# Plastic Deformation of the Regenerated Cellulose Fibers. I. Dichroic Study of the Deformation of Freshly Prepared Fibers

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## I. Introduction

The authors studied quantitatively the dichroic behaviors of the natural and artificial fibers and found that dichroism can reasonably show their inner structures.(1) The deformation process of the regenerated fiber was also studied by using this phenomenon and it was concluded that the results confirm Kratky's second theory(2) in the early stage of stretching in the case of the freshly prepared and swollen state. But this conclusion was made by neglecting the volume change of the fiber during stretching, and P. H. Hermans(3) has recently pointed out the importance of this volume effect. So we also repeated the study taking this effect into consideration and found that the previous conclusion must be changed a little, so it is reported here especially about the case of the freshly prepared and not yet dried fibers. That of the reswollen sample will be given in the following papers.

## II. Experiment

(1) **Sample.**—Isotropic model filaments of regenerated cellulose were prepared by the cuprammonium process as already described(4) in the study of the refractive indices. One or two days were necessary to prepare a sufficient amount of the sample, but the degradation of cellulose did not occur if the spinning solution was kept from air (oxygen) and light during spinning. For this purpose the whole apparatus were placed in a closed box controlled at a definite temperature and the surface of the spinning solution was covered with a thin layer of oil. The conditions of preparation and some properties of the fibers are summarized in Table 1. Their cross sections are almost completely circular.

Table 1

| Sample No. | Spinning solution | | | Fiber | | |
|---|---|---|---|---|---|---|
| | Cellulose (%) | Cu (%) | $NH_3$ (%) | $DP$ | Swelling deg. | $v_L$ |
| 14 | 13.4 | 4.9 | 10.1 | 380 | 4.5 | 2.00 |
| 6a | 11.8 | 5.5 | 21.5 | 380 | 7.1 | 1.91 |
| 15 | 9.3 | 3.1 | 6.1 | 370 | 4.6 | 1.93 |
| K | 4 | 1.7 | 4 | 300 | 13.6 | 1.97 |
| 20 | 3 | 1.5 | 8 | 580 | 14.5 | 1.95 |

(2) **Measurement of the Dichroic Constant *D*.**—The samples are stretched in water and dyed without drying, in a methanol solution of congo red (0.10-0.05%) for half an hour at room temperature, excepting No. 6a, which was dyed after drying in an aqueous dye solution after the old method(1) and then $D=K_{\parallel}/K_{\perp}$ was measured; $K_{\parallel}$ and $K_{\perp}$ are the absorption coefficients of the dyed fiber for the plane polarized D-line oscillating in the directions parallel and perpendicular to the fiber axis. $D$ is the dichroic constant of Preston,(5) exhibiting the inner structure of the fiber.

For this measurement a new microphotometer has been constructed according to the principle of the Leipho-microphotometer (Leitz) used in the previous study. The new photometer has the same accuracy as that of the previous one.

## III. Experimental Results

(1) $v_{1w} \sim v_{2w}$.—An isotropic specimen of the original length $l_{0w}$ was stretched to $l_{1w}$ and kept for one to two days at that length, and then it was released and the residual length $l_{2w}$ was read with a calipers after it had relaxed to the equilibrium state. During these operations the specimens were kept always in the water of the room temperature. Then the total ($v_{1w}$) and the residual ($v_{2w}$) stretching degrees are calculated as follows:

$$v_{1w} = l_{1w}/l_{0w} \quad \text{and} \quad v_{2w} = l_{2w}/l_{0w}.$$

The relation between $v_{1w}$ and $v_{2w}$ is very characteristic as shown by a typical example in Fig. 1; in the early stage of stretching

(1) S. Okajima and others, *J. Soc. Chem. Ind. Japan*, **49**, 38, 128 (1946); *J. Soc. Textile and cellulose Ind. Japan*, **3**, 89, 94 (1947); **4**, 21 64 (1948).
(2) O. Kratky, *Kolloid- Z.*, **84** (1938).
(3) P. H. Hermans, J. J. Hermans, D. Vermaas and A. Weidinger, *J. Polymer Science*, **3**, 1 (1948).
(4) S. Okajima and others, *J. Soc. Chem. Ind. Japan*, **43**, 355 (1940); etc.
(5) J. M. Preston, "Modern Textile Microscopy," Emmott and Co., London, 1933.

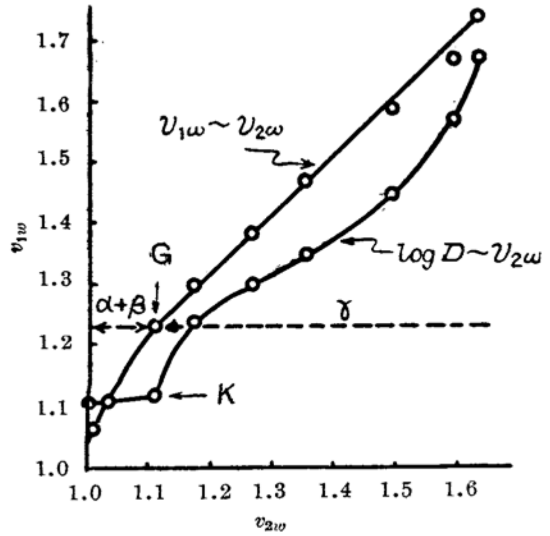


Fig. 1.—No. 15.

($\alpha+\beta$-range) the larger part of $v_{1w}$ is recovered but when $v_{1w}$ goes beyond this range $v_{2w}$ grows in the linear proportion to $v_{1w}$ ($\gamma$-range). This transition point from $\alpha+\beta$-range, G, can be recognized clearly.

$\alpha+\beta$-range is generally about 10% as shown by the above example although there exist some fluctuations.

**(2) Volume Change during Stretching.**— The diameters of the specimen, $b_{0w}$, $b_{1w}$ and $b_{2w}$, corresponding to the lengths $l_{0w}$, $l_{1w}$ and $l_{2w}$ respectively, were measured microscopically and the corresponding volume ratios were calculated as below:

$$R_{1w} = b^2{}_{1w} \cdot l_{1w} / b^2{}_{0w} \cdot l_{0w} = V_{1w}/V_{0w}$$

and

$$R_{2w} = b^2{}_{2w} \cdot l_{2w} / b^2{}_{0w} \cdot l_{0w} = V_{2w}/V_{0w},$$

and similarly the ratio $R_{2d}$ from the corresponding dry volume $V_{2d}$ and $V_{0w}$

$$R_{2d} = b^2{}_{2d} \cdot l_{2d} / V_{0w} = V_{2d}/V_{0w}.$$

The swelling degrees before and after stretching $q_0$ and $q_2$ were given by

$$q_0 = V_{0w}/V_{0d} \quad \text{and} \quad q_2 = V_{2w}/V_{0d},$$

where $V_{0d}$ is the air-dried volume of the isotropic fiber.

In the above notation the suffixes 0 and 1 mean the states before and after stretching respectively and 2 especially the equilibrium state after relaxing. The suffixes $w$ and $d$ denote the wet and air-dried states respectively.

The volume change also corresponds to its $v_{1w} \sim v_{2w}$ curve as shown in Fig. 2. $R_{1w}$ increases slightly (4∼10%) till $v_{1w} = 1.1$ ($\alpha$-range) and decreases slowly to the original

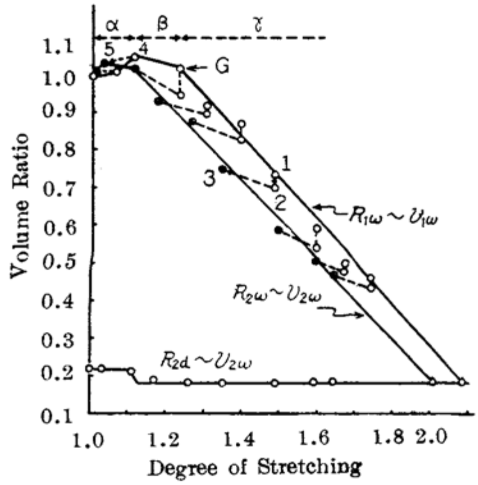


Fig. 2.—No. 15.

value ($\beta$-range) and then suddenly and linearly decreases with the increase of $v_{1w}$ till breaking ($\gamma$-range). When the fiber is kept at a certain length ($l_{1w}$) in the $\gamma$-range for two days at room temperature, its diameter and the volume decrease slowly, though they increase again when the fiber is released and allowed to shrink freely. In the $\alpha$- and $\beta$-ranges the volume does not change while being kept at $l_{1w}$ but decreases slightly after releasing. These changes are shown in the figure by the two representatives 1→2→3 and 4→5.

Such multiphase deformation is also seen in the change of $R_{2d} \sim v_{2w}$ *i. e.*, it remains unchanged in the $\alpha+\beta$-range ($v_{2w} = 1.0 \sim 1.1$ or $v_{1w} = 1.0 \sim 1.23$) but decreases at G and again is kept constant thereafter ($\gamma$-range). Therefore $q_2/q_0$ is not always equal to $R_{2w}$.

In Fig. 2 the points $R_{1w}$ or $R_{2w}$ are not always on the smooth lines but small fluctuations can be seen, which are thought to be due principally to the slight fluctuations among the specimens of the same sample. If we trace $R_{1w}$ of the same specimen every time we stretch it a little same remarkable phenomena can be seen as Fig. 3 shows:

(i) The $\beta$-range extends to 1.2∼1.3 of $v_{1w}$.

(ii) The curves of No. 15 of lower swelling degree is zig-zag and it is clearly beyond the scope of the experimental error, and it may be supposed that the deformation did not happen uniformly in the exact sense, while this tendency is slight in the case of the highly swollen fiber as No. K.

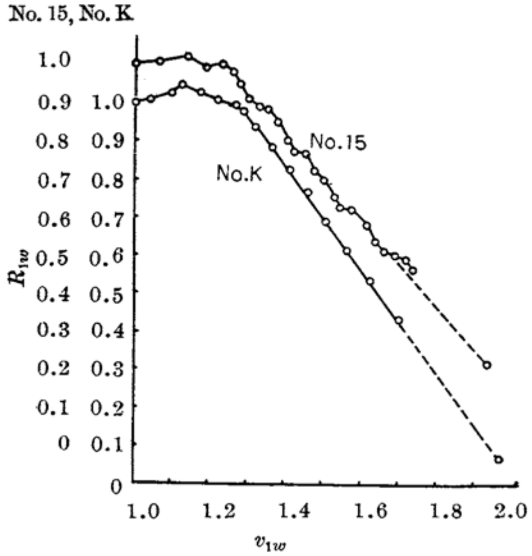


Fig. 3.

(iii) Extrapolating the lines further, beyond the breaking points and reading the values of $v_{1w}$ at $R_{2d}=V_{2d}/V_{0w}$ they are 1.9~2.0 and nearly constant, and correspondingly $v_{2w}$ obtained by extrapolating $R_{2w}$-line are 1.8~1.9. This means that the stretching follows the expelling of the intermicellar free water and if the stretching can be continued without breaking, the complete dehydration of the free water occurs when the fiber is stretched by nearly 100%. As this is very suggestive the values of these $v_{1w}$ are specially denoted by $v_L$ and shown in the last column of Table 1. We shall return to this point later.

(3) $D \sim v_{2w}$.—As $\log D/\Gamma$ is equal to 20 according to our calculation[1] $\log D$ is plotted against $v_{2w}$ in the present study. Then it is convenient to know also the relation $\Gamma \sim v_{2w}$ directly from the same curve; $\Gamma$ is the intrinsic double refraction of the fiber and measured as reported previously.[5]

As an example, No. 15 is shown in Fig. 1; there appears a kinck point K on the $\log D$-curve, which corresponds completely to the point G on the $v_{1w} \sim v_{2w}$ curve already described and in the $\alpha+\beta$-range the increase of $D$ is very slight. Fig. 4 shows other examples, which have similar discontinuities and their curves are slightly sigmoid. In the case of No. 6a the values of $\Gamma$ determined by the retardation method are also given in the figure by the mark +. They were determined by mounting the air-dried specimens into tricresylphosphate, so the values gained are the total double refractions, and the curve of $\Gamma$ does not coincide completely with that of $\log D$, but runs parallel.

## IV. Comparison of the Data with the Theoretically Calculated Curves

In the previous study the above discontinuity was missed due to too small points of observation in the first stage of deformation, and $n_{\parallel}$ and $n_{\perp}$[6] are plotted against $v_{2w}$ which was corrected only in the slight intrinsic anisotropy of the original samples. The same treatment applied to the present data leads to the same conclusion as before (Fig. 5), where the curves 1 and 2 are calculated ones on the

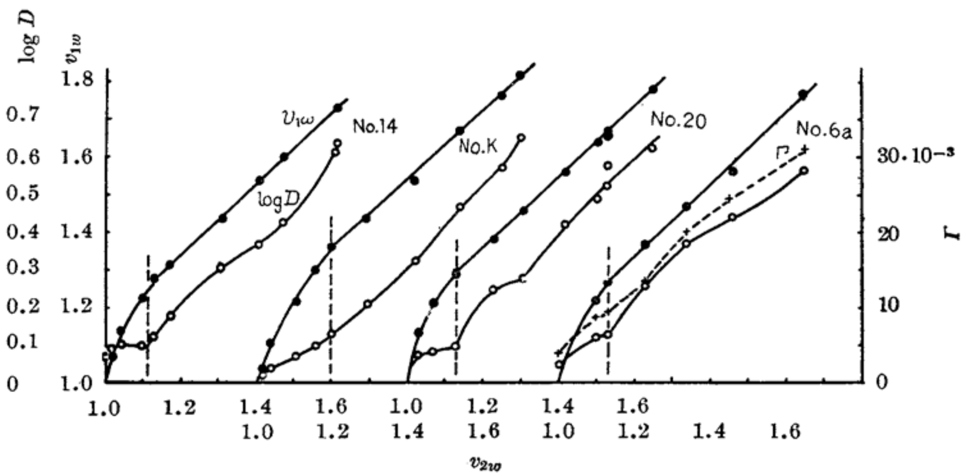


Fig. 4.

(5) S. Okajima and Y. Kobayashi, *J. Soc. Chem. Ind. Japan*, **46**, 941 (1941).

(6) The refractive indices of fiber for the plane-polarized D-line, oscillating parallel and perpendicular to the fiber axis.

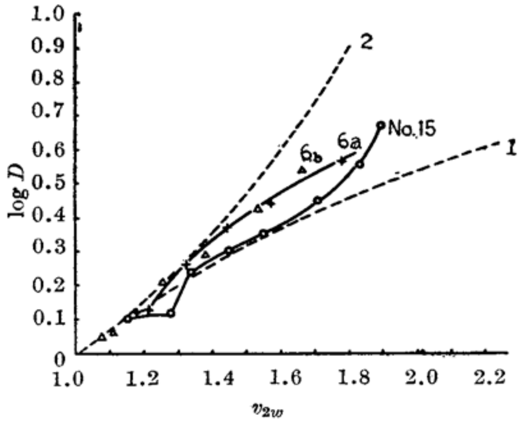


Fig. 5.

assumptions of the first and second theories of Kratky respectively. The point corresponding to the knick point also deviates clearly in this treatment, which has been overlooked carelessly.

Now such discontinuity showing a multiphase deformation was found out in the present stage of our knowledge the authors must be satisfied with discussing the deformation in the last stage only. And in this case stretching degree must be corrected not only from the smallest intrinsic anisotropy of the original sample but also from the volume decrease due to stretching.

As to the theoretical relation assuming the volume change during the stretching, an affined deformation has been described by J. J. Hermans[7] and discussed experimentally by P. H. Hermans and others;[8] it will be discussed later also in this paper. The Kratky's theories also assume the constancy of the fiber volume, so in order to compare with the observed data it is necessary to extend the theories to the case where the volume is changed.

(1) **The First Theory of Kratky.**—It is assumed in the original paper of Kratky that micells are thin rods and a cube is considered in the fiber, each of which contains a micell in it and whose diagonal coincides with the direction of the micell as shown in Fig. 6.

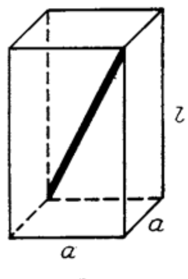


Fig. 6.

Now stretching the isotropic filament by $v$-fold this cube also deforms and the length $l$ is stretched to $lv$ and $a_0$ shrinks to $a_2$, when the volume also shrinks to $V_2$ from $V_0$, then the volume of each cube changes as follows:

Before stretching: $V_0 = a_0^2 \cdot l$ (1)

After stretching: $V_2 = a_2^2 \cdot l \cdot v$ (2)

From Fig. 6, $\tan\theta_0 = \sqrt{2}\, a_0/l$ (3)

$\tan\theta = \sqrt{2}\, a_2/vl$ (4)

The initial intensity of the micells in the isotropic fiber, $J_0$, is constant and indepemdent of the micellar inclination $\theta_0$ relative to the fiber axis but it changes to $J$ by stretching as shown in the next relation.

$$J \sin\theta\, d\theta = J_0 \cdot q_0/q_2 \cdot \sin\theta_0\, d\theta_0 \quad (5)$$

From (1), (2), (3) and (4)

$$\tan\theta = \{(V_0/V_2)^{1/3} \cdot v\}^{-3/2} \tan\theta_0 \quad (6)$$

Now from (5) and (6) the desired relation is obtained.

$$J = q_0/q\, J_0 v_a^3/(v_a^3 \sin^2\theta + \cos^2\theta)^{3/2} \quad (7)$$

where

$$v_a = v(V_0/V)^{1/3} = v \cdot R_2^{-1/3} \quad (8)$$

The refractive indices and $D$ can be calculated from (7) and (8) as already carried out using the original relation of Kratky, but from the formula (7) it can be easily seen that the new relations $n_\parallel$, $n_\perp \sim v_a$ or $D \sim v_a$ coincide with the relations $n_\parallel$, $n_\perp \sim v$ or $D \sim v$ respectively, so even when the volume changes during stretching, the experimental data can be compared with the already calculated relations by using $v_a$ instead of $v$.

For calculation of $v_a$, $v_{2w} \cdot R_{2w}^{-1/3}$ is generally used excepting a few cases, where $v_{2w} \cdot (q_0/q_2)^{1/3}$ is used. These two values are not always equal to each other as pointed out in the paragraph III—(2), but the differences are very slight. $R_{2w}^{-1/3}$ requires only the wet volumes and they are obtained more accurately.

In Fig. 7 the knick point K is placed on the theoretical curve and each value of $v_a$ is corrected being multiplied by $v_k/(v_a$ at the knick point) where $v_k$ is the theoretical abscissa of the point K on the calculated curve. Moreover, the origins of the curves are shifted one by one upward in the order of the decreasing degree of swelling for the sake of avoiding confusion. Then some interesting facts are seen:

(i) The curves nearly correspond to the

(7) J. J. Hermans, *J. Colloid Science*, **1**, 235 (1946); *Trans. Faraday Soc.*, **43**, 591 (1947).
(8) P. H. Hermans and D. Vermaas, *Trans. Faraday Soc.*, **42**, 155 (1946).

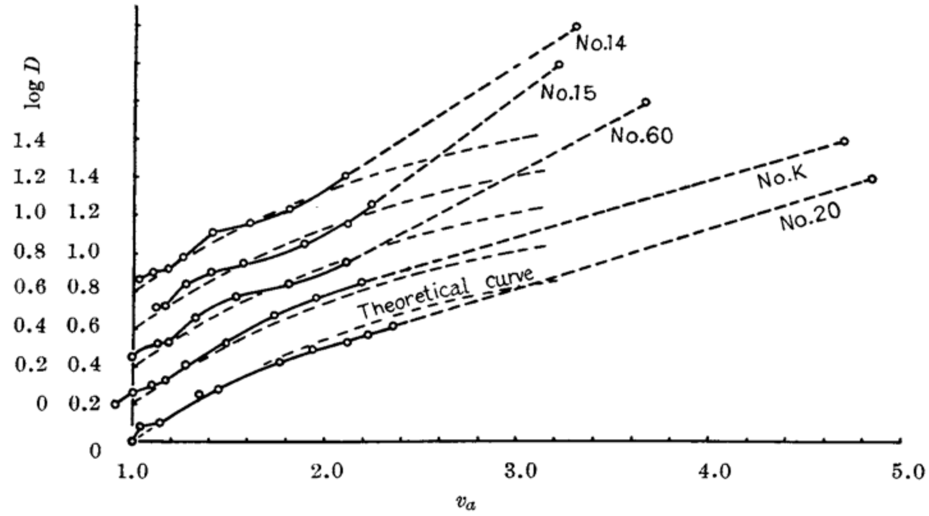


Fig. 7.

theoretical one, but on precise observation the coincidence is not perfect, and the curves are more or less sigmoid. This tendency is more remarkable when the cellulose concentrations of the spinning solutions are larger and the swelling degrees of the filaments are lower (see Table 1). We may consider therefore that the filaments spun from the solutions of the higher concentration have denser structures and their particles (aggregates or parts of molecules) rotate predominantly rather than flow, but in the middle stage of deformation they flow rather easily. This may be due to the change of the relative easiness of the two types of the motion, rotation and flowing, which is caused by the change of the inner structure, depending upon the dehydration, and packing and orientation degrees of the particles. Those three factors, dehydration, orientation and packing, may act dependently to each other. The fibers spun from the dilute solutions are thought to be less dense and flow governs predominantly. Even in this case the curves deviate upward from the theoretical one in the last stage of deformation.

(ii) The authors defined $v_L$ in the paragraph III-(2)-(iii). This is the imaginative degree of stretching, where accompanied with orientation, the free water in the fiber may be expelled completely. So now we suppose that the orientation may also be complete at this point and plot its $\log D = 1.415$ (complete orientation) against the corrected $v_L$ according to the same principle as above. Then those points, marked by ○, can be recognized to be on the extrapolating curve of each sample as shown in Fig. 7. This illustrates that there is an intimate relation between orientation and dehydration due to stretching. But when and how this characteristic of deformation is given duriug the fiber is regenerated is an interesting problem to be studied further.

(2) **The Affined Deformation Theory of J. J. Hermans.**—A new theory of deformation is proposed for the case of the rubberlike polymers, assuming the constancy of volume. This is given as follows:

$$\beta_{\parallel} - \beta_{\perp} = k(v^2 - v^{-1}),$$

where $\beta_{\parallel} - \beta_{\perp}$ is the orientation of the network, $k$ a constant and $v$ the stretching degree relative to the isotropic state. When the volume changes during stretching this is modified to

$$\beta_{\parallel} - \beta_{\perp} = k(q_2/q_0)^{2/3} \cdot (v_a^2 - v_a^{-1})$$

by J. J. Hermans. So for our present case

$$\log D = k'(V_{2w}/V_{0w})^{2/3}(v_a^2 - v_a^{-1})$$

If this theory is right, $\log D$ must be linearly proportional to $(V_{2w}/V_{0w})^{2/3}(v_a^2 - v_a^{-1})$ and its inclination must be independent of the degree of swelling. And actually plotting our data a linear relationship can be considered nearly applicable on the whole as in Fig. 8. Of course this happens in the $\gamma$-range and all the points in the $\alpha+\beta$-range deviate upwards from the line. But precise observation shows that the relations of the samples No. 14, 15 and 6a are slightly sigmoid and there is the same trend as pointed out in Fig. 7, while in the cases of the highly swollen fibers, No. 20 and K, they are exactly linear also in this case.

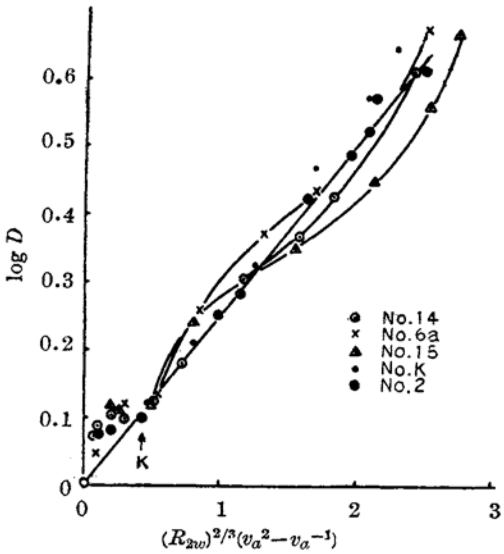


Fig. 8.

## V. Conclusion

The results can be concluded as follows:

(1) When a freshly spun fiber is stretched its volume increases slightly at first together with a very slight orientation. When the fiber is further stretched beyond this range, the orientation becomes very remarkable and, at the same time, the volume decreases due to dehydration which proceeds in proportion to the stretching degree.

(2) In the $\gamma$-range the deformation may generally be considered to proceed nearly according to the first theory of Kratky in the case of the highly swollen fiber. The curve $\log D \sim v_a$ of the sample of low swelling degree is sigmoid around the theoretical one and this tendency is more remarkable as the swelling becomes lower.

(3) As to the affined deformation theory the same trend can be seen. It holds good nearly completely in the case of the fiber of higher swelling degree.

Thus the deformation mechanism of the cellulose seems to be very complicated to be expressed by a single mechanism on the whole range. It requires more abundant and more direct experimental data as well as the precise theory.

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