

# Kinetics of Swelling of Cotton Fibers in Aqueous Ethylenediamine Solutions Using X-Ray Diffraction Data

P. K. CHIDAMBARESWARAN and N. B. PATIL, *Cotton Technological Research Laboratory (ICAR), Matunga, Bombay 400 019, India*, and A. D. PAWAR, S. R. SHUKLA, and H. T. LOKHANDE, *Department of Chemical Technology, University of Bombay, Matunga, Bombay 400 019, India*

## Synopsis

Kinetics of swelling of cotton cellulose with 75% (w/w) ethylenediamine (EDA) solution has been studied using X-ray diffraction. Apparently, the swelling reaction proceeds at three different rates, all obeying the first-order kinetics. The first rate ( $k_1$ ), which is the fastest one, is hypothetically attributed to the swelling action of EDA-monohydrate in the amorphous region of cellulose; the second rate ( $k_2$ ), which is extremely slow, is responsible for the penetration of swelling species into the crystallites, accompanied by breakage of the hydrogen bonds in these regions; and the third rate ( $k_3$ ), which is faster than  $k_2$  but slower than  $k_1$ , has been assigned to the decrystallization of the crystalline regions. The increase in temperature of swelling (from 10°C to 55°C) brought about increase in all these three rates with shortening of their respective periods. Thus, at temperatures of 35°C and above,  $k_2$  and  $k_3$  merge, giving a combined rate ( $k_{2+3}$ ). These results were confirmed from the data on the activation energy values. The changes in crystallinity were comparatively less, when 65% (w/w) EDA solution was used for swelling cotton fibers. The ineffectiveness of 65% (w/w) EDA solution was explained on the basis of the absence of powerful swelling species in the solution. An attempt has also been made to examine the kinetic data on the basis of the model for cotton fiber fine structure consisting of crystalline elementary fibrils and surfaces or regions of varying extents of hydrogen bonding.

## INTRODUCTION

The presence of sensitive linkages or segments of the microfibrils in cellulose has been studied by various workers, mainly using acid hydrolysis of unmodified and modified cotton fiber.<sup>1,2</sup> Lokhande,<sup>3</sup> from his swelling and decrystallization studies on cotton fibers, reported three types of fractions present in cotton cellulose, namely, low order ( $L$ ), intermediate order ( $I$ ), and high order ( $H$ ) fractions.

Results of kinetic studies on swelling of cotton fibers in aqueous ethylenediamine (EDA) solutions using moisture regain data were reported in an earlier paper from our laboratories.<sup>4</sup> The changes in crystallinity of EDA-treated cotton samples, as evaluated by X-ray diffraction technique, are presented in this communication. As is well known, the moisture regain technique provides an estimate of accessibility of the hydroxyl groups to water vapor, while X-ray crystallinity gives a physical measure of the 3-dimensional order in the fiber. The present investigation was, therefore, carried out to get a more complete picture of the swelling action of EDA on cotton fibers.

## EXPERIMENTAL

### Materials

Good quality long staple Sudanese cotton in loose form was used after purification using a standard procedure.<sup>5</sup> The purification of fibers essentially involved scouring and bleaching under specified conditions. EDA was of CP grade. It was distilled twice before use.

**Preparation of Swollen Cotton Fibers:** The methods used have been described in the earlier paper.<sup>4</sup>

**Determination of X-Ray Crystallinity:** Cotton fibers, weighing about 150 mg and treated in EDA as described in detail in the earlier paper,<sup>4</sup> were cut into fine powder, filled in the standard specimen holder, and mounted in place in the goniometer set up in the reflection geometry. Ni-filtered  $\text{CuK}_\alpha$  radiation from a stabilized Philips X-ray generator was used for recording the ratemeter scans. The diffraction patterns were used to derive estimates of decrystallization brought about by the treatments in the cotton fibers. Quantitatively, the decrystallization was expressed through the crystallinity index of Segal et al.<sup>6</sup> defined as

$$\text{CI} = \frac{I_{002} - I_{\text{am}}}{I_{002}} \times 100$$

where  $I_{002}$  and  $I_{\text{am}}$  are the intensities at the (002) peak and at  $2\theta = 18^\circ$ , respectively in the diffraction pattern. The conversion of cellulose I lattice into cellulose II type was evaluated using the lattice conversion ratio of Vigo et al.<sup>7</sup> defined as

$$\text{LCR} = I(2\theta_{002} - 2)/I_{002}$$

where the numerator represents the intensity at an angle which is two degrees less than the  $2\theta$  position of the (002) peak in the diffractogram.

The error limits for CI and LCR were  $\pm 1\%$  and  $\pm 0.01\%$ , respectively.

## RESULTS AND DISCUSSION

### Swelling with 75% (w/w) EDA Solution

The kinetic aspects of the decrystallizing action may be evaluated better using Figure 1, where  $\log(\text{crystallinity})$  has been plotted as a function of time. For treatment at  $10^\circ\text{C}$ , the initial fast rate of decrystallization ( $k_1$ ) is followed by an extremely slow rate ( $k_2$ ) and, subsequently, by a faster rate ( $k_3$ ). The three rates persist during the swelling reaction at  $20^\circ\text{C}$  also, although the duration for  $k_2$  is reduced to a certain extent. With further increase in temperature to  $35^\circ\text{C}$  (which seems to be the transitional temperature) and above, the rates  $k_2$  and  $k_3$  seem to merge to yield a single rate, which may be designated as  $k_{2+3}$ . It may also be observed that the levelling off of crystallinity is reached within shorter reaction periods at higher swelling temperatures. It can be seen that the reaction follows the first-order kinetics.

The quantitative data on the rate constants and the corresponding activation energies are presented in Table I. It may be seen that the rate constants increase with increase in temperature. In addition, it may be also noted that the ratio

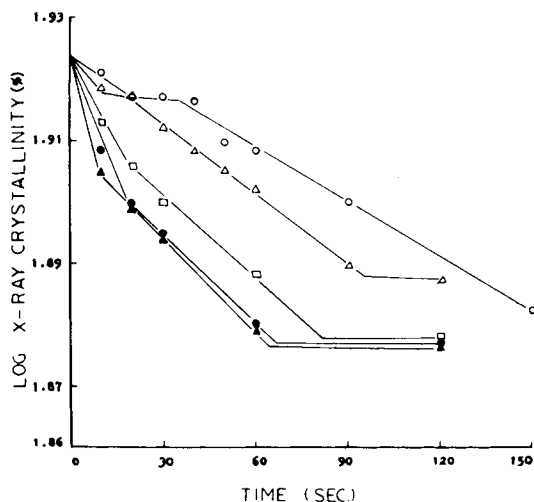


Fig. 1. Rate curves for swelling reaction of cotton fibers with 75% (w/w) EDA: (○) 10°C; (△) 20°C; (□) 35°C; (●) 45°C; (▲) 55°C.

$k_1/k_3$  increases with increase in temperature from 10°C to 35°C; the same is true for the ratio  $k_1/k_{2+3}$  in the temperature range 35°C to 55°C. By comparing the values of the rate constants and their ratios, it may be concluded that  $k_1$  is favored, in comparison to  $k_3$  and  $k_{2+3}$ , at higher temperatures. As regards data on activation energies, it may be noted that the value of  $E_1$  (temperature range 10–55°C) is 7.37 kcal/mol, while  $E_3$  (temperature range 10–35°C) and  $E_{2+3}$  (temperature range 35–55°C) have the identical value 2.53 kcal/mol. The relevant Arrhenius plots are given in Figure 2.

For the purposes of discussion, the results obtained using moisture regain data<sup>4</sup> may be briefly recalled. It was observed in the above work that the decrystallization was characterized by three rate constants,  $k_1$ ,  $k_2$ , and  $k_3$  at lower temperatures (10°C <  $T$  < 35°C); only  $k_1$  and a combined rate,  $k_{2+3}$ , could be evaluated at higher temperatures (35°C <  $T$  < 55°C). On the basis of the results obtained, it was suggested that (a)  $k_1$  corresponds to swelling of amorphous and mesomorphous regions, (b)  $k_2$  refers to the penetration of the EDA-monohydrate into the crystallites, (c)  $k_3$  pertains to the decrystallization resulting from the breakage of H bonds, and (d)  $k_{2+3}$  results from merging of  $k_2$  and  $k_3$  at high temperatures.

TABLE I  
Rate Constant and Activation Energy Values for EDA<sup>a</sup>-Swollen Cotton Fibers<sup>b</sup>

Temp (°C)	Rate constant $\times 10^{-5} \text{ s}^{-1}$			$k_1/k_3$	$k_1/k_{2+3}$	Activation energy (kcal/mol)		
	$k_1$	$k_3$	$k_{2+3}$			$E_{1(10-55^\circ\text{C})}$	$E_{3(10-35^\circ\text{C})}$	$E_{2+3(35-55^\circ\text{C})}$
10	63.33	73.69	—	0.86	—			
20	103.63	85.21	—	1.22	—		2.53	
35	213.02	100.75	100.75	2.11	2.11	7.37		
45	287.87	—	115.15	—	2.50			
55	426.05	—	124.36	—	3.43			2.53

<sup>a</sup> 75% (w/w) EDA, washed with water.

<sup>b</sup> From X-ray diffraction data.

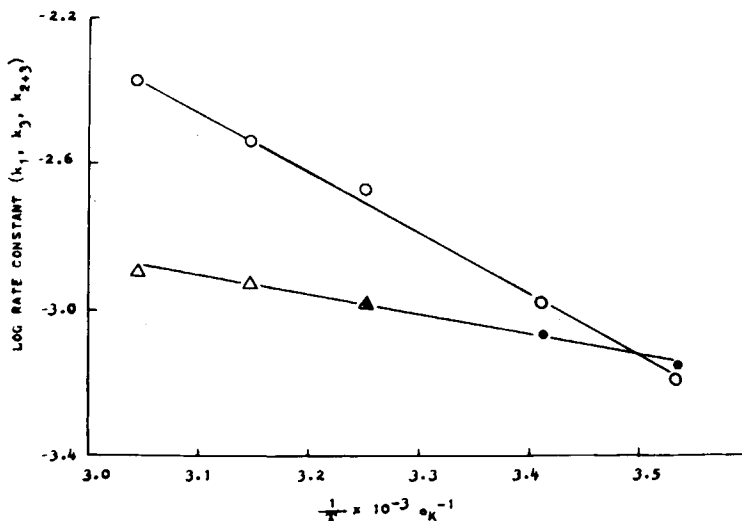


Fig. 2. Arrhenius plots for the reactions. (O)  $E_1$ , 10–55°C; ( $\Delta$ )  $E_{2+3}$ , 35–55°C; ( $\bullet$ )  $E_3$ , 10–35°C.

The X-ray diffraction data are qualitatively similar insofar as observations of the three rate constants at lower temperatures ( $10^\circ\text{C} < T < 35^\circ\text{C}$ ) and two rate constants at higher temperatures ( $35^\circ\text{C} < T < 55^\circ\text{C}$ ) are concerned. However, some differences in the temperature dependence of the ratios of rate constants (such as  $k_1/k_3$ ) exist. Besides, the magnitudes of the rate constants obtained by the two methods are considerably different, the maximum difference being shown by  $k_1$  and the minimum by  $k_{2+3}$ . In view of this, it becomes necessary to have some working model of fiber structure encompassing both moisture sorption and X-ray diffraction phenomenon to clarify the issues involved.

If we assume a simplistic picture in which moisture sorption is decided by the availability of cellulosic hydroxyl groups and X-ray scattering by the proportion of crystallites capable of contributing to the diffraction maxima, we should expect correspondence in results obtained using the two methods, only for that phase of reaction which involves disruption of the crystalline structure. In other words, the main common feature should correspond to the reaction represented by  $k_{2+3}$ . To a smaller extent, some similarity of behavior of the rate curves may result in the region characterized by  $k_1$  also, (a) if the "mesomorphous" part in the fiber structure is fairly significant as compared to the "amorphous" portion and (b) if these parts have dimensions of the minimum order required for effectively contributing to the diffraction maxima.

As regards  $k_2$ , it is doubtful whether penetration of the swelling agent, which can affect the availability of hydroxyl groups for moisture sorption, will be reflected in the X-ray diffraction results, unless the process induces considerable strains and distortions in the crystallites. This phase can be visualized as a prelude to the actual decrystallization, which could easily occur in a strained crystallite.

The above hypothesis would explain (i) the observation of the rate constant  $k_1$  in both the methods, (ii) the maximum closeness of values of  $k_{2+3}$  in comparison to other corresponding rate constants, obtained by the two methods, and

(iii) the comparatively shorter duration of the phase  $k_2$  in the X-ray data as compared to the moisture regain data. Thus, they provide the means for unified interpretation of the results obtained using the two experimental techniques.

The identical value of  $E_3$  and  $E_{2+3}$  indicates the similarity of the mechanism of decrystallization of the high-ordered regions.  $E_3$  and  $E_{2+3}$  represent the activation energies for the breakage of hydrogen bonds in the high-ordered regions by the swelling species which have already penetrated the crystallites.  $E_1$ , on the other hand, represents activation energy for the swelling reaction in the comparatively low-ordered regions. Here, the mechanism of decrystallization seems to be the initial penetration of the swelling species, followed by the hydrogen bond-breaking action in these regions. Hence,  $E_1$  is greater than  $E_3$  and/or  $E_{2+3}$ .

It may be interesting to view the above model of fine structure, involving mesomorphous regions and straining of crystallites, against the concepts put forward by Lokhande<sup>3</sup> and Rowland and Roberts.<sup>2</sup> Lokhande,<sup>3</sup> from swelling and decrystallization studies, visualized three levels of hydrogen bonding in cotton cellulose, viz., low (*L*) intermediate (*I*), and high (*H*) order. Rowland and Roberts<sup>2</sup> also envisaged essentially three levels of order, viz., low (*C*), intermediate (*B*) and high (*A*) order, and correlated these with reaction surfaces of different types in the microstructure built up by completely crystalline elementary fibrils. The present results of kinetic studies can be fitted into the above models, if regions *L* (or *C*) are taken to represent the "amorphous" and "mesomorphous" regions represented by the rate constant  $k_1$ , and those of predominantly type *I* (or *B*) and partly *H* (or *A*) are assigned to the swelling reaction corresponding to the rate constant  $k_2$ . The disruption of the structure of the elementary fibrils may correspond to  $k_3$ .

On the basis of the above, the swelling and decrystallization of cotton fibers in 75% (w/w) EDA solution may be visualized to proceed as follows. The swelling agent first acts upon the regions of high accessibility, containing weak hydrogen bonds, which may be taken to represent amorphous and mesomorphous structures. The interaction between the reagent and these regions is extremely fast. Subsequently, the interfibrillar hydrogen bonds of higher strength are affected. Penetration of the swelling agent into these regions is predominantly controlled by temperature-dependent diffusion processes. In the last stage of this phase, disruption of the still stronger hydrogen bonds in the tightly coalesced interfibrillar regions may be initiated. The fibrils would be, thus, almost fully exposed to the swelling species. This situation, combined with the powerful donor-acceptor interaction between EDA and cellulose, leads to the observation of rapid decrystallization in the fibrillar units of cellulose structure.

The differences, observed in the magnitudes of the corresponding rate constants and their temperature-dependent behavior may be partly due to the different bases of moisture regain and X-ray diffraction measurements. Besides, the swelling with EDA also brings about noticeable changes in the values of lattice conversion ratio of the samples, as shown in Figure 3. It has been mentioned that the accessible surface on elementary fibrils in the mercerized fiber is about double of that of the native fiber and that the number of segments of low order, or of type *C* per unit length of elementary fibril is about 60% greater in the former.<sup>2</sup> Such factors may influence sorption phenomena to a greater extent compared to the X-ray diffraction observations. They may also account for the

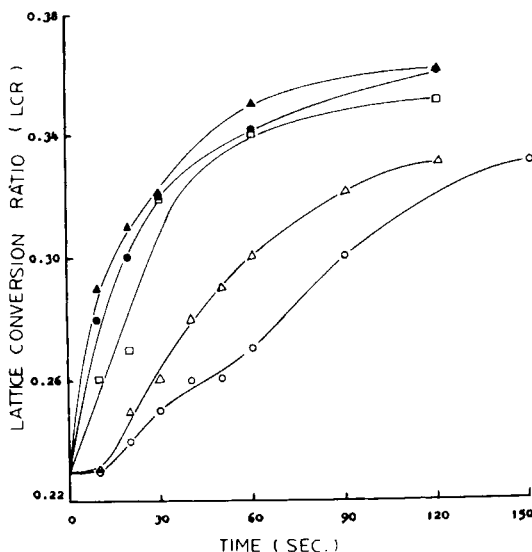


Fig. 3. Lattice conversion ratio vs. time of swelling reaction of cotton fibers with 75% (w/w) EDA: (○) 10°C, (△) 20°C; (□) 35°C; (●) 45°C; (▲) 55°C.

maximum decrease of nearly 22% "crystallinity" shown by moisture regain data,<sup>4</sup> as compared to the corresponding figure of only 8.4% maximum decrease evident in X-ray data.

Thus, although exact correspondence of the phases of swelling reaction, as obtained by the two techniques, may not be obvious, the present studies indicate qualitative similarities which can be understood in terms of cellulose crystallites (or microfibrils) possessing substructures. More specifically, it seems that the swelling process, after affecting the relatively more disorganized regions, has to cross a barrier before the crystalline portions in the fiber can be disrupted.

### Swelling with 65% (w/w) EDA Solution

Our earlier studies on swelling of cotton fibers in 65% (w/w) EDA solutions had indicated that the increase in moisture regain was considerably less as compared to the treatment with 75% (w/w) EDA, even at higher temperatures. Only two rate constants were observed for swelling with 65% (w/w) EDA solutions, and these were assigned to (i) opening up of the accessible portions of the fibers and (ii) opening up of the mesomorphous portions as well as surfaces of crystallites. Regions containing very weak hydrogen bonds (*L*) or surfaces of type (*C*) were suggested to represent the amorphous and mesomorphous phases in the earlier discussion. If the mechanisms suggested on the basis of moisture regain data are correct, the X-ray results should reveal (i) absence of any change in crystallinity when the swelling agent acts initially on the truly amorphous cellulose and (ii) a consequent small disordering when the mesomorphous regions are attacked.

Figure 4 shows typical data obtained on treatment of cotton fibers with 65% (w/w) EDA solution at 45°C, a temperature at which the effects should be fairly pronounced.

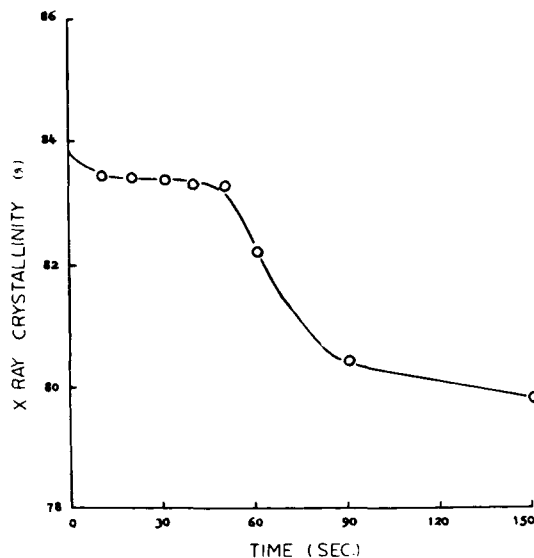


Fig. 4. X-ray crystallinity vs. time of swelling reaction of cotton fibers with 65% (w/w) EDA at 45°C.

It may be noticed that the results are close to expectations, there being little decrystallization up to about 50 s and about 3% decrystallization from 50 to 90 s. For the sake of completeness, it is to be added that the lattice conversion ratio did not register any major changes after this treatment, confirming thereby that the strongly hydrogen-bonded or crystalline regions were not brought into the picture. Besides, the X-ray diffraction data also confirm the comparatively poorer action of 65% (w/w) EDA solution in comparison to 75% (w/w) EDA solution on cotton fibers, perhaps due to the absence of EDA-monohydrates in the former solution.

The present studies seem to generally corroborate conclusions based on moisture regain data.<sup>4</sup> Besides, they also suggest a new way of considering X-ray diffraction results in terms of the concepts of fine structure of cotton cellulose based on crystalline fibrils.

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