

# Mercerization of Cellulose. I. X-Ray Diffraction Evidence for Intermediate Structures\*

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## Synopsis

A study of the mercerization of ramie cellulose was begun using x-ray diffraction, in order to determine the types of alkali-cellulose structures that occur as intermediates during the conversion of cellulose I to cellulose II. A total of five unique alkali-celluloses (Na-celluloses) could be generated reproducibly, depending only on the alkali concentration used. The reproducibility was enhanced by slowing down the mercerization process, by laterally compressing the fibers in capillary tubes. The five structures, named Na-celluloses I, IIA, IIB, III, and IV, were of two types based on their crystallographic fiber repeats. The first type was represented by Na-celluloses I, III, and IV, all exhibiting a ca. 10 Å repeat. The second type was represented by Na-celluloses IIA and IIB, with a ca. 15 Å repeat. The latter structures are possibly based on a threefold helical chain conformation, which has not been seen in crystalline celluloses. All Na-cellulose structures exhibited a reasonable degree of crystallinity and high degree of fibrous orientation. They formed a definite interconversion scheme, marked by crystalline-to-crystalline phase transformations.

## INTRODUCTION

When native ramie cellulose is mercerized with alkali, its crystal structure undergoes an irreversible transformation which is not accompanied by an evident outward alteration in the morphology of the fiber (cf. Fig. 1). During this transformation, the original, parallel-chain crystal structure of cellulose I changes to that of cellulose II, which is based on antiparallel chains. Because the crystal structure of cellulose II is more stable than that of cellulose I, the reverse transformation does not occur.<sup>1</sup> In spite of the fact that the process of mercerization has been known and used for a long time, its mechanism on the molecular scale is not known. At least two mechanisms have been proposed: One involves the folding of cellulose chains,<sup>2</sup> while, in the other, a sliding of hydrogen-bonded sheets of chains is presumed to take place.<sup>3</sup>

The present study was undertaken to obtain further information on the structural transformations that occur during mercerization. Previous studies had shown that many alkali-celluloses were produced during the process<sup>4</sup>; consequently, a systematic characterization of these intermediate structures was an appropriate starting point of the study. In this first report,

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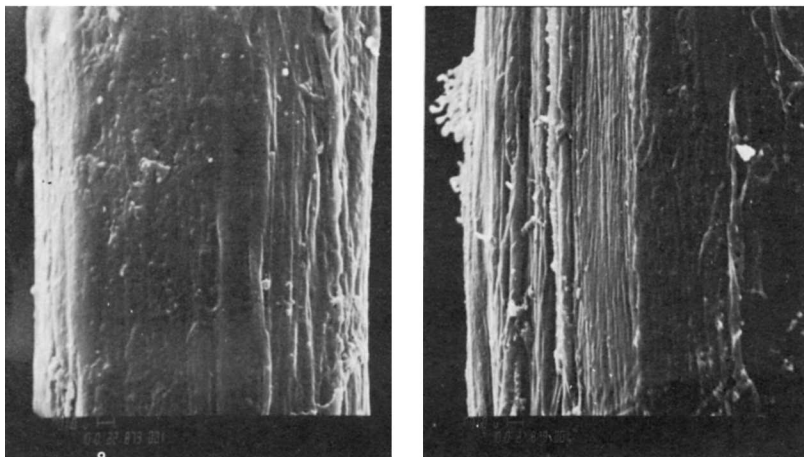


Fig. 1. Scanning electron micrographs of (left) untreated ramie fiber and (right) mercerized fiber.

we describe the formation, some interconversions, and preliminary x-ray diffraction characteristics of alkali-celluloses that can be isolated during mercerization. The starting material was purified native ramie cellulose. As described below, the intermediate structures were obtained in a reproducible fashion by slowing down the mercerization process.

### EXPERIMENTAL

**Materials.** Before its use in mercerization experiments, native ramie was purified using the following procedure. The fibers were boiled in an excess of 0.25*N* aqueous NaOH for 6 h, with a change of solution after 3 h. This was followed by a room-temperature wash in 0.05*N* HCl overnight and a thorough wash in distilled water. The fibers were subsequently either stored in distilled water or air-dried.

**Mercerization.** Although some mercerizations were done simply by soaking the cellulose in an excess of aqueous NaOH solution of the desired concentration, most mercerization experiments were conducted with bundles of fibers contained in glass capillary tubes of 0.5–1.0 mm diameter, such as are normally used for preparing samples for x-ray diffraction. In some other cases, bundles of fibers were soaked while held under tension at constant length in a stainless steel clamp. The concentration of NaOH solutions ranged from 1.6 to 16.3*N* (saturated solution), although most mercerizations were carried out with 3.5 and 8.0*N* solutions. The recording of the x-ray diffractograms of the samples during mercerization was usually performed while the samples remained in contact with the NaOH solution. Whenever a sample required washing and drying, this was done in a number of ways. For example, some samples were quickly neutralized with 0.1*N* HCl, followed by washing with distilled water and drying in air or in vacuum. Other samples were washed with either pure methanol or methanol saturated with NaOH, followed by drying. (The drying methods are further

described under Results). All conversions, washing, drying, etc., processes were carried out at room temperature.

**X-Ray Diffraction.** Samples prepared in capillary tubes, as described above, were already in a convenient form for x-ray diffraction. The diffraction patterns were obtained in a Searle toroidal focusing camera mounted on a Rigaku RU-100, rotating anode (copper target), x-ray generator. The patterns were recorded on Kodak SB x-ray film, at a film-to-sample distance of 3 cm. The operation of the generator at 50 kV and 100 MA allowed the patterns to be obtained in less than 20 min for most samples, thus making it convenient to follow the samples throughout the entire mercerization treatment.

Other samples, which were not mercerized in capillary tubes, were either mounted "as is" or were placed in capillary tubes prior to mounting in the x-ray camera.

## RESULTS

According to earlier literature, a variety of crystalline soda-celluloses (hereafter referred to as "Na-celluloses") can be obtained by soaking cellulose I in aqueous NaOH solutions of different concentrations and for varying times.<sup>4</sup> These structures have been classified as Na-celluloses I, II, IIh, III, IV, V, X, etc., principally on the basis of their x-ray diffraction diagrams. Because there is considerable disagreement in the literature concerning the classification of these Na-celluloses, the conditions required to produce them, as well as their unit cells, the first objective of this study was to determine the formation conditions of all unique Na-cellulose structures. Since it was known from earlier work that conditions which were necessary to obtain a given Na-cellulose appeared to vary, depending on the amount of tension under which the sample was kept, the latter condition also became a variable. During preliminary experiments it was found that the effects of tension could be reproduced and more easily controlled by packing the fibers into capillary tubes prior to the addition of the NaOH solution. Apparently, the lateral pressure developed in response to the swelling of the fibers by NaOH either duplicated or mimicked the effects due to longitudinal tension. A desirable consequence of swelling the cellulose fibers in capillary tubes was the slowing down of the mercerization process, permitting continued observation of the sample by x-ray diffraction while it was undergoing conversion. This, coupled with controlling the concentration of NaOH, allowed the generation of the desired Na-cellulose structure in a reproducible manner. (Samples prepared under such conditions are hereafter frequently referred to as "laterally constrained" or "laterally compressed" samples.)

As shown below, five different Na-cellulose structures could be observed during the mercerization process. The structures exhibited a considerable degree of crystallinity and a high degree of fibrous orientation, and could be classified into two types. Rather than depend on the often confusing older nomenclature of Na-celluloses, the five structures were named Na-celluloses I, IIA, IIB, III, and IV. (The renaming really represents only a

simplification of the older nomenclature.) The characteristics and the conditions responsible for the formation of these Na-celluloses are summarized in Table I; in addition, the formation of each structure is described in detail below.

**Na-Cellulose I.** When ramie was treated with NaOH solutions ranging in concentration from 1.6 to 16.3*N*, the effects were, predictably, dependent upon both the NaOH concentration and the degree to which the samples were constrained. With 1.6*N* NaOH, no conversion of cellulose I was observed with any of the samples, even with treatment times as long as 3 months. Increasing the concentration to 1.8*N*, however, could produce the conversion of cellulose I to a crystalline structure first identified by Hess and Trogus as Na-cellulose I.<sup>5</sup> With this NaOH concentration, the conversion of an unconstrained sample took place over a period of several days, but no conversion was observed with laterally constrained samples (or fibers kept under tension). The x-ray diffraction pattern of Na-cellulose I, shown in Figure 2, developed gradually and coincidentally with a decrease in the intensity of the original pattern of cellulose I. As shown in Figure 3, a mixed pattern could be observed before conversion had gone to completion. Increasing the NaOH concentration both increased the rate of conversion and allowed converting samples that were laterally constrained. For example, with 3.5*N* NaOH, laterally lightly constrained samples (i.e., in less than fully packed capillary tubes) converted in approximately 1 h, whereas samples that were severely compressed did not convert at all. With 8 or 16.3*N* NaOH, even the severely constrained samples converted rapidly, as fast as in a few minutes with the higher concentration. In all cases, however, the first step in conversion was to Na-cellulose I. As shown in Table I, the crystallographic fiber repeat of Na-cellulose I is very near the 10.3 Å repeat seen in all crystalline celluloses.

**Na-Celluloses IIA and IIB.** When Na-cellulose I was further treated with alkali, it slowly changed into a structure with a 15.4 Å repeat, earlier named Na-cellulose II or Natron cellulose.<sup>5,6</sup> In our nomenclature, and for reasons that are clarified below, this structure has been renamed Na-cellulose IIA. Its formation depended on both the strength of the alkali solution and the compression of the sample. For example, a lightly constrained Na-cellulose I, formed from cellulose I by the action of 3.5*N* NaOH, gradually changed into Na-cellulose IIA when left in the same solution. The higher the concentration of NaOH, the faster was the rate of conversion, viz., when

TABLE I  
Typical Preparation Conditions and Crystallographic Fiber Repeats of the  
Five Na-Celluloses

Na-Cellulose	Alkali (or other) treatment	Degree of constraint	Fiber repeat (Å)
I	3.5 <i>N</i> NaOH	Moderate	10.1
IIA	8.0 <i>N</i> NaOH	Moderate	15.4
IIB	8.0 <i>N</i> NaOH	Light	15.4
III	Drying after 3.5 <i>N</i> NaOH	None	10.1
IV	Water or methanol wash	None	10.2

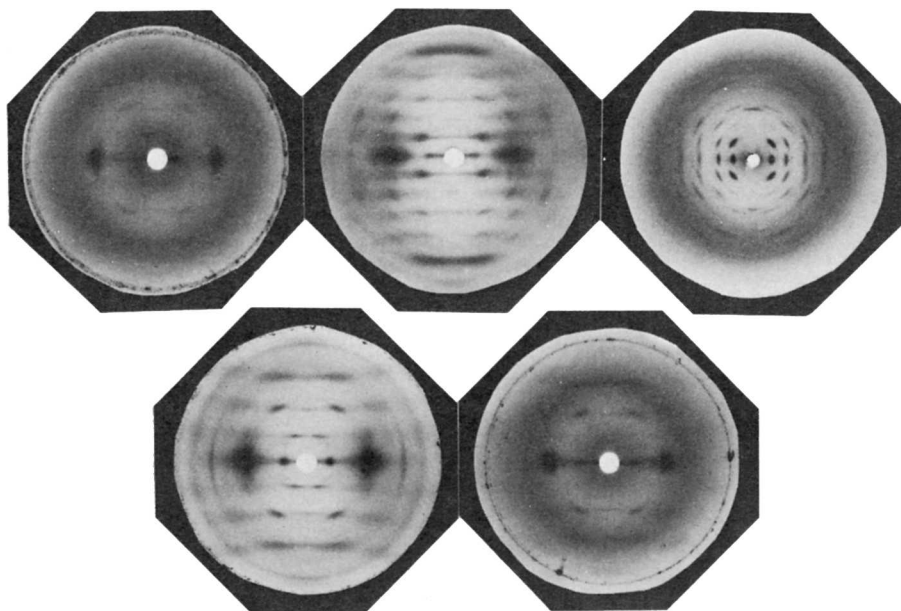


Fig. 2. X-ray diffraction diagrams of: (top, left to right) Na-celluloses I, IIA, IIB; (bottom, left to right) Na-celluloses III, IV. Fiber axis is vertical.

an unconstrained sample of cellulose I was treated with 8.0*N* NaOH, the conversion was complete so quickly as to appear to have gone directly to Na-cellulose IIA. In most cases, however, the conversion could be followed easily, and mixed patterns of Na-celluloses I and IIA (shown in Fig. 3) could be obtained. Such mixed patterns had previously been observed by Sobue, Kiessig, and Hess, who mistakenly identified them as Na-cellulose II + III.<sup>7</sup> On the other hand, the conversion of Na-cellulose I to IIA could be entirely prevented by increased lateral compression of the sample.

Under certain conditions, treatment of Na-cellulose I with alkali resulted in the formation of another Na-cellulose with a fiber repeat of 15.4 Å. Because this Na-cellulose had previously not been described, and because

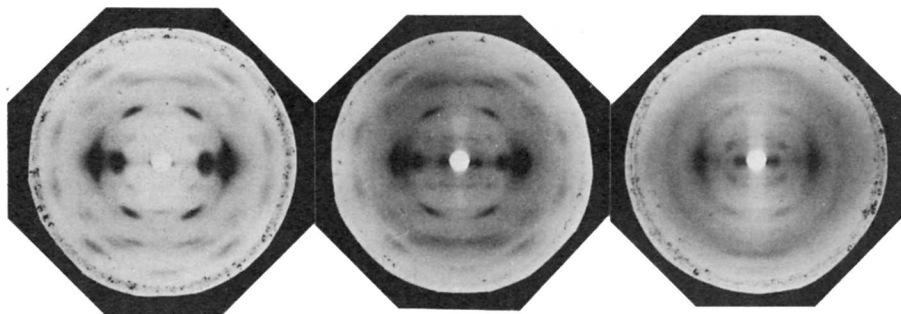


Fig. 3. X-ray diffraction patterns of mixed crystal structures observed during conversions: (left to right) cellulose I, shown for comparison; cellulose I + Na-cellulose I; Na-celluloses I + IIA.

its diffraction pattern was similar to that of Na-cellulose IIA (cf. Fig. 2), we have named it Na-cellulose IIB. Typical conditions for the formation of Na-cellulose IIB were as follows. When ramie fibers were soaked in 3.5*N* NaOH, compressed laterally to an extent which allowed conversion to Na-cellulose I in about 1 day, subsequent removal of constraints and continued soaking in the same concentration of alkali resulted in a complete conversion of Na-cellulose I to IIB within a period of several days. The important difference in the conditions favoring conversion of Na-cellulose I to either IIA or IIB was the degree of lateral constraint: More compression favored IIA and less compression favored IIB.

Na-celluloses IIA and IIB differ from Na-cellulose I (and all other Na-celluloses) in that their fiber repeats are approximately 15 Å (cf. Table I). This suggests a threefold helical chain conformation for both structures, in contrast with the 10.3 Å, twofold conformation usually seen in celluloses. Another interesting feature of Na-cellulose IIB is that it is bright blue in color, while other Na-celluloses are colorless.

**Stability of Na-Celluloses I, IIA, and IIB: Na-Celluloses III and IV.** All three Na-celluloses—I, IIA, and IIB—are stable while they remain in contact with NaOH of a concentration necessary for their formation. In order to determine whether the three structures are also stable when not in contact with the alkali solution, they were dried either before or after various washing treatments.

In response to drying in vacuum at 20°C, without prior washing, Na-cellulose I converted to Na-cellulose III (first identified by Hess and Trogus<sup>5</sup>) or sometimes to a mixture of Na-cellulose III and other unit cells. As shown in Table I, the fiber repeat of Na-cellulose III is also near the usual 10.3 Å. On the other hand, both Na-celluloses IIA and IIB remained unchanged after the same drying procedure. The instability of Na-cellulose I under such conditions is probably due to the fact that it is stable only at lower concentrations of alkali, in contrast with Na-celluloses IIA and IIB which can also exist at higher alkali concentrations. During drying, the concentration of NaOH in the sample increases, which causes the conversion of Na-cellulose I to Na-cellulose III, which is stable under higher NaOH concentrations. Apparently, increasing the alkali concentration by drying is not identical with conditions under which Na-celluloses IIA and IIB can form, because the latter were never observed to form, *a priori*, under drying conditions.

These observations agree with the results obtained after washing the three Na-celluloses with methanol saturated with NaOH, which produced no changes in the respective crystal structures. When the alkaline methanol wash was followed with pure methanol, Na-celluloses I and IIA both changed into Na-cellulose IV (first described by Schramek and Succolowsky<sup>8</sup>), and Na-cellulose IIB became entirely amorphous. It appears that the NaOH content and not the water content of these structures is an important variable, contrary to Sobue, Kiessig, and Hess, who advanced the opposite point of view.<sup>7</sup> It is likely that the three crystal structures of Na-cellulose I, IIA, and IIB contain varying amounts of NaOH, but probably an undetermined amount of water which is not part of the crystal structure. This conclusion is also supported by the results obtained after washing all

three Na-celluloses with distilled water, which resulted in Na-cellulose IV as the sole end product in all three cases (Na-cellulose IIB proceeded again through an amorphous stage). Because the diffraction pattern of Na-cellulose IV resembles that of cellulose II (in fact, simply drying Na-cellulose IV converts it to cellulose II), and only washing with water or methanol produces it, the crystal structure of Na-cellulose IV is likely to contain little, if any, NaOH.

**Effects of Lateral Compression on the Conversion of Cellulose I to Na-Cellulose I.** In order to determine the effects of an increasing degree of lateral compression of the fibers on the rate of formation of Na-cellulose I, the following experiment was performed. A bundle of approximately 550 ramie fibers was placed in a tapered glass capillary tube, and 3.5*N* NaOH solution was drawn into the tube by suction. Obtaining x-ray diffraction diagrams at three different positions in the tube, having diameters 0.8, 1.0, and 1.2 mm, respectively, showed that the extent of conversion to Na-cellulose I was markedly less at the position of the smallest diameter and considerably more at the largest diameter. Clearly, the higher the degree of sample compression, the slower was the rate of conversion. That this result was not due to the physical inability of the alkali to penetrate the sample was shown by repeating the experiment with 16.3*N* NaOH, which, despite the higher viscosity of the fluid, effected the conversion in only a few minutes at all positions in the sample tube. Similarly, holding the fibers under a high degree of tension, but not otherwise encased, gave results analogous to those obtained with 3.5*N* NaOH under high compression. The ability of the fluid to penetrate the unencased sample should not be affected by the degree of tension. The explanation of the observed effects of constraining the sample is probably to be found on a molecular level, i.e., in how swelling affects molecular mobility under different degrees of compression or tension.

## DISCUSSION

Despite indications in the early literature that many different Na-celluloses could be obtained during mercerization, our results show the number of unique structures to be small and their interconversion scheme—as shown in Figure 4—to be relatively simple.

Within this scheme, there appear to be two different types of Na-celluloses. To the first type belong Na-celluloses I, III, and IV, all having an approximately 10 Å fiber repeat, which is common to twofold helical cellulose conformations. The second type is represented by Na-celluloses IIA and IIB which exhibit an approximately 15 Å fiber repeat and thus, possibly a threefold helical chain conformation.

All other Na-celluloses described in earlier literature are likely to be poorly crystalline or incompletely formed structures, exhibiting ill-defined diffraction diagrams, or are mixtures of two or more structures. An example is a mixed 10–15 Å diffraction diagram that we have occasionally seen during the conversion of Na-cellulose I to Na-cellulose IV. This diagram may be representative of what Schramek and Succolowsky identified as Na-cellulose IIh.<sup>8</sup>

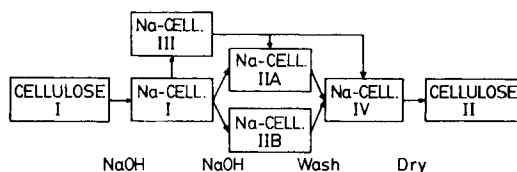


Fig. 4. Interconversion scheme of Na-celluloses during mercerization.

Several interesting features associated with the conversion scheme became apparent. One was that during the conversion of almost every structure to its successor in the scheme, the conversion did not proceed through an amorphous phase. In such cases, mixed crystal structures could be observed part way through the conversion. This was particularly clearly seen during the cellulose I to Na-cellulose I and the Na-cellulose I to Na-cellulose IIA or IIB conversions, as illustrated by the diffraction diagrams shown in Figure 3. These observations suggest crystalline-to-crystalline phase transformations, the significance of which is not yet clear.

Another interesting feature observed during these conversions concerns Na-celluloses IIA and IIB—the structures with an approximately 15 Å fiber repeat. It is significant that both form only from Na-cellulose I and not directly from cellulose I. Further, the more crystalline Na-cellulose IIB forms only in the absence of strong lateral compression or tension applied to the fibers, which, otherwise, would cause the formation of the less crystalline Na-cellulose IIA. These facts suggest that during the normal course of cellulose mercerization, the chain conformation undergoes a major change in response to the incorporation of NaOH in the crystal structure. The stability of the Na-celluloses IIA and IIB further suggests that the ca. 15 Å repeat structure may be the true intermediate occurring during the mercerization of cellulose. The shift of chain conformation away from the normal, twofold helical one with a 10.3 Å repeat may further allow larger changes to occur in the morphology of the crystalline fiber. Such changes may explain some of the gross changes that occur in the fiber during mercerization, for example, its longitudinal shrinkage, although, at this time, an adequate explanation does not exist. More information on the significance of this intermediate may be forthcoming once its crystal structure has been determined.

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