

Fine Structural Probes for the Evaluation of the Structure and Development of Cotton Fibers

The use of aqueous solutions of alkali metal hydroxides for evaluating the lateral order distribution (LOD) in cellulosic fibers has been known for a very long time.¹ An investigation on the lattice conversion behavior of cotton fibers was carried out more recently² which indicated that semioordered regions exist in the fibers. Similar work³ on jute has also led to interesting conclusions on the concept of the degree of crystallinity in cellulose fibers. Using kinetic data on the swelling of cotton fibers in aqueous ethylene diamine solutions collected employing x-ray diffraction methods, evidence for the existence of at least three types of fibrillar surfaces or regions of varying extents of hydrogen bonding has been presented.⁴ The results corroborated findings based on moisture regain data.⁵ In general, the conclusions were in agreement with the concepts discussed by Rowland and Roberts.⁶ All these studies have established the inadequacy of the crystalline-amorphous model for precisely describing the fine structural ramifications present in cotton fiber. The very early attempts to evaluate the LOD in cotton fiber,¹ it was felt, were likely to have been unsuccessful in revealing its finer aspects due to the employment of photographic film techniques and densitometer instrumentation, which were very poor methods compared with the sophisticated equipment now available. Furthermore, recent studies mentioned above pointed to the need for a fresh look into the LOD aspects with the main objective of assessing its potential in explaining physicochemical properties of the fiber which are not easily explained by conventional approaches adopting an oversimplified two-phase model.

Since reproducibility of results is very important in LOD studies, fiber treatment conditions were standardized through repeated experimentation and confirmation. Aqueous NaOH solutions were used in the experiments. Fibers of Giza-7 cotton were treated at $29 \pm 0.1^\circ\text{C}$ for 30 min in a thermostatted water bath with different concentrations of alkali. The strategy adopted was to employ wider intervals of normality initially to determine the range in which maximum changes in lattice conversion ratio (LCR)⁷ occurred and then narrowing down the interval within this range to the extent of 0.01 N. Identical washing and drying conditions were strictly adhered to for all samples, which were washed with flowing tap water and subsequently with distilled water. The samples were dried at the same temperature as washing.

The above scheme of treatment gave LCR values within the error limits ± 0.01 .

The x-ray diffraction (XRD) patterns of the sample were obtained from pellets of Wiley-mill cut fibers passed through a 40-mesh screen. A nominal pressure of 5 kg was applied for preparing the pellets in the standard sample holder. Ni-filtered Cu K α radiation from a stabilized x-ray generator with scanning diffractometer and recording arrangements formed the set-up for recording XRD patterns. The divergence and antiscatter slits were 0.5° and the receiving slit was 0.1 mm. All intensities were measured above the background level at $2\theta = 30^\circ$.

The results are presented in Figure 1. The broad details of normality versus LCR curve for cotton obtained for swelling with NaOH is fairly well known.¹ The present results indicate that the structural units within the fiber are more sensitive to alkali treatment in the range 3.50 to 3.80 N, in general agreement with earlier reports.^{1,8} What seems to be new information arising from the present study, however, is related to the LOD curve itself (Fig. 2). Four distinct regions can be clearly noticed in this curve. The regions marked A and B are identical to the two peaks mentioned for cotton in the literature.¹ The present data collected by careful and repeated experiments and using a well-aligned modern diffractometer scrutinized for reproducibility of intensities as well as diffraction angles, revealed that at least two more regions on the higher order side are present in the fiber. The regions in the fiber represented by C must be only a little higher in structural order compared with those responsible for peak B, while the regions of highest order marked D must have varying degrees of fine structural compactness within a rather broad range. To the first approximation, regions of intermediate order (B and C) quantitatively predominate over zones having very low (A) and very high hydrogen bonding (D). The ratios of the heights of the peaks

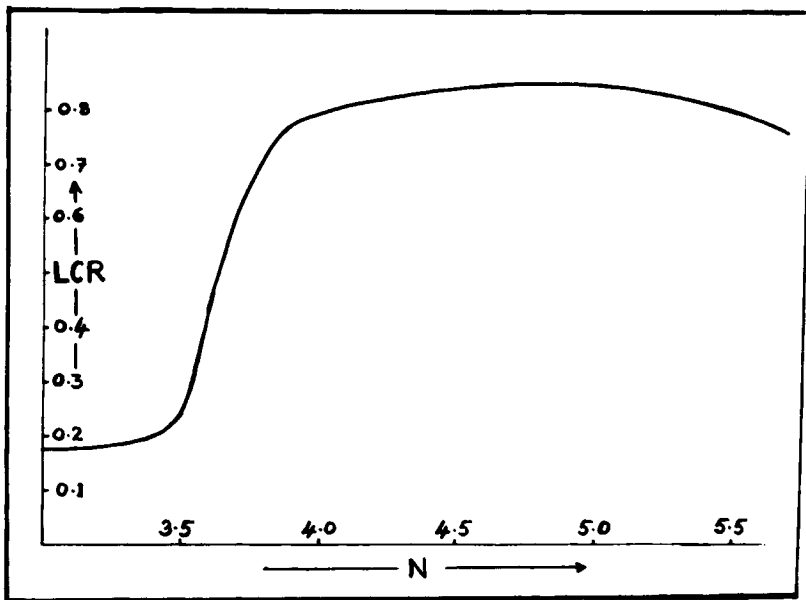


Fig. 1. Response of LCR to normality (N) of NaOH solution.

A, B, C, and D are in the order 1:16:9.375:0.875, which shows that regions of extreme order (A and D) have nearly the same peak heights. However, areawise comparison indicates that extremely well-ordered regions (D) may be quantitatively a little more. It may also be noted that very low-ordered regions tend to show up as a peak (A).

The present findings thus strengthen the concept of the existence of a spectrum of order in cotton fibers.^{1,2,8} The studies are being continued with other alkali metal hydroxides to evolve more

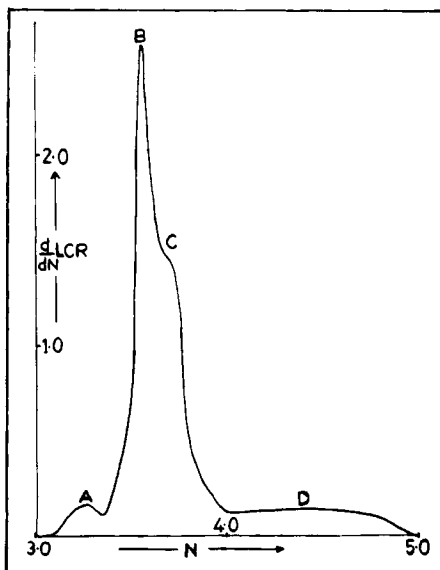


Fig. 2. The LOD curve obtained using NaOH.

suitable means to reveal still finer details of the LOD. The implications of the findings on fine structural aspects and reactivity of the cotton fiber will be discussed with these additional data.

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