Pore Structure Analysis of Purified, Sodium Hydroxide-Treated and Liquid Ammonia-Treated Cotton Celluloses

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Synopsis

To characterize the pore structures of purified cotton, NaOH-treated cotton, and liquid-NH_3-treated cotton, we have (1) investigated the feasibility of preparing useful chromatographic columns from whole cotton fibers and (2) studied the elution behavior (penetration) of three selected classes of water-soluble solutes from columns of the three types of cotton fibers. The solutes were series of common oligomeric sugars, oxyethylene glycols, and oxyethylene glycol dimethyl ethers having molecular weights or dimensions in the range of conventional dyes and finishing agents. Substantial differences in dyeing performance and in resilience have been reported for the cottons under study. Differences in performance qualities of these fibers in fabric form are explained in terms of the substantial differences in sizes and abundance of pores in the fibers.

INTRODUCTION

A direct approach to information on porosity of wet cotton fibers and to penetration of solutes into cotton fibers makes use of reverse gel filtration: i.e., application of solutes of known molecular weight and/or size to columns packed with the substrates to be characterized for relative abundance and sizes of pores. Preceding studies[1-3] dealt with cotton fibers chopped to pass 20–80-mesh screens; columns were packed with these particles in a conventional manner.

The desire for measurements on the whole cotton fiber as it exists in a yarn or fabric led to this exploratory study of the preparation and assessment of whole-fiber cotton columns packed by nonconventional means. The realization of a packing mode for columns for which discrete elution peaks were obtained for the selected solutes was followed by an assessment of the behavior of three types of cotton fibers. These cottons were selected for their pertinence to durable-press finishing and to the realization of optimum balances of textile performance qualities.

Substantial improvements in performance qualities of cotton result from swelling of cotton fibers with NaOH (> 13% concentration) or liquid NH_3 prior to chemical finishing.[4,5] Improvements of performance qualities that result from swelling in one or both of these swelling media and that are of interest to the textile industry occur in dimensional stability, luster, dye uptake, fiber light diffusion, fabric softness or handle, and fabric smoothness and resilience. The two swelling agents often generate similar effects, but there are substantial differences in the degree of some of their contributions

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to performance qualities. Our particular concern in this report lies in the fact that NaOH is superior in increasing depth of dyeing and that liquid NH_3 is superior in generating resilience. It is desirable to understand the causes of these differences with the subsequent possibility of achieving both of these qualities as a result of a single swelling treatment.

Conventional commercial swelling of fabric with NaOH commonly employs 23% caustic, and swelling of fabric with liquid NH_3 involves evaporative removal and recovery of the agent. Our choice of fibers for characterization of pore structure includes these considerations and consists of purified cotton, NaOH-treated cotton, and liquid-NH_3-treated cotton.

This report describes the operations that led to useful whole-fiber cotton gel filtration columns, and it concerns differences in pore structures among the three types of cotton fibers noted above.

EXPERIMENTAL

Materials

Cotton was used in a variety of forms, i.e., batt, sliver, ball, yarn, and fabric. The form employed in the bulk of the study was sterile absorbent cotton batting, U.S.P., Acme, White Cross, or ACCO brands. The batting was immersed and soaked in 23% NaOH at room temperature followed by extensive rinsing in water at ambient temperature. To facilitate handling of the batting, it was supported on a plastic grid and contained in an open-weave cotton fabric. The product was characterized by X-ray diffraction and shown to be converted essentially completely to lattice II pattern. The treatment with liquid NH_3 was conducted as described by Calamari et al.[4] with evaporation of almost all of the ammonia before final quenching in and rinsing with water. The X-ray diffractogram for this cotton was intermediate between those reported by these authors for the product from evaporation of NH_3 and that from water quenching of the NH_3–cellulose; the nature of the diffractogram indicated substantial disorder and showed the 002 peak at slighly lower 2θ angle than that for lattice I cellulose. The original absorbent cotton exhibited a clean-cut lattice I pattern. The lattice I and lattice II diffractograms from the samples of cotton noted above were near identical to those illustrated by Calamari et al.[4]

All water to make up solutions or for elution of the columns was deaerated, deionized, and filtered through a 0.45-μm Millipore filter for removal of particulate material and for cold sterilization. Most of this water contained 0.02% sodium azide as a preservative of a microbiological-free system.

Glucose, maltose, raffinose, and stachyose were commercial products, some obtained in hydrate form.[1] Mono-, di-, tri-, and tetraethylene glycols and the corresponding oxyethylene glycol dimethyl ethers were also commercial products. Dextran T-40 (MW 40,000) was from Pharmacia and D_2O was from Stohler Isotope Chemicals. These compounds appeared as single, discrete peaks in column chromatography on Sephadex -15.

Methods

The Cheminert columns were glass, 60 cm long × 2.54 cm internal diameter and were packed over a minimum height of 40 cm. Columns, whether packed wet or dry, were subjected to circulation of water for periods adequate to allow swelling and removal of trapped air. Solutes were introduced individually as 1% aqueous solutions through a 0.5-mL sample loop into the columns. Elution was at a linear flow rate of 26 mL/cm²/h. The eluates were monitored continuously with a Pharmacia differential refractive index unit. Volumes of eluate were measured gravimetrically by collecting 10-mL fractions in tared test tubes and then summing weights of fractions and proportional parts of fractions between solute injection and peak elution for each sample. D-Glucose was included as a reference standard with each set of about six samples. This procedure is similar to those described earlier.[1-3,6,7]

RESULTS

Preparation and Assessment of Whole-Fiber Cotton Columns

Among the various trial preparations of columns were (1) settling of loose fibers into a column, (2) random or ordered packing of chunks, balls, and sliver, (3) ordered wrapping of sliver, roving, yarn, and fabric prior to or during insertion into the column, and (4) ordered packing of die-cut disks of batting and fabric. Encouraging leads were not uncovered relative to items 1 and 3. Columns prepared by packing wet-out chunks or plugs of cotton showed visual stratification and resulted in a diffused broad indistinct dye band, but discriminated in elution volume (V_e) among dextran T-40, glucose, and D_2O. The peaks were not symmetrical, and replication of V_e's was poor. Columns packed with vertical rolls of fabric, with vertical strands of sliver, with die-cut disks of fabric, etc. failed to discriminate in V_e's among the solutes noted above; channeling in some of these packings, such as in the case of die-cut fabric, might be eliminated or at least reduced by precisely adjusting the die or column diameter, fabric construction, or taking shrinkage into consideration. Columns packed with die-cut disks of batting offered greater potentiality than others noted above. These columns were packed in the dry state from disks cut with a die having the same diameter as the interior of the column. Dry plugs were pressed together tightly (6–8 lb/in.²) with a dowel rod. Subsequent performance of the column was improved by additional compression after thorough wetting and by addition of more disks of cotton. Columns compressed in the dry state were characterized by high values of V_0 (measured with dextran T-40): e.g., 173 mL. But this value was reduced as much as 30% by compaction. The columns packed with disks of batting gave elution peaks that were less symmetrical and broader than those from Sephadex G-15 or chopped cotton; it was not unusual to observe a miniature peak or skew on the leading side of each solute peak with the whole fiber cotton columns. After several days use or soaking, these cotton columns stabilized, and results were very reproducible.

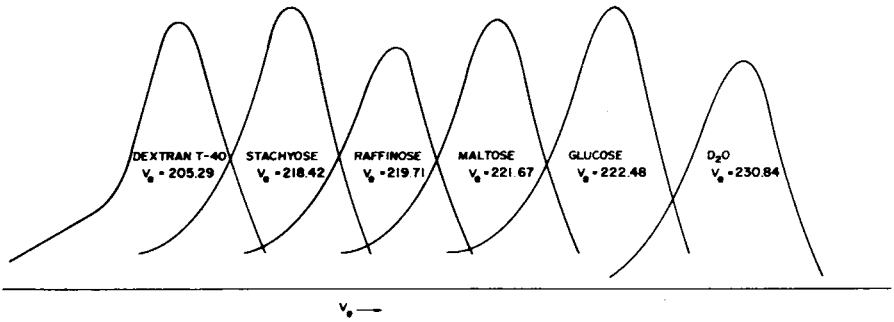

Fig. 1. Elution curves reproduced as obtained in a series of tests for the indicated solutes arranged with increasing elution volume (V_e) from left to right.

Accessible water for these columns ranged from 18 to 26 mL compared to about 90 mL for corresponding Sephadex G-15 columns.

Typical curves for solutes eluted from a whole-fiber cotton column are illustrated in Figure 1. These elution curves are shown with increasing V_e and decreasing molecular weight of the solute from left to right side of the figure. Typical values of V_e for each solute are shown in the figure. Standard deviations for V_e's generally fell in the range of 0.01 with a predominance of values below 0.01 and as low as 0.002 for some columns. Thus, the small difference in V_e's from one to another solute did not detract from the value of the measurement, as will become evident in the following section. It is emphasized that these columns were not suitable for separations of compounds and that all measurements resulted from injections of individual solutes into the columns. An elution curve is shown for D_2O; however, the V_e's for D_2O on the various cotton columns proved unacceptable substitutes for corresponding values for H_2O without thorough investigation of the relationship. The V_e's for D_2O were 4–6% higher than the V_e's estimated for H_2O by extrapolation of the sugar lines (Fig. 2) back to MW 18. Differences are due to—OD/—OH interchange.

Characterization of Whole-Fiber Cottons in Gel Filtration Columns

Accessible internal fiber water, V_i(mL/g), serves as a primary means of characterizing and comparing columns packed with three different cotton celluloses. The V_i is derived from measured data as follows[1]:

$$V_i = (V_e - V_0)/W$$

where V_e is the elution volume of the specific solute, V_0 is the elution volume of a solute (dextran T-40) that is excluded from internal pores, and W is the dry weight of fiber in the column.

Experimental data are summarized in Figure 2 for the V_i's of the three types of solutes on the purified (A), NaOH-treated (B), and liquid-NH_3-treated (C) cotton columns. V_i, a measure of accessible pore volume or accessible solvent water in the pores, was lowest for A cotton, highest for B cotton, and intermediate for C cotton. The slopes of the curves for sugars are increasingly negative in the order: A cotton < B cotton < C cotton.

The curve for sugars on C cotton intersected the curve for A cotton at a molecular weight about 750.

Differences in slopes of the plots of V_i vs. molecular weight for sugars (Fig. 2) are consistent with earlier observations[7,8] from measurements on purified and mercerized cottons in the form of 60–80-mesh chopped fibers. In those cases the curve for mercerized cotton displayed the steeper slope and the two curves crossed at a molecular weight (of sugar) about 1500 with intercepts of the horizontal axis (permeability limits) at molecular weights of about 2150 (chopped mercerized fibers) and 2900 (chopped purified fibers). The curves for sugars on whole-fiber cottons had intercepts with the horizontal axis at about 2350 (B) and 2440 (A) with a crossover close to these estimated permeability limits. There are, therefore, general similarities but quantitative differences between V_i's for sugars from chopped and whole-fiber cottons.

The curves of V_i's for glycols and glycol dimethyl ethers as a function of their molecular weights (Fig. 2) show regular patterns among the three variations of cotton celluloses. Curvatures are visably different between the glycols and the glycol dimethyl ethers; this is emphasized by the fact that curves for the glycols are fit slightly better by a power equation ($y = Ax^B$), whereas curves for the glycol dimethyl ethers are fit slightly better by an exponential equation ($y = Ae^{Bx}$).

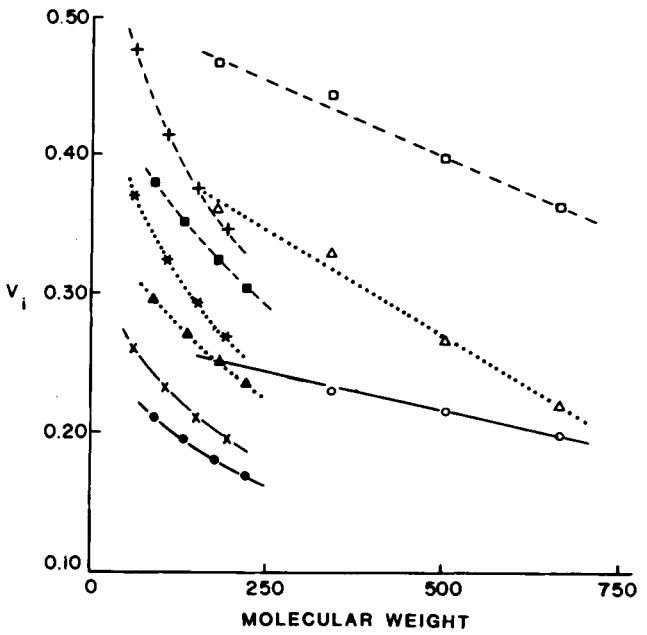

Fig. 2. V_i for each specific solute as a function of molecular weight of that solute for each of the whole-fiber cotton columns: (A) purified cotton; (B) NaOH-treated cotton; (C) liquid NH_3-treated cotton. Curves for sugars are denoted by (○) A, (□) B, and (△) C; curves for the glycols are denoted by (x) A, (+) B, and (*) C; and curves for the glycol dimethyl ethers are denoted by solid symbols comparable to those for the sugars.

Further analysis of the V_i data is facilitated by considering the V_i of each of the sugar, glycol, or glycol dimethyl ether solutes as a function of the molecular diameter of the hydrated solute. Molecular diameters of the sugars were reported by Stone and Scallan.[9] Estimates of the molecular diameters of glycols are based on extrapolations from measurements of Nelson and Oliver.[10] Measurements of molecular diameter of the glycol dimethyl ethers are not available in the literature; they have been approximated here by assuming that molecular sizes of the hydrated molecules are the same as those of the glycols at the same molecular weight. V_i's as a function of molecular diameter are summarized in Figure 3 for the sugars and glycols. It is evident that lines for sugars and glycols on A cotton are close together and have identical slopes: i.e., these quite different types of solutes (i.e., highly polar, slightly stiff, bulky sugars vs. less polar, very flexible, slender glycols) penetrated pores in very similar manners. The lines for these solutes on B cotton are more widely separated with little or no difference in slope, perhaps indicative of slightly greater discrimination between the sugars and glycols by the B cotton. The lines for the sugars and glycols on C cotton crossover near 12 Å (1.2 nm) molecular diameter (MW ca. 500 for sugars, ca. 175 for glycols) with indication of quite different tolerance of the pores in C cotton for the two types of solutes.

Lines for glycol dimethyl ethers (low polarity) on each of the three variations of cotton fibers fall systematically below these for the glycols and are characterized by slopes that are slightly less negative than those of the glycols. These lines are not shown in the Figure 3, because they congest the figure but primarily because the molecular diameters for the solutes are approximations derived from published data for the glycols.[10]

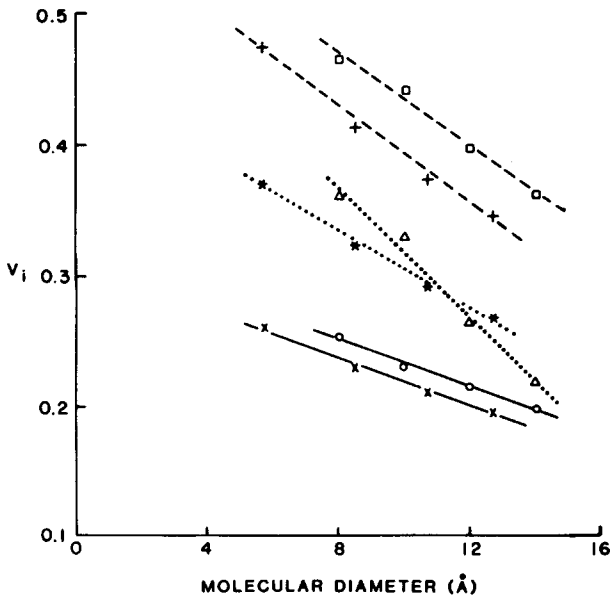

Fig. 3. V_i for each sugar or glycol solute as a function of molecular diameter of that solute on whole fiber cotton columns from purified cotton [A: (○) sugars; (x) glycols], NaOH-treated cotton [B: (□) sugars; (+) glycols] and liquid NH_3-treated cotton (C: (△) sugars; (*) glycols).

The estimated permeability limits (Å) from extrapolation of the lines in Figure 3 are as follows:

A cotton: 35.9 from sugars;	33.8 from glycols;	(38.0 from glycol ethers)
B cotton: 34.7 from sugars;	30.9 from glycols;	(39.0 from glycol ethers)
C cotton: 23.0 from sugars;	30.7 from glycols;	(38.1 from glycol ethers)

These values are indicative of the directions and slopes of the lines, but the values may be in substantial error due to the length of the extrapolation. Only the differences measured with sugars for the C cotton vs. A and B cottons are considered significant and meaningful at this time.

Appearance of Fibers

Photomicrographs of the three variations of cotton fibers are shown in Figure 4. The segments of fibers, which were selected for the figure, illustrate common (but not statistically proven) differences among A, B, and C cottons. The A cotton fibers are frequently characterized by surface irregularities such as "scaliness," reflections of underlying macrostructural units, and crevices and cracks, some of which are shown in the figure. The B cotton fibers are generally more even and round with substantial "healing" of surface imperfections. The C cotton fibers are less expanded and rounded than B fibers, show substantial "healing" of surface imperfections, and often display a considerable smoothing (compared to A cotton) of the type shown in the figure.

DISCUSSION AND CONCLUSIONS

From a research standpoint, the realization of an effective gel filtration column from plugs of whole-fiber batting represents a substantial advance

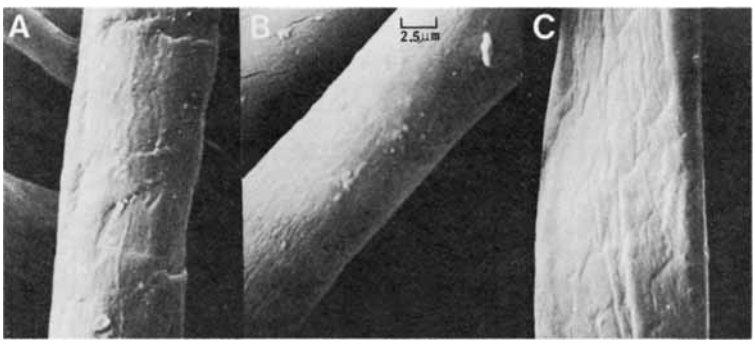

Fig. 4. Scanning electron photomicrographs of segments of cotton fibers: (A) purified cotton; (B) thrice-mercerized cotton, (C) liquid-ammonia-treated cotton.

in this line of endeavor, a significant simplification in column preparation compared to conventional procedures, and a real improvement in column stability. In this case it makes possible the characterization of cotton (or other textile) fibers as they might ultimately behave in yarn or fabric structures. In other cases, it could prove an appropriate path to readily prepared, stable columns for conventional chromatographic separations or preparative work. Batting is generally available from a variety of textile fibers and could be made from other fibrous materials.

Results measured on purified and NaOH-treated (mercerized) whole-cotton fibers are numerically different from those values reported earlier from measurements on the corresponding chopped fibers,[2,8] but differences are small. V_i's extrapolated to molecular weight 18 (H_2O) are 0.27 mL/g and 0.29 mL/g for whole and chopped fibers, respectively, indicating that the chopped fibers have slightly higher pore volume, probably as a consequence of cutting of and damage to fibers during the chopping.

The primary effect of NaOH treatment on whole cotton fibers was to raise V_i by 45–55% as measured by penetration of sugars or glycols with molecular weights in the range of chemical agents that are commonly applied to cotton for durable press or flame retardancy. The V_i's of purified and NaOH-treated cotton fibers converge at higher molecular weights, if the long extrapolation of V_i as a function of molecular weight (or molecular diameter) can be ascribed significance. The indication is that the NaOH treatment has lesser effect on the size and abundance of the large pores than it does on the smaller pores.

In contrast to the effect of NaOH, the effect of the liquid-NH_3 treatment is to cause a greater change in the slope of the V_i–molecular weight (or molecular diameter) curve as measured by bulky, semirigid sugars; but there is little effect on this slope, as measured by the flexible glycols. The glycol dimethyl ethers followed the same relative change as the glycols (assuming the same molecular weight–molecular diameter relationship as for the glycols). It is tentatively concluded that pores in liquid-NH_3-treated cotton fibers are less tolerant of bulky, semirigid sugars than are the pores of the two other forms of cotton. The effect is not evident for the glycols (at least in this range of molecular weight or size). The difference in behavior of sugars and glycols could be caused by a change in shape of pores, as well as size, in the NH_3-treated cotton and the greater ability of flexible oxyethylene chains to conform to the new requirements.

Photomicrographs of the three cottons were searched for significant differences, primarily evidence of fewer or smaller crevices or cracks on the fiber surfaces, since pores such as discussed above are too small for detection. With a predisposition in this direction, it is possible to point toward appearance that seems to indicate the presence of fewer crevices and cracks and generally smoother surfaces of fibers following liquid NH_3 treatment. The NaOH treatment seems also to account for smooth surfaces but not for the same decrease in crevices and cracks.

Thus, the major difference delineated between cotton fibers swollen in NaOH (23%) and those swollen in liquid NH_3 (with evaporative removal of NH_3) lies in the abundance of large pores. Arbitrarily, we define large pores as those into which sugars of molecular weight > 800 or molecular diameter

> 16 Å are capable of penetration: i.e., above the crossovers of the curves for liquid NH_3 and purified cottons (Figs. 2 and 3). Actual diameters of pores to accomodate these solutes would be substantially larger, by a factor of 2–4 according to Nelson and Oliver.[10] Bredereck and Saafan[11] concluded from equilibrium dye adsorption that pores having diameters in the region of 20–60 Å are of special importance relative to dye response.

The loss of large pores in the NH_3-treated cotton fiber is balanced in part by the increase in small pores, but it results in a significant decrease in total pore volume. Since pores constitute voids between elementary fibrils or microfibrils, the disappearance of these voids brings microfibrillar units into closer lateral association, i.e., into lateral hydrogen bonding which amounts to a natural type of crosslinking. This natural crosslinking accounts for the resilience that is inherent in the cotton fiber, that may be accentuated by drying the cotton fiber,[12] and that may be supplemented by chemical crosslinking.

With this background of data and reasoning, it follows that among the three cottons under examination the greatest depth of color or dye yield is associated with the abundance of large pores in NaOH-treated cotton and that the highest level of resilience is associated with the lowest level of large pores or highest level of lateral fibrillar association in the NH_3-treated cotton.

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