of the fibroin, if we neglect the vacant portion of the narrow intermicellar space into which the water molecules may have intruded.

Silk fibre expands by swelling in water as well as in saturated water vapour. The mean lateral and longitudinal swellings in water of the silk fibroin as used in the present experiment was measured by Prof. Ohara microscopically; and the values of 19.7% and 1.3% were obtained respectively.

Now let V_2 be the volume of the intermicellar space in the air when the expansion of the silk fibre by swelling is negligible, and $\alpha V_2''$ be the vacant portion of the intermicellar space into which the water molecules can not intrude in the fully swollen state, then we have from the above data of swelling,

$$V_1+V_2''+\alpha V_2''=(1.197)^2(1.013)(V_1+V_2),$$
$$=1.451(V_1+V_2), \qquad (10)$$

$$\therefore \quad 1+\frac{V_2''}{V_1}(1+\alpha)=1.451+1.451\frac{V_2}{V_1}. \qquad (10)'$$

By substituting the value of $\frac{V_2''}{V_1}$ into (10)′ we get

$$1.446+0.446\alpha=1.451+1.451\frac{V_2}{V_1} \qquad (11)$$

If we take $\alpha=0.17$ as will be stated later this equation becomes

$$1.522=1.451+1.451\frac{V_2}{V_1},$$

and we get

$$\frac{V_2}{V_1}=0.049.$$

Next let us consider the reason why the net densities of the fibroin in alcohols are greater than in water. As already explained, the main cause for it is of course the fact that when the silk fibroin dried fully by evacuation is put into the water, one molecule of water per unit cell penetrates into the lattice of the fibroin. In the net density measurement in water before stated this structural change was disregarded. But a second cause lies in the fact that there are some very narrow, vacant cavities in the intermicellar space which can not be occupied by the water molecules even of liquid water.

Let the mass of the silk fibroin dried perfectly in vacuum be M, the mass of water which penetrated into the crystal lattice of fibroin be m, net volume of the silk fibroin which absorbed one water molecule per its unit cell be V_1, the volume of the vacant cavities into which the water molecules can not penetrate be aV_2'' and the net density of the wet silk fibroin be D, then the calculation of the density measurement by evacuation in which we had disregarded the intramicellar swelling was made with the equation

$$\frac{M}{M-\{(M+m)-(V_1+aV_2'')\}}=\frac{M}{M-\left\{(M+m)-\frac{M+m}{D}\left(1+a\frac{V_2''}{V_1}\right)\right\}}=1.426,$$

i. e.

$$\frac{D}{\left(1+\frac{m}{M}\right)\left(1+a\frac{V_2''}{V_1}\right)-\frac{m}{M}D}=1.426$$

By putting $D=1.512$ and $\frac{m}{M}=0.035$ as is stated before in the above equation we get

$$a\frac{V_2''}{V_1}=0.0764;$$

and by giving the value of $\frac{V_2''}{V_1}=0.446$ we have

$$a=0.17=17\%.$$

This shows that the volume of the vacant intermicellar space is 17% of the water which has penetrated completely into the intermicellar space; and consequently that the volume of the vacant intermicellar space is 14.5% of the total volume of the whole intermicellar space when the silk fibroin is swollen completely.

In the above consideration we have assumed that the number of

the water molecules which penetrated intermicellarly into the crystal lattice of fibroin was one per unit cell. If we take the number of water molecules as two or more, then the value of α becomes more than 0.39. This seems to be too large for the volume of the vacant intermicellar space into which the water molecules can not penetrate; and consequently it seems to be more accurate to take the number of the water molecules as one per unit cell of the fibroin crystal, as assumed before.

It may be considered from the above investigation that there are intermicellar spaces of various widths in silk fibroin; and the upper limit of their width is estimated to be of about 10 A. U. from the value of its density measured in alcohols.

When the density of the silk fibroin in alcohols is measured, the swelling has taken place only in the intermicellar manner; and the difference in the values of the densities obtained with different kinds of alcohols seems to be caused by the difference in the degree of intrusion of the alcohols into the intermicellar space as was considered before.

Let V_1 be the net volume of the fibroin, V_2'' the volume of the intermicellar space, $\alpha V_2''$ the volume of the intermicellar space into which alcoholic molecules can not penetrate, and d be the densities of the silk fibre which we measured in primary normal alcohols; then we get

$$\frac{1.665 V_1}{V_1 + \alpha V_2''} = d,$$

or

$$\frac{1.665}{d} = 1 + \alpha \frac{V_2''}{V_1}.$$

The numerical value of $\frac{V_2''}{V_1}$ is obtained from the equation (5)

$$\frac{V_2''}{V_1 + V_2''} = 0.171,$$

$$\therefore \quad \frac{V_2''}{V_1} = 0.206$$

and then we get

$$\frac{1.665}{d} = 1 + 0.206\alpha.$$

Table VI shows the values of α thus obtained for various kinds of alcohols.

Table VI

Alcohol	Density	α %
Methyl	1.483	59.2
Ethyl	1.445	44.3
n Propyl	1.382	98.2
n Butyl	1.380	100.1
n Amyl	1.382	98.2

Summary

The main results obtained from the present experiment are summarised below.

(1) The lattice constant of the silk fibroin in the perfectly dried state is less than that in the wet state; and consequently it may be said that the fibroin brings about the intramicellar swelling by absorbing water.

(2) In the wet state one molecule of water penetrates into the unit cell of perfectly dried fibroin.

(3) This change is reversible.

(4) Even with the evacuation method the density measurement by dipping a fibrous substance into a liquid is not perfect, owing to the presence of very narrow intermicellar spaces into which the liquid molecules can not intrude.

(5) The width of the intermicellar space of different fibrous substances such as ramie cellulose, silk fibroin and viscose rayon is not uniform; and in the case of silk fibroin it varies from zero to about 10 A. U.

In conclusion the writer wishes to express his sincere gratitude to Pr f. U. Yoshida for his kind guidance and invaluable suggestions during the course of his research. His hearty thanks are also due to his friend Mr. T. Matsumoto for his kindness in examining the powder photographs with the microphotometer and he further wishes to say that he is grateful to Prof. K. Ohara for the pains he has taken in measuring the swelling of silk fibre in water with the microscope.

Industrial Physical Laboratory, Nagoya Commercial College.

(April 29, 1937)

Plate I

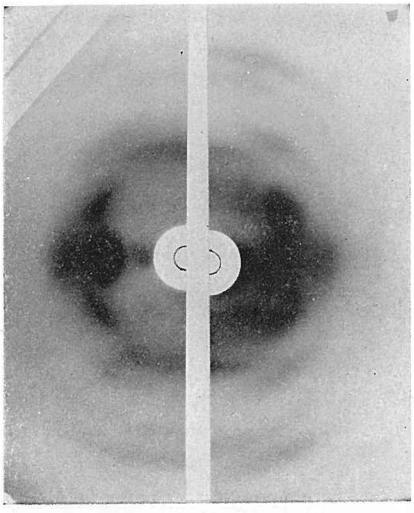


Fig. 1
(wet)

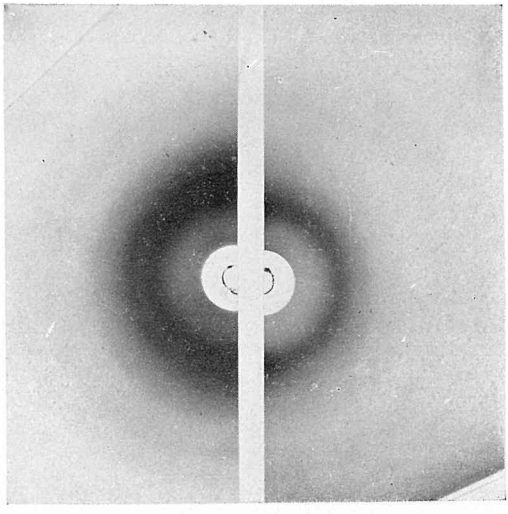


Fig. 2
(dry)

Fig. 3
(wet)

Fig. 4
(dry)

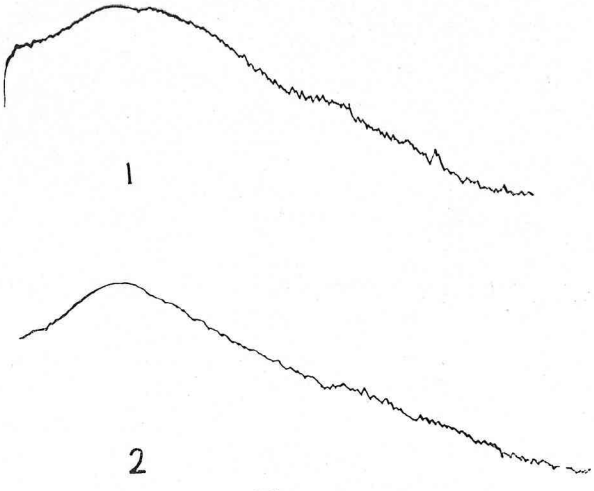


Fig. 5

1 : Microphotometer curve of Fig. 3.
2 : Microphotometer curve of Fig. 4.