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Small-Angle X-Ray Scattering of Cellulose. II. Intensity of Scattering in Some Fibers and Films

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Synopsis

It was shown that the realization of a straight log I–h^2 curve may be a coincidence depending on the relative influence of heterogeneity of distribution and non-independent scattering, and a concave log I–h^2 curve can represent a nonhomogeneous system amenable to Shull and Roess's method of analysis. The results indicate: (*1*) The I–h curve for a jute holo-cellulose film has a maximum, and that for a ramie film an inflexion point, each superimposed on a background of gradually declining intensity, and in either case the singularity is accentuated and shifted to a region of larger angle on alkali-treatment. (*2*) The log I–h^2 plots for untreated, alkali-treated and stretched jute fibers give straight sections in the low-angle, and convex, concave, and straight sections, respectively, in the high-angle region. An interesting feature of the results for ramie is the realization of a straight logarithmic curve on mercerization. The curves for alkali-treated and stretched Fortisan fibers have also each of them two discernible linear parts, indicative of two groups of scatterers. (*3*) An evaluation of the log I–log h^2 curves by Shull and Roess's method leads to figures for the diameters of the scattering elements in ramie comparable to those estimated from the corresponding log I–h^2 plots.

INTRODUCTION

The study of the intensity of small-angle x-ray scattering in cellulose shows that native and regenerated cellulose fibers in the dry state generally yield progressively declining I–h curves; when wetted with water or alkali or wetted with water after hydrolytic treatment, etc., some fibers show maxima or inflection points in their I–h curves, a few give straight log I–h^2 curves, and the rest curved logarithmic plots,[1–8] where $h = 4\pi \sin \theta/\lambda = 2\pi/\lambda \sin 2\theta = 2\pi/\lambda \tan 2\theta$, for very small values of θ.[9]

The maximum or inflection point of the I–h curve can be explained as due to either closeness of packing or frequent realization of an average distance between the neighboring units.[7,9] But for cellulose the explanation is usually based on the latter hypothesis, and it is suggested that the necessary organization is either produced or facilitated by the swelling action of water or alkali.[7]

Generally, when exposed to a beam perpendicular to their long axes, a system of homogeneous and isolated elongated particles will, to a first approximation, give rise to a straight log I–h^2 curve. If the particles are homogeneous, not isolated, but closely packed so as to produce mutual interference of the scattered rays, the log I–h^2 curve will be convex, and in special circumstances the corresponding I–h curve may exhibit a maximum or an inflection point. However, if the particles are isolated but not homogeneous in respect to size, shape, or orientation, the log I–h^2 curve will be concave.[9] This means that the factors of inhomogeneity and compactness may produce effects opposed to each other and occasion a straight logarithmic curve. Therefore, the realization of a straight logarithmic plot does not necessarily imply an isolated homogeneous system, although it is not clear what physical significance is to be attached to the size parameter determined, on the basis of Guinier's approximation, from such a straight plot. But contrary to these considerations, a sample of cellulose giving a concave logarithmic curve has been taken to represent a close-packed system of scattering elements, and the realization of a straight logarithmic curve following an apparently swelling treatment of the sample has been taken to be due to changing of the system into an isolated or dilute one, despite the observation that similar swelling treatments often lead to singularities in the intensity I–h curve.[4–9] On the other hand, since a straight logarithmic curve may be a coincidence resulting from the influence of different factors, it is conceivable that a given sample can give a straight logarithmic curve under more than one condition of treatment. That the swelling treatment may not lead to a dilute system is indicated by the example of Fortisan, which does not give a straight log I–h^2 curve under any of the experimental conditions tried by Heyn; in fact, the intensity curves for Fortisan and ramie swollen in plain water have been found to be characterized by a maximum.[4–8] In this connection, one can refer to the experiments of Heikens et al., in which only one out of 25 samples examined gave a straight logarithmic plot, and that too, when the sample was swollen in plain water.[5] It is also noteworthy that a straight logarithmic plot is realized in jute at a higher concentration of alkali than in ramie,[6] whereas in both microscopic and gravimetric methods the swelling of jute at a given strength of alkali in the dilute range is much higher than that of ramie, [10,11] which would suggest that the realization of a straight logarithmic plot may not be directly related to the swelling action of alkali. On the other hand, the results on Cordura as reported by Heyn clearly indicate the influence of tension in changing the shape of the logarithmic curve.[6] If it is remembered that when plasticized in water or alkali, ramie is more susceptible to tension than jute,[12] one would wonder if some small tension required to keep the swollen sample taut during x-ray exposure could produce an orientation or organizational change in the system which would facilitate the realization of a straight plot and thus explain the apparently anomalous behavior of jute and ramie. In view of these considerations we confined our experiments only to those samples which may be assumed to remain organizationally unaffected when mounted for x-ray exposure.

It can be assumed from what has been stated above that the samples which give concave log I–h^2 curves represent inhomogeneous systems amenable to Shull and Roess's method of analysis.[13] The assumption is supported by the fact that the shape of the resulting log I–h^2 curve becomes more and more concave as more and more groups of uniform and identical particles are mixed together,[9] and that it can be shown that the logarithmic curves for the nonhomogeneous samples analyzed by Shull and Roess[13] are clearly concave. Assuming, then, that the particles of such a system are all geometrically similar, optically independent, and obey the Maxwellian type of distribution, it can be shown that the arithmetic mean of their radii of gyration is given by

$$R = r_0 \Gamma[(n/2) + 1]/\Gamma[(n/2) + {}^1/_2] \qquad (1)$$

in which the parameters r_0 and n are determined by a graphical (or analytical) solution of eq. (2)

$$\log I = \text{constant} - [(n + 4)/2] \log [h^2 + (3/r_0^2)] \qquad (2)$$

which is derived from Guinier's exponential relation after incorporating Maxwell's distribution function.[9,13] It can be shown that when the system consists of parallel oriented, elongated elements, as in cellulose fibers, the corresponding expressions are

$$D = r_0 \Gamma[(n/2) + 1]/\Gamma[(n/2) + {}^1/_2] \qquad (3)$$

and

$$\log I = \text{constant} - [(n + 4)/2] \log [h^2 + (1/r_0^2)] \qquad (4)$$

where D now stands for the arithmetic mean of average inertial distances.[9]

Shull and Roess have observed that the method is likely to introduce some ambiguity as regards the correct type of distribution, but it leads to definite values of the average particle size for those cases in which the particle geometry is such that the Guinier's scattering function can be used, and thus there is no particular point in insisting upon the correct distribution function unless very accurate and extensive data can be secured.

EXPERIMENTAL

The materials were untreated jute, ramie, and Fortisan fibers, and the same (*1*) treated freely in mercerizing NaOH solution and (*2*) stretched while swollen in mercerizing alkali and washed and dried under tension.[12] The other samples were untreated and alkali-treated films of jute holocellulose,[14] ramie and cotton prepared from the dialyzed colloidal solutions of these fibers, disintegrated by immersion in concentrated H_2SO_4 (950 g./l.) for 45 hr. at 40°C., by allowing the water to evaporate from a small pool of the solution on a glass plate.[15] The equipment consisted of a demountable x-ray tube, a system of three linear slit diaphragms, a lithium fluoride plane crystal monochromator,[16] an optical bench, and a flat camera. The nominal specimen–film distance was 10 cm., and in order to minimize the air scattering the beam-catch was placed about one-third the total distance from the film.[17] The fibers were exposed to x-ray with their axes parallel to the vertical slit length, and the films with their surfaces either parallel or perpendicular to the horizontal direction of the beam. The exposure was so adjusted that the intensity could be taken as proportional to the optical density. The microphotometering of the x-ray photographs was carried out in a Kipp and Sohnnen instrument. The smallest angle accessible to observation corresponded to a Bragg spacing of about 150 A.

RESULTS AND DISCUSSION

The reproducibility of the results was ensured by repeating the x-ray exposure of a few samples and comparing the log I–h^2 plot of our jute sample with that of Heyn explored with a highly monochromatized focussed beam.[6] We were convinced that (*1*) intensity contribution by the $\lambda/2$ component was negligibly small,[16] and (*2*) for the well-oriented fibers as used in these experiments[12] and exposed with their fiber axes parallel to the slit diaphragms there was no significant distortion of intensity by the slit. As regards the latter point, Heikens et al.[5] have shown that even some deviations from complete orientation, e.g., when the orientation factor falls from 0.99 to 0.80, have no significant effect on the intensity distribution.

In analyzing the intensity distribution the procedure was first to draw I–h curves for all the samples and find out which of these curves show a singularity, i.e., an inflection point or a maximum. Log I–h^2 plots were then attempted for the rest of the samples. In cases where the log I–h^2 curves showed decided upward concavity, the corresponding log I–log h^2 curves were plotted. Figures 1–7 represent some of the I–tan 2θ, log I–tan^2 2θ,[9] and log I–log h^2 curves.[13] The results of studying these curves are summarized in Tables I–III.

I–tan 2θ Curves

When exposed to an x-ray beam parallel to the film surface, the untreated jute holocellulose film has its I–tan 2θ curve characterized by a maximum, and the untreated ramie film has in its I–tan 2θ curve an inflection point, either (maximum or inflection point) superimposed on a declining intensity distribution; the corresponding Bragg spacings are 49.7 and 61.6 A., respectively. The I–tan 2θ curve of the alkali-treated ramie film also shows a maximum which is much accentuated and shifted to a larger angle when compared with the inflection point of the curve for the untreated sample. It was not, however, possible to obtain a monochromatic photograph of the treated jute film, but when examined by a very fine, highly collimated, filtered point-beam, corresponding to a Bragg spacing of 250 A., the treated jute and ramie films both showed a maximum, and compared to the untreated sample, the curve for the treated sample had its maximum more accentuated and occurring at a larger angle. The shift was less in jute than in ramie. No singularity was observed in the scattering pattern of untreated and treated cotton films (Fig. 1 and Table I).

It does not appear possible to interpret the results shown in Table I in detail. Assuming the presence of a singularity as due to an often-recurring distance between the neighboring elements, its accentuation and shift-

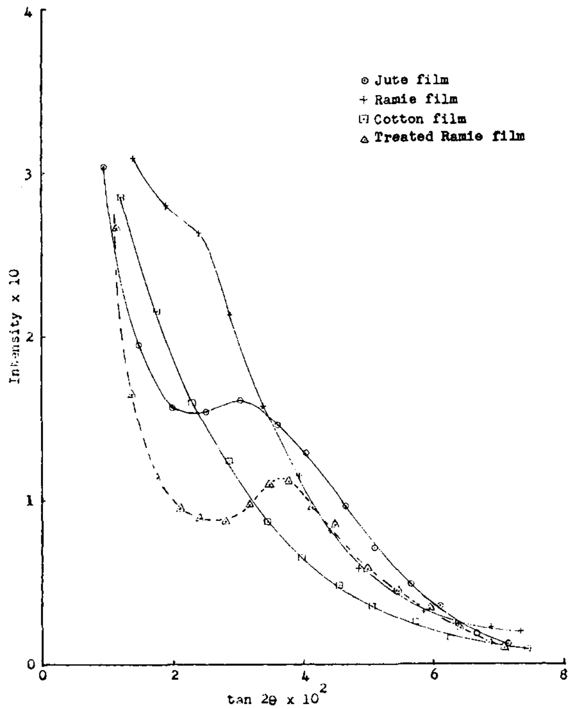

Fig. 1. I–tan 2θ curves for films.

TABLE I

Analysis of the I–h curves for the Films of Jute Holocellulose, Ramie, and Cotton

Sample	Type of Singularity	Location of singularity	
		2θ	A.
Untreated jute holocellulose film	Maximum	1.75°	49.68
Untreated ramie film	Inflection point	1.43°	61.60
Untreated cotton film	—	—	—
Treated jute holocellulose film	Maximum	1.92°	45.90[a]
Treated ramie film	"	2.12° (2.05°)[a]	41.62 (43.06)[a]
Treated cotton film	—[a]	—	—

[a] From filtered beam pattern.

ing to a larger angle would indicate an improved organization and drawing together of the elements resulting from the alkali treatment. But as the exposure was parallel to the film surface the change should refer to a direction perpendicular to it, whereas the observed dimensional change in the film on treatment refers to a direction parallel to the surface. Accordingly, it is not possible to correlate the changes in the position and intensity of the singularity with the dimensional changes in the film, although the linear contractions along the film surface were quite appreciable, viz., 17.5, 14.5, and 10.5% in jute, cotton, and ramie, respectively.

log I–tan² 2θ Curves

The untreated, alkali-treated, and stretched samples of jute, ramie, and Fortisan fibers were examined by analyzing their log I–tan² 2θ curves

TABLE II
Analysis of the Log I-h^2 Curves for Untreated and Treated Jute, Ramie, and Fortisan Fibers

Sample	Diameter of the scattering elements (assumed cylindrical), A. From slope at low-angle region of curve	From slope at high-angle region of curve
Untreated jute	48.36	—
Mercerized jute	49.95	—
Mercerized and stretched jute	50.20	—
Untreated ramie	33.48	—
Mercerized ramie	25.00[a]	
Mercerized and stretched ramie	—	18.38
Untreated Fortisan	54.31	—
Alkali-treated Fortisan	61.49	22.88
Alkali-treated and stretched Fortisan	51.79	20.59

[a] From the complete curve.

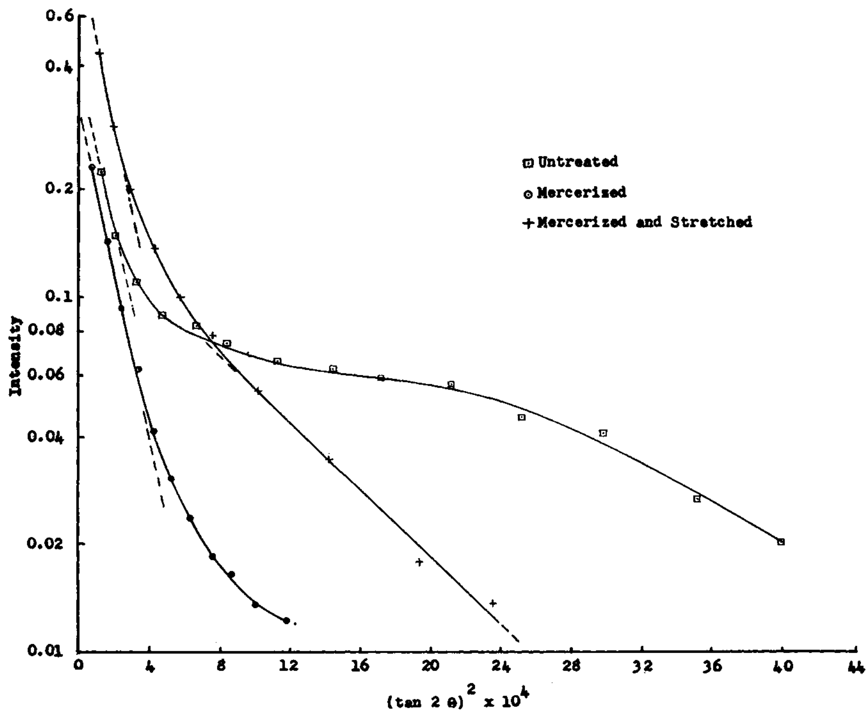

Fig. 2. Log I–tan² 2θ curves for jute fiber.

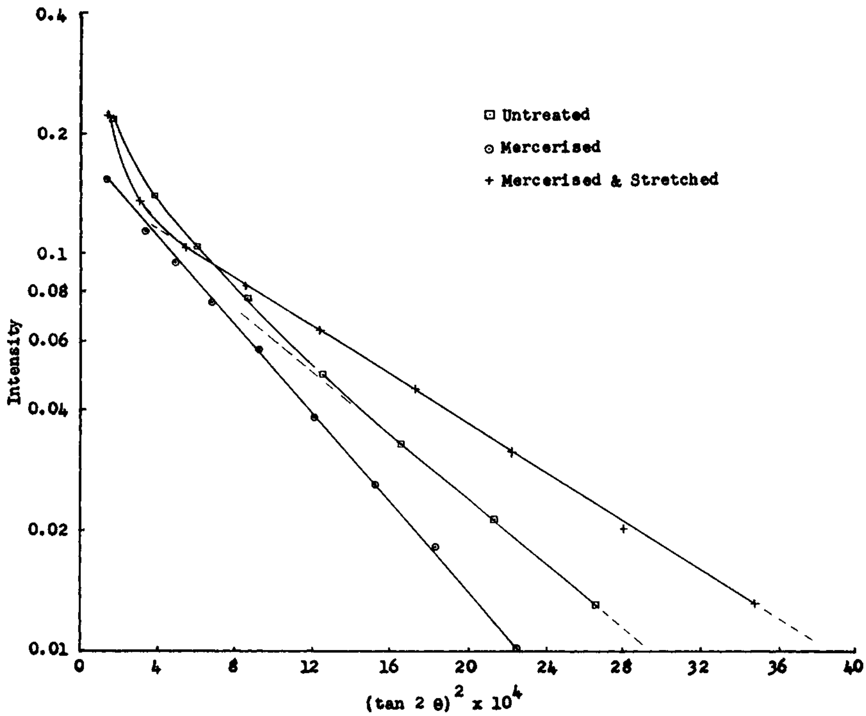

Fig. 3. Log I–$\tan^2 2\theta$ curves for ramie fiber.

drawn on semilogarithmic scales (Figs. 2–4), and the diameters of the scattering units, assumed cylindrical, were calculated (Table II).

It will be seen (Fig. 2) that the logarithmic curves for the three samples of untreated, alkali-treated, and stretched jute have each of them two discernible parts. The part corresponding to the minimum-angle region is practically straight in each curve, but that in the large-angle region is different in the three samples, viz., a little convex in the untreated, concave in the alkali-treated, and mostly straight in the stretched sample. Referring to Figure 3, the curve for untreated ramie is a little concave, but that for alkali-treated ramie is practically straight. The curve for the sample of stretched ramie is also approximately straight, except at very low angles. On the other hand, the curves for the alkali-treated and stretched Fortisan fibers consist of two discernible linear parts (Fig. 4). It has been recorded that the logarithmic plot for untreated Fortisan is slightly concave.[5–7]

The above results for the untreated samples of jute, ramie, and Fortisan fibers appear to be in fair agreement with those of the previous workers,[5–8] but some new and interesting results are obtained for the treated fibers in the present experiment. One of these is the realization of a straight logarithmic plot in alkali-treated ramie in the dry state, which is different from what has been reported before, and the value of the average inertial

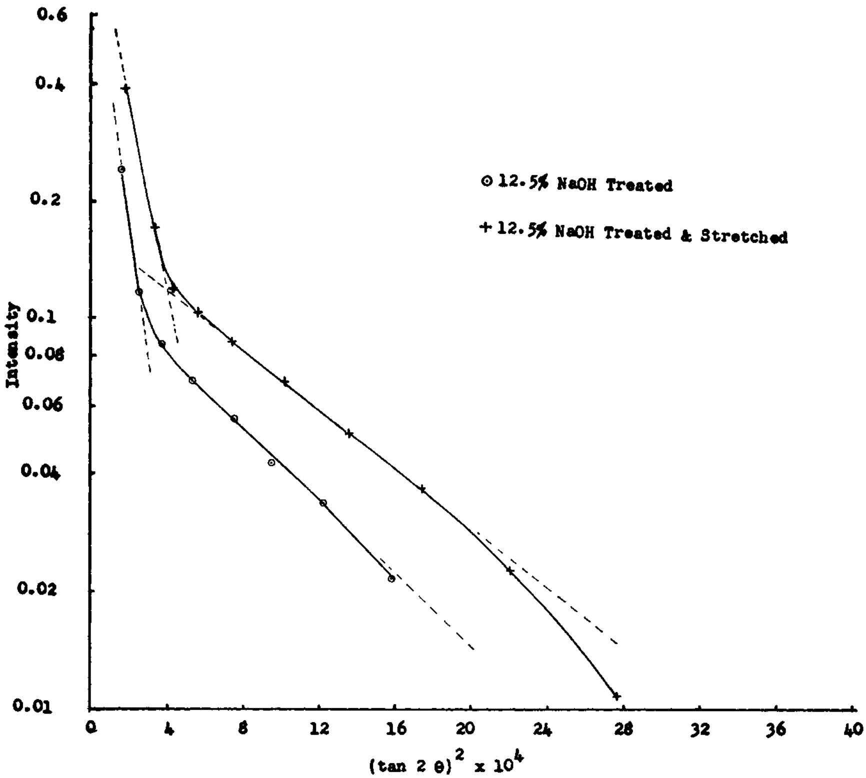

Fig. 4. Log I–$\tan^2 2\theta$ curves for Fortisan fiber.

distance is also different. While it does not seem possible to give a satisfactory explanation of all these observations, a brief discussion of the same may be worthwhile. Accepting that the low-angle region of the logarithmic curve refers to the larger, and the large-angle region to the smaller particles, the linear shape and unchanged slope of the low-angle part of the curves in untreated and treated samples of jute would indicate that the larger elements in these fibers remain unaffected by treatment in respect of size and density of packing. As regards ramie, its elements are probably subject to a more continuous size distribution than those of jute. Similarly, the presence of two discernible linear sections in the logarithmic curve for alkali-treated and stretched Fortisan fibers would indicate two groups of scattering elements which are effectively homogeneous. In this connection, one may refer to the communication by Heikens et al. in which the logarithmic curves of certain samples (Nos. 8, 10, 17) clearly indicate two distinguishable linear regions, one at low and another at high angles, although these authors applied Guinier's evaluation only to the former region.[5] It is also interesting to note that the diameters of the scattering elements in the three fibers, particularly the diameters of the smaller elements, tend to increase on swelling and decrease on stretching treatment.

log I–log h^2 curves

The log I–log h^2 curves plotted on double logarithmic scales were analyzed by the method of Shull and Roess.[9,13] The results are shown in Figures 5–7 and Table III. As it has been stated before (Introduction), the Maxwellian type of distribution was assumed and the parameters r_0 and n were determined by both graphical and analytical procedures.

TABLE III
Analysis of the Log I–Log h^2 curves for Fibers and Films

Sample	Diameter of the scattering elements (assumed cylindrical), A. From complete curve	Diameter of the scattering elements (assumed cylindrical), A. From major high-angle region of curve
Untreated ramie fiber	—	21.72
Mercerized ramie fiber	23.90	—
Mercerized and stretched ramie fiber	—	18.07
Untreated ramie film (⊥ beam)	—	37.08
Untreated cotton film "	—	28.93
Treated ramie film "	—	42.96
Treated cotton film "	—	29.22

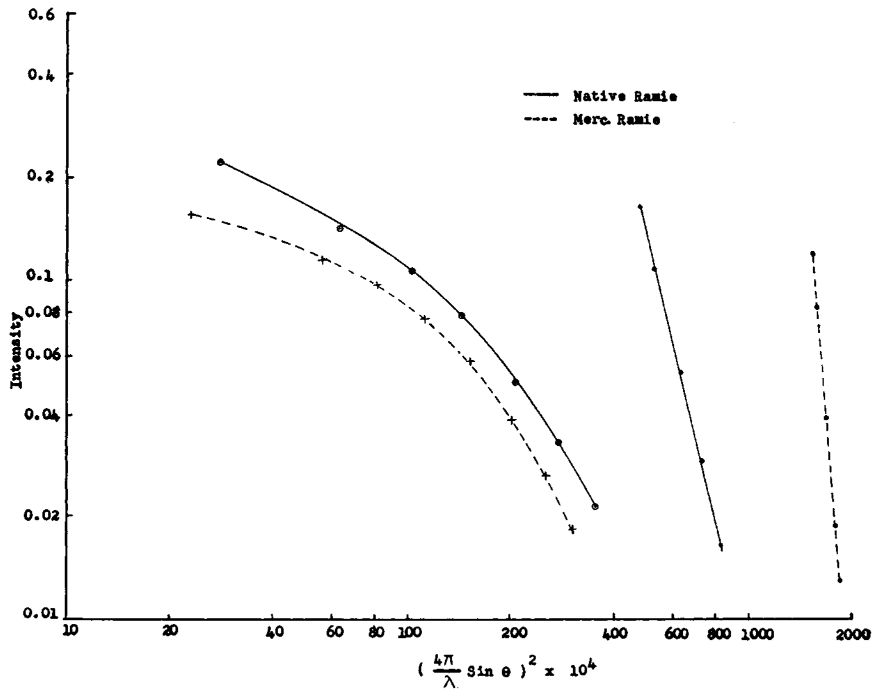

Fig. 5. Log I–log h^2 curves for ramie fiber.

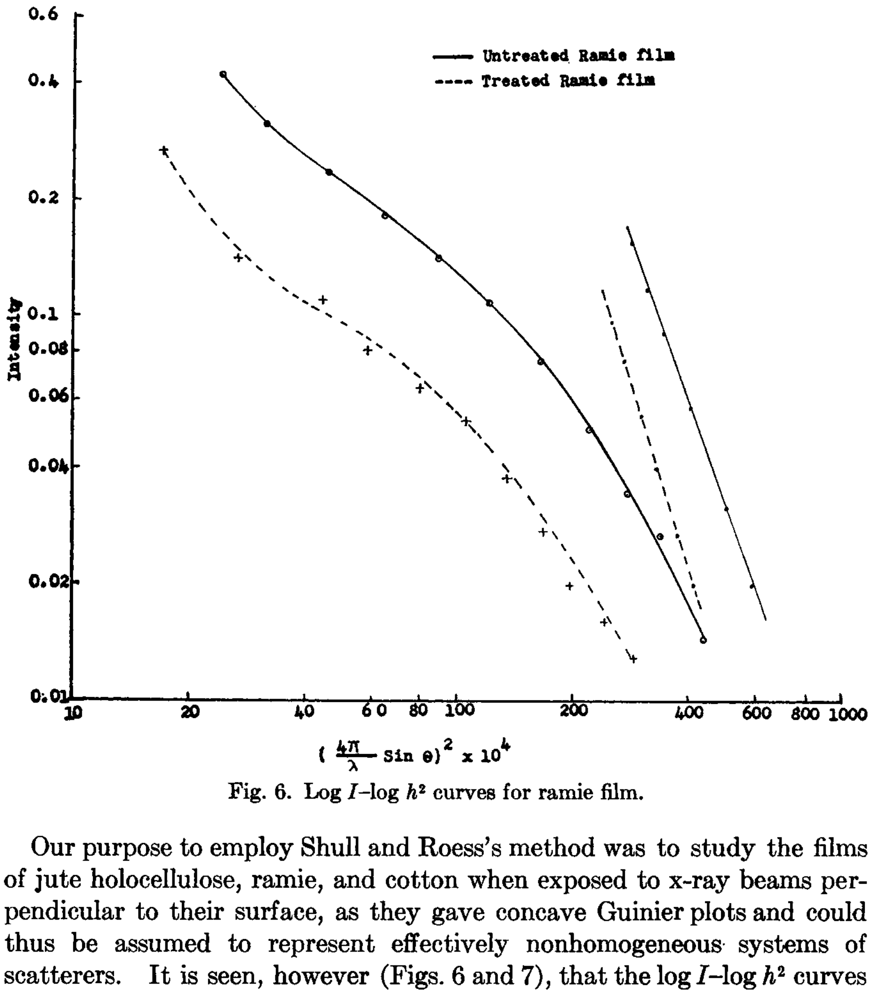

Fig. 6. Log I–log h^2 curves for ramie film.

Our purpose to employ Shull and Roess's method was to study the films of jute holocellulose, ramie, and cotton when exposed to x-ray beams perpendicular to their surface, as they gave concave Guinier plots and could thus be assumed to represent effectively nonhomogeneous systems of scatterers. It is seen, however (Figs. 6 and 7), that the log I–log h^2 curves of ramie and cotton films consist of two distinguishable sections joined by an infection region and only the sections at the high-angle region could be converted into straight lines by means of the shifting procedure of Shull and Roess. Accepting the validity of the method, we can think of two possible reasons for this deviation. One is that the curve is of composite character and would probably fit into two or more components as suggested by the authors; another is that there is some intensity error due to slit distortion, which could only be neglected in case of well-oriented fibers when the orientation of the particles is parallel to the slit length. But although the sample of native ramie gives a concave log I–h^2 curve, its log I–log h^2 curve cannot be adjusted to a single straight line by the shifting procedure. A similar difficulty arises in case of untreated Fortisan. In fact, the only sample which is found to be completely analyzable by the method of Shull and Roess, i.e., the whole of whose log I–log h^2 curve is convertible into a straight line, is mercerized ramie; and we have seen be-

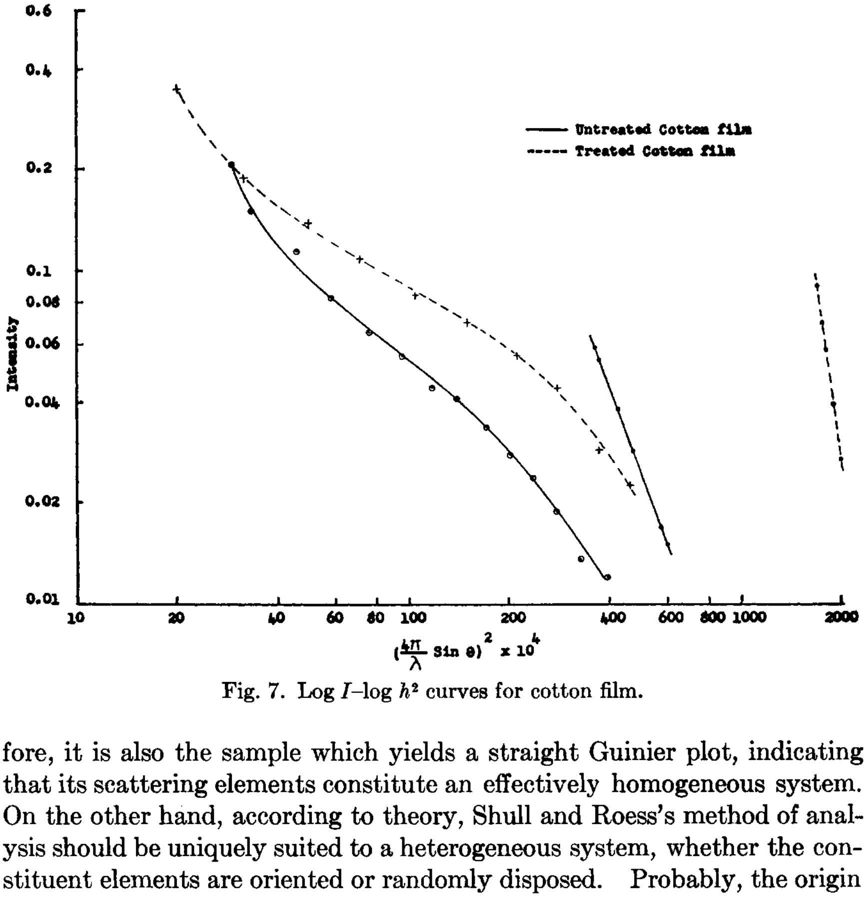

Fig. 7. Log I–log h^2 curves for cotton film.

fore, it is also the sample which yields a straight Guinier plot, indicating that its scattering elements constitute an effectively homogeneous system. On the other hand, according to theory, Shull and Roess's method of analysis should be uniquely suited to a heterogeneous system, whether the constituent elements are oriented or randomly disposed. Probably, the origin of the discrepancy lies in nonfulfillment of the basic assumptions of shape similarity and optical independence of the scattering particles, the third assumption regarding the type of distribution being not so critical. However, it may be interesting to compare the diameters of the smaller particles as estimated from the large-angle regions of the Shull and Roess curves with those obtained from the corresponding log I–h^2 plots (Tables II and III).

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Résumé

On a démontré que la réalisation d'une courbe droite log I–h^2 peut être une coïncidence qui dépend de l'influence relative de l'hétérogénéité de distribution et la diffusion non-indépendante, et qu'une courbe concave log I–h^2 peut représenter un systéme non-homogène qui correspond à la méthode d'analyse de Shull et Roess. Les résultats indiquent: (*1*) la courbe I–h d'un film de jute d'holo-cellulose présente un maximum, celle d'un film de ramie un point d'inflexion, chacun étant superposé à un fond continu d'intensité décroissante; dans chaque cas la singularité est accentuée et déplacée vers une région à angle plus grand par traitement aux alcalis. (*2*) les diagrammes log I–h^2 pour les fibres de jute non-traitées, traitées aux alcalis et étirées donnent des sections droites à angles faibles, et annexes, concaves et droites, respectivement, dans le domaine des grands angles. Une donnée intéressante pour la ramie est l'obtention d'une courbe logarithmique droite lors de la mercérisation. Les courbes des fibres fortisan traitées aux alcalis et étirées ont aussi chacune deux parties linéaires distinctes, indiquant deux groupes de centres diffusants. (*3*) une évaluation des courbes log I–log h^2 par la méthode de Shull et Roess fournit des valeurs pour les diamètres des éléments diffusants dans la ramie, comparables à ceux estimés au départ des diagrammes log I–h^2 correspondants.

Zusammenfassung

Es wurde gezeigt, dass die Realisierung einer geraden log I–h^2-Kurve eine vom relativen Einfluss der Heterogenitätsverteilung und der nicht unabhängigen Streuung abhängige Koinzidenz sein kann und dass eine konkave log I–h^2-Kurve ein nichthomogenes, der Shull-Roess-Methode zugängliches System repräsentieren kann. Die Ergebnisse zeigen: (*1*) Die I–h-Kurve eines Juteholozellulosefilms besitzt ein Maximum, diejenige eines Ramiefilmes einen Wendepunkt, welche beide einem Untergrund mit graduell abnehmender Intensität überlagert sind; in beiden Fällen tritt die Singularität bei Alkalibehandlung stärker hervor und wird zum Bereich grösserer Winkel verschoben. (*2*) Das log I–h^2-Diagramm für unbehandelte, alkalibehandelte und gedehnte Jutefasern liefert gerade Abschnitte im Kleinwinkelbereich und konvexe, konkave bzw. gerade Abschnitte im Grosswinkelbereich. Ein interessanter Zug der Ergebnisse an Ramie ist die Realisierung einer geraden logarithminchen Kurve bei der Mercerisierung. Die Kurven für alkalibehandelte und gedehnte Fortisanfasern besitzen ebenfalls zwei unterscheidbare lineare Anteile, was für zwei Gruppen von Streuzentren spricht. (*3*) Eine Auswertung der log I–log h^2-Kurven nach der Methode von Shull und Roess führt zu Werten für die Durchmesser der Streuungselemente in Ramie, welche mit den aus den entsprechenden log I–h^2-Diagrammen bestimmten vergleichbar sind.