Layer Morphology and Its Relation to Swelling and Structure: II. Cotton Fibers Treated with Ethylenediamine and Zinc Chloride

INTRODUCTION

Layered cross-sectional morphology of cotton fibers treated with different alkali metal hydroxides was reported earlier.[1] It was noted that structural variations and cross-sectional morphology showed good correspondence and the structural parameters such as residual cellulose I (CI) content and the resolution parameter (RP) of the residual cellulose could be utilized to predict the layered structure and vice versa, though qualitatively. The present study has been undertaken with a view to see whether the structure–layer relationship remains valid when entirely different class of swelling agents are used. The investigation has brought out some interesting aspects of swelling with reagents like ethylenediamine (EDA) and zinc chloride ($ZnCl_2$). The results are presented here and discussed briefly.

MATERIALS AND METHODS

Kier-boiled cotton fibers were swollen in 80% (v/v) EDA and 65% (w/w) $ZnCl_2$ for different intervals and cycles. Fibers were also swollen in 3.7*N* NaOH, 3.5*N* KOH, and 4.0*N* LiOH at room temperature (RT).

The X-ray diffractograms of the treated fibers were obtained and the structural parameters were evaluated following the methods described earlier.[2] The layered cross sections of the treated fibers prepared by standard procedure[3] were coated with platinum and examined using a Hitachi HU11E electron microscope at 75 kV.

RESULTS AND DISCUSSION

Structural parameters of the differently swollen fibers are given in Table I. It is obvious from the table that all the swelling treatments have produced a partial conversion of the native lattice into cellulose II (CII). However, the layered cross-sectional morphology of fibers treated with metal hydroxides are different from that of fibers treated with other swelling agents. Partial lattice conversion after swelling in lower alkali concentrations revealed very clearly the bilateral structure in the layered section and contained CI and CII in the same cross section.[4] The layered sections of fibers once treated with EDA are given in Figure 1. These do not reveal any bilateral structure and probably indicate uniform swelling. The ultra-structure of the layers show fibrillar texture as in native cellulose fibers. The interesting observation is that the layered cross section is highly swollen within the lamellae and hence the layers showed a higher separation than that observed for normal cotton fibers. This probably is the result of high swelling and subsequent decrystallization that weakened some of the interfibrillar binding forces leading to the breakdown of a few fibrils bridging the lamellae.

Layered cross sections of fibers swollen in EDA for five cycles are shown in Figure 2. Structurally, as regards the amounts of CI and CII, this sample is very close to that obtained after 3.7*N* NaOH treatment, although the RP of residual CI is poorer for the former (Table I). Low RP for CI suggests that EDA is able to penetrate even the highly ordered crystalline regions and produce extensive swelling. As a result we observe no bilateral structure and the honey-combed structure is sparingly seen. Layers show

Table I X-ray Data of Fibers Treated in Various Swelling Agents

	X-ray Data				
Treatment	CI	CII	Total	Am	RP of CI
1. None	70	0	70	30	2.6
2. 4.0*N* LiOH RT	34	34	68	32	4.6
3. 3.7*N* NaOH RT	33	34	67	33	5.0
4. 3.50*N* KOH RT	26	37	63	37	3.4
5. 80% (v/v) EDA RT					
(a) 30 min once	42	13	55	45	2.7
(b) 30 min 5 times	29	29	58	42	2.7
6. 65% (w/w) $ZnCl_2$ RT					
(a) 15 min once	20	19	39	61	—
(b) 1 h once	18	18	36	64	—
(c) 15 min, 5 times	13	22	35	65	—

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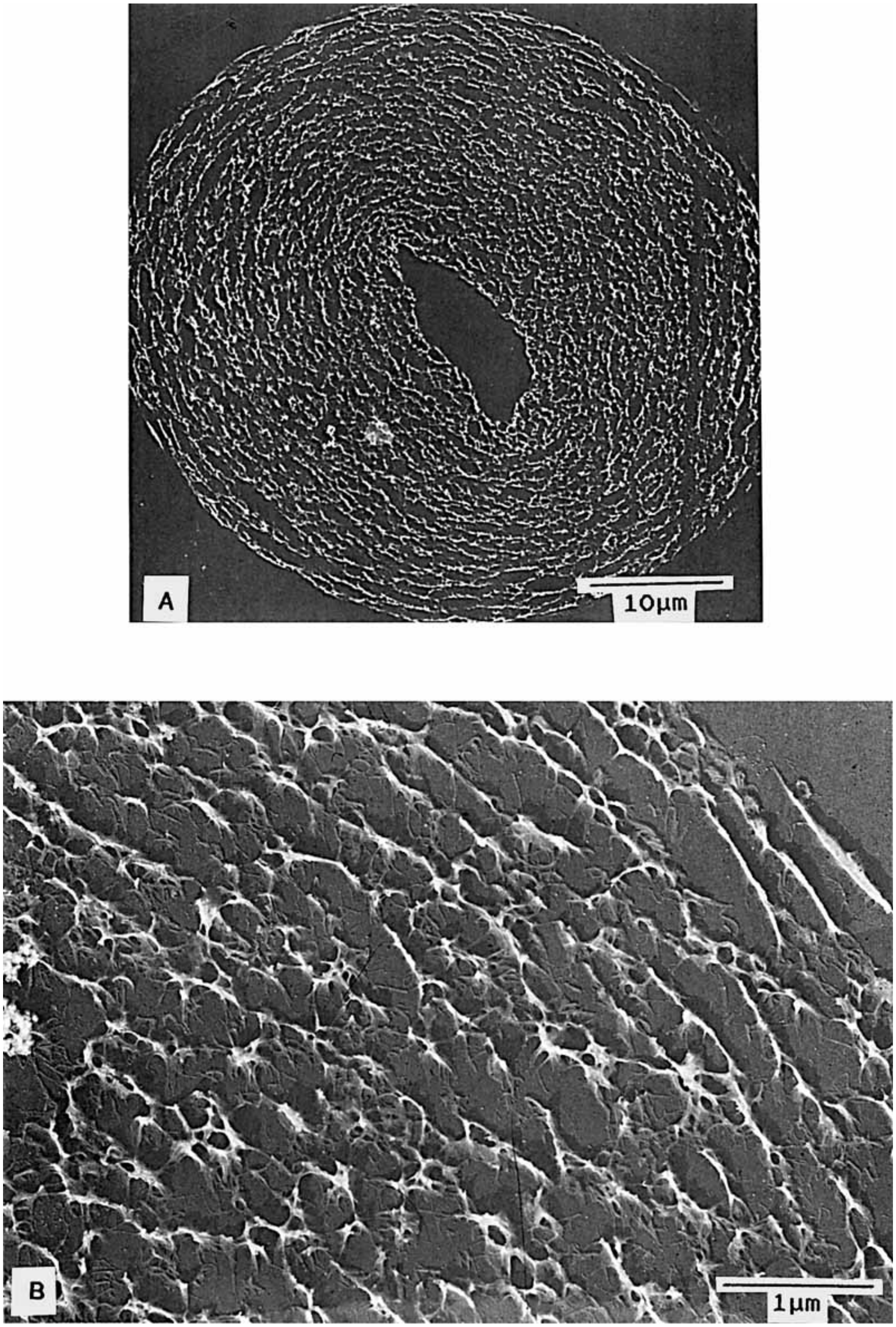

Figure 1 Layered cross section of fibers swollen in 80% (v/v) EDA at room temperature once: (a) low magnification and (b) fibrillar texture of terminal zone at high magnification.

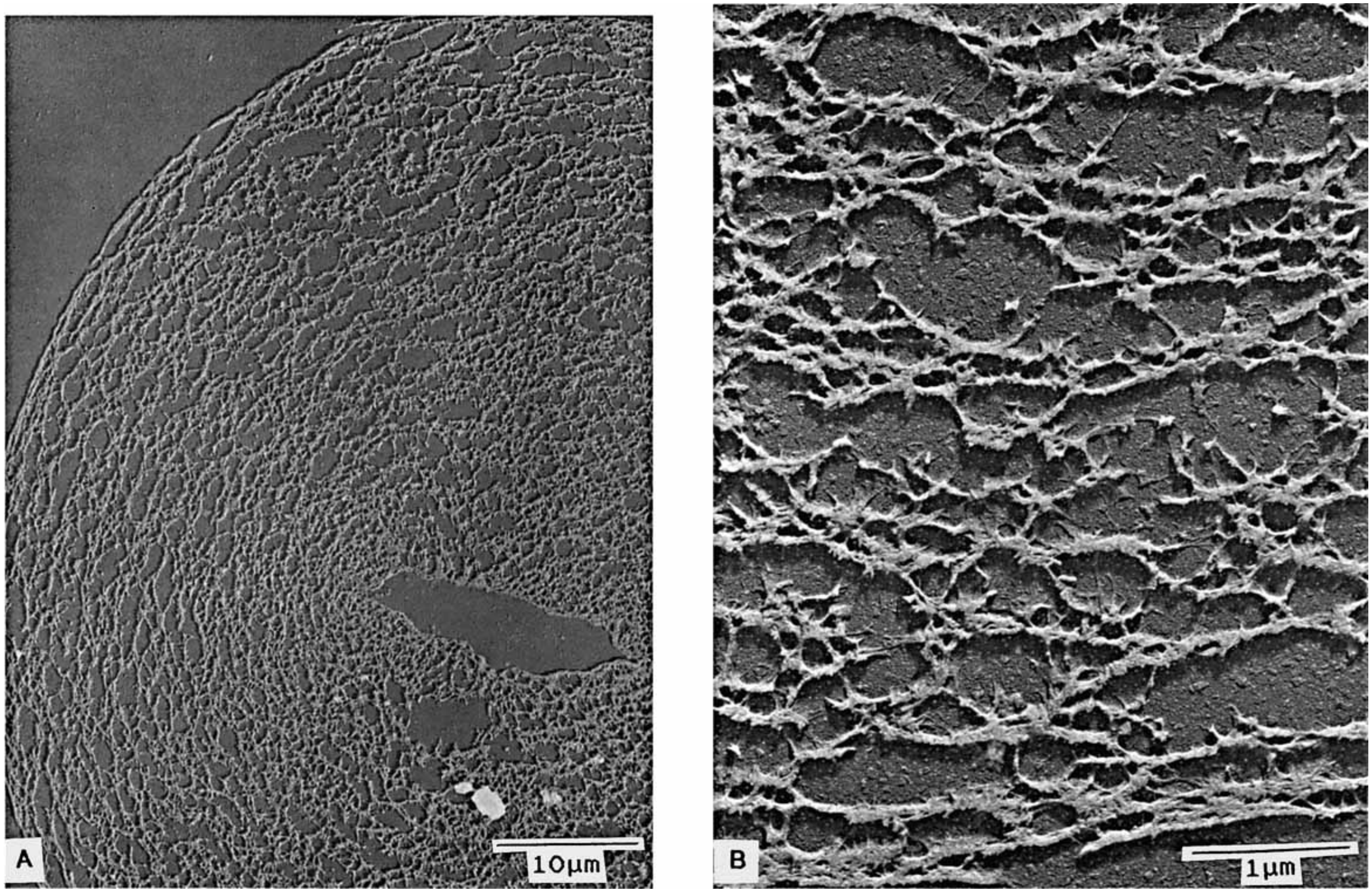

Figure 2 Layered cross section of fibers treated with 80% (v/v) EDA at room temperature five times: (a) low magnification and (b) fibrillar texture of terminal zone at high magnification.

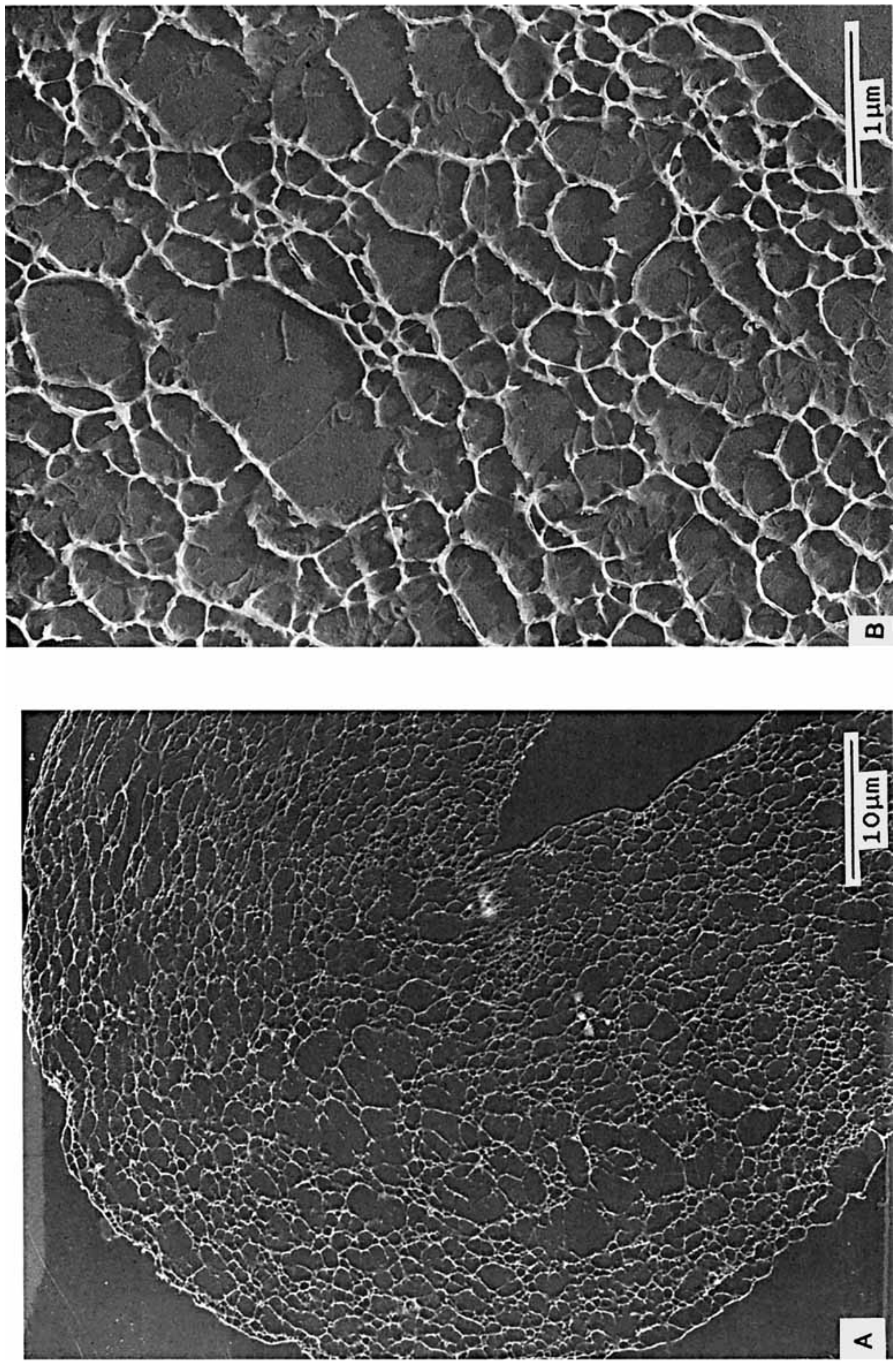

Figure 3 Layered cross section of fibers treated with 65% (w/w) $ZnCl_2$ at room temperature, once: (a) low magnification and (b) layer structure of middle zone at high magnification.

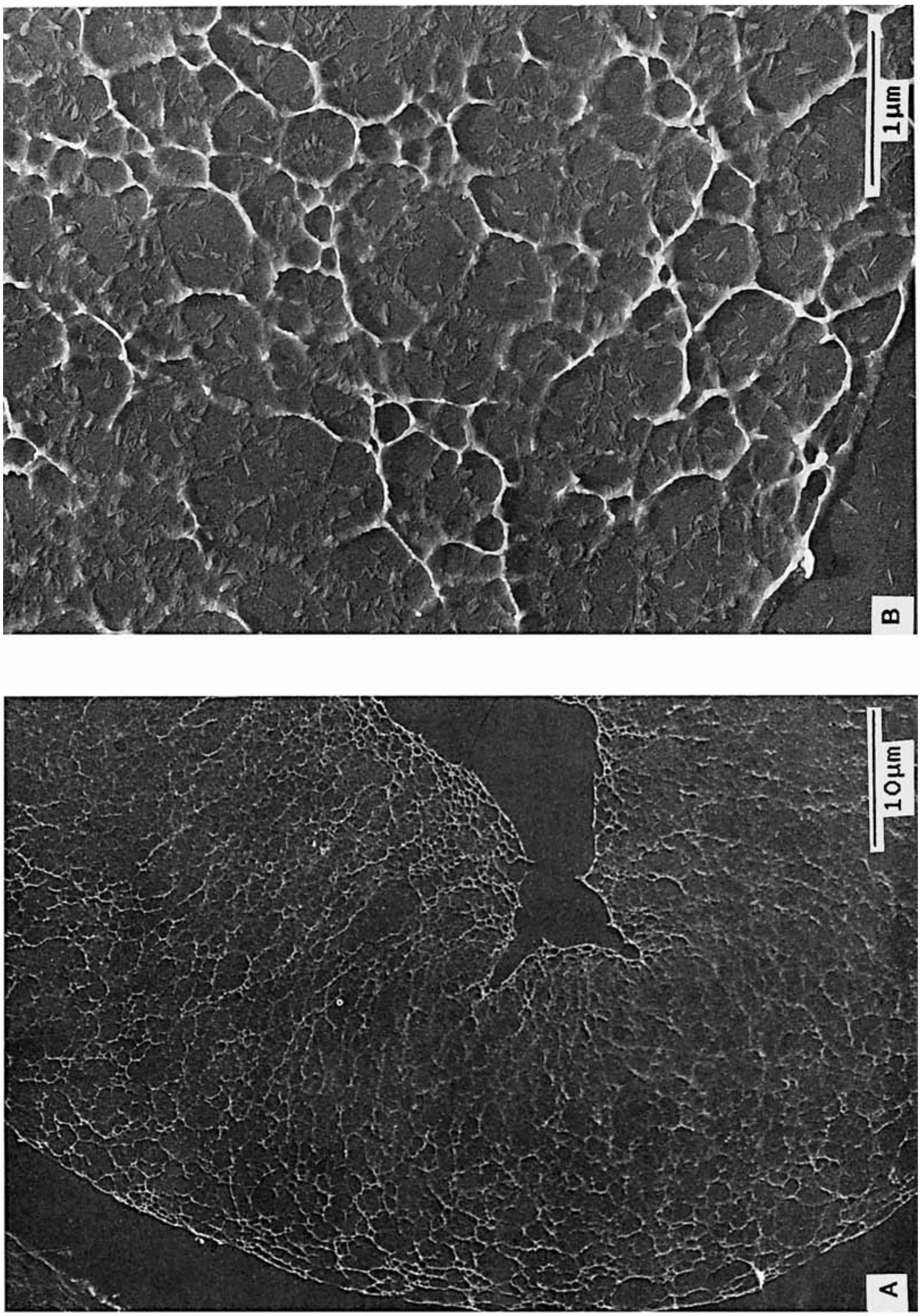

Figure 4 Layered cross section of fibers swollen in 65% (w/w) $ZnCl_2$ at room temperature, five times: (a) low magnification and (b) structure of layers at high magnification.

predominantly fibrillar texture, and the separation between layers is much higher than that observed for untreated cotton fibers. Further, this highlights an important criterion for observing the bilateral structure. The bilateral structure would be preserved after swelling: If and only if (a) CI and CII are present in sufficient amounts and (b) swelling is predominantly intercrystalline and intracrystalline only for the less ordered regions.

In Figure 3 we have layered sections of 65% (w/w) $ZnCl_2$ treated fibers. Here the layer morphology shows honey-comb structure with fibrillar texture. XRD data (Table I) for this sample shows 20% CI, 19% CII, and 61% amorphous (Am). This high decrystallization did not produce any remarkable change in layer morphology, except that it showed higher layer separation than that observed in raw and alkali treated fibers. Fusion of layers during $ZnCl_2$ treatment was reported by earlier workers.[5] However, no structural data was given that could help in an accurate comparison of the present treatment with that reported earlier. Fusion of layers appears a remote possibility even in cases of very high swelling as discrete microfibrils were observed during fragmentation.[5] Hence we feel that a proper layer expansion micrograph should show a layered section revealing fibrils and lamellae as obtained in the present investigation.

To confirm that $ZnCl_2$ treatment does not inhibit layering, fibers were swollen at room temperature for an extended period of time and also repeatedly up to five cycles. Micrographs of the layered fiber sections for these multiple swollen samples (Fig. 4) show layers with honey-comb structure. The layers are well separated and show fibrillar texture [Fig. 4(a)] though there are fusion of smaller fibrils [Fig. 4(b)]. Dissolution of some of the layers is also observed. Needle-shaped fibrillar fragments are seen spreading all over the section indicating some disintegration brought about by extreme swelling. If $ZnCl_2$ had helped to form permanent bonding between the cellulose chains, then the layering would not have taken place. Since layering is observed even in the highly swollen fibers, it can be inferred that though $ZnCl_2$ is a powerful intracrystalline swelling agent, it does not form any new chemical bond within or between the chains. In other words, the swelling action of $ZnCl_2$, though more severe, is more or less similar to that produced by alkali metal hydroxides, and that differences are noted predominantly in the layered structure and amorphous content.

CONCLUSIONS

Fibers swollen in both EDA and $ZnCl_2$ could be layered by the layer expansion technique, although the layer separations are much higher as compared to those normally obtained with raw cotton fibers. In spite of a lot of residual CI, swelling by both these reagents does not preserve the bilateral structure existing in cotton and made more visible by partial mercerization in alkali metal hydroxides. This indicates that they produce an extensive and uniform swelling although the phenomenon is very much time dependent. The ultra-structure of the layers show fibrillar texture after EDA swelling while the layers showed honey-comb structure with fibrillar texture after $ZnCl_2$ swelling.

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