

Effect of Mode of Agent Removal on Pore Structure of Liquid Ammonia Treated Cotton Cellulose

N. R. BERTONIERE, WALTER D. KING, and STANLEY P. ROWLAND,
Southern Regional Research Center, Agricultural Research Service, U. S.
Department of Agriculture, New Orleans, Louisiana 70179*

Synopsis

The pore structures of three liquid-ammonia-treated cottons were compared via a reverse gel permeation chromatographic technique. Cotton battings were treated with liquid ammonia which was removed by volatilization at ambient temperature or at elevated temperature and by water exchange. Three series of water-soluble solutes were used to study the elution characteristics of whole fiber columns prepared from these battings. The solutes were oligomeric sugars, ethylene glycols, and glymes (ethylene glycol dimethyl ethers) having molecular dimensions in the range of conventional finishing agents for cotton. All three liquid ammonia treatments increased the internal pore volumes accessible to small molecules. The greatest increase was noted when the ammonia was removed by water exchange and the least when volatilization at elevated temperature was employed. Ambient temperature volatilization had an intermediate effect. Decreases in the volumes of large pores were effected by ammonia treatment followed by volatilization at ambient or elevated temperature. Water exchange of the ammonia resulted in an increase in the volume of large pores as well as of the small pores.

INTRODUCTION

Swelling pretreatments for cotton fabrics are utilized to improve dimensional stability, dyeability, luster, softness, and textile performance both before and after crosslinking to impart smooth drying properties. Such pretreatments include caustic mercerization and liquid ammonia treatment. Processing in liquid ammonia causes complex changes in the cotton fiber which are only partially understood. Liquid ammonia penetrates the cotton fiber effecting intra- and inter fibrillar swelling which disrupts the hydrogen bond structure and leads to the formation of a cellulose-ammonia complex.¹ Destruction of this complex by evaporative removal of the ammonia leads to the formation of cellulose III, but removal by water exchange results in regeneration of cellulose I. In both instances disorder is introduced into the structure.²⁻⁵ The removal technique alters the physical properties of the treated celluloses as well as their crystal structure. Enhanced textile performance is realized when dry volatilization is employed⁶ whereas dyeability is better when water exchange is used.⁷ Commercially ammonia is removed from treated yarns by means of hot water in the Prograde process⁸ and from fabrics by dry volatilization followed by steaming in the Sanfor-Set process.⁹

* One of the facilities of the Southern Region, Agricultural Research Service, U.S. Department of Agriculture.

An earlier report¹⁰ described a technique for preparing chromatographic columns from whole cotton fibers along with elucidation of the effects of caustic mercerization and liquid ammonia treatment on the pore structure of cotton celluloses. A reverse gel permeation chromatographic technique was utilized. The liquid ammonia treatment consisted of immersion of cotton batting in liquid ammonia followed by evaporative removal of the ammonia at room temperature. The present study expands this knowledge by distinguishing differences in the pore size distribution in liquid-ammonia-treated cottons resulting from evaporative removal of ammonia at ambient temperature or at elevated temperature and from water exchange.

EXPERIMENTAL

Materials

The cotton was ACCO Absorbent Cotton U.S.P. 96-9117 from Absorbent Cotton Co., Division of Dart Industries.† Dextran T-40 (MW = 40,000) was from Pharmacia; glucose was from Mallinkrodt Chemical Works; maltose and raffinose were from Calbiochem; and stachyose was from Aldrich Chemical Corp.

The water used to elute solutes through the chromatographic columns was deionized and then further purified by passage through a Water-I system from Gelman Sciences. It was degassed by sonication under reduced pressure for 20 min.

Methods

The batting was quilted between cheesecloth for treatment with liquid ammonia. Quilts were loosely rolled and tied before immersion in liquid ammonia for 5 min in a large Dewar flask. In one case the ammonia was removed by heat in an oven at 96°C for 3 h. In another the ammonia was allowed to evaporate at room temperature while hanging in a well-ventilated hood. In the third case the ammonia was removed by immersion in water at room temperature followed by air drying. These samples will be designated ammonia-96°C, ammonia-25°C, and ammonia-water, respectively.

The columns were Chromatronix, precision bore (2.54×45 –50 cm between top and bottom bed supports). The columns were packed with disks cut with a die having the same diameter as the interior of the column. Dry plugs were pressed together tightly in the dry state with a dowel rod. The column was wet, further compressed, and additional disks added. Columns exhibited maximum performance when they contained approximately 75 g of cotton. Water was pumped through the column for approximately 5 days to remove all of the entrapped air before evaluation. The procedure for packing these columns was described in our earlier report.¹⁰

Dextran T-40, glucose, maltose, raffinose, and stachyose were applied

† Names of companies or commercial products are given solely for the purpose of providing specific information; their mention does not imply recommendation or endorsement by the U.S. Department of Agriculture over others not mentioned.

individually as 2% solution through a 0.5 mL sample loop. The flow rate was 26mL/cm²/h. The eluate was monitored continuously with a Pharmacia differential refractometer. Elution volumes were determined gravimetrically by collecting the eluate in tared test tubes and summing the weights of fractions and proportional parts of fractions between the injection and the peak of the recorded elution curve for each solute. Gel permeation chromatographic results are obtained in terms of elution volume for each specific solute V_e , total void volume for the column V_0 (elution volume of a high molecular weight solute such as Dextran T-40, molecular weight 40,000, which is totally excluded from the internal pore structure), the total column volume V_t , and the weight (dry basis) of material in the column W . Calculated results are expressed as accessible internal volume V_i (mL/g), specific gel volume V_g (mL/g), and total internal water V_w (mL/g). These terms (per g dry cellulose) were defined by the following equations¹¹:

$$V_i = (V_e - V_0)/W \quad (1)$$

$$V_g = (V_t - V_0)/W \quad (2)$$

$$V_w = V_g - 0.629 \quad (3)$$

The specific volume occupied by the solid cellulose in the water-wet fiber [required to calculate V_w , eq. (3)] was taken as 0.629 mL/g, which corresponds to a density of 1.59 g/mL.^{12,13} V_i 's were averages of six replicates having standard deviations from 0.001 to 0.012. Data were fit to straight lines via the method of linear least squares.

Water of imbibition was determined by a modification¹⁴ of the method of Welo.¹⁵ Results are expressed as g water/g cotton.

RESULTS AND DISCUSSION

The crystallographic changes effected by the ammonia treatments were essentially those reported for similarly treated cotton fibers by Rousselle.¹⁶ Removal of the ammonia through water exchange resulted in reversion to cellulose I but with an increase in the amorphous fraction. Evaporative removal either at ambient or elevated temperatures gave mixtures of cellulose I and cellulose III also with increases in the amorphous component. All of the samples were eventually immersed in water, the chromatographic solvent.

V_g and V_w of the three liquid-ammonia-treated cotton battings and the original purified batting are listed in Table I. V_g and V_w were higher in the liquid-ammonia-treated samples than in the original purified batting. Differences were evident for the three methods of ammonia-cellulose complex destruction. The smallest increases in V_g and V_w were noted when the ammonia was removed in the dry environment of the oven. The largest increases in V_g and V_w occurred when water exchange was employed. Volatilization at ambient temperature in a hood gave intermediate results. Condensation of water in the cotton fiber in this relatively high humidity environment effects some water exchange in addition to volatilization. The percent increase in V_w was three times that of the increase in V_g .

TABLE I
Specific Gel Volumes (V_g) and Total Internal Water (V_w) of Liquid-Ammonia-Treated Cotton Battings

Ammonia removal	V_g (mL/g)	V_w (mL/g)
Original batting	0.924 ± 0.018	0.295 ± 0.018
96°C	1.020 ± 0.017	0.393 ± 0.017
25°C	1.058 ± 0.011	0.429 ± 0.011
Water	1.076 ± 0.028	0.447 ± 0.028

The relationship between V_i and molecular weight is linear for the sugars but curvilinear for both the ethylene glycols and the glymes.¹⁰ Within a homologous series molecular weight is an indicator of relative molecular size. When comparing different series it is desirable to do so on a molecular size basis. The molecular diameters of the sugars have been reported by Stone and Scallan.¹⁷ Estimates of the molecular diameters of the lower molecular weight ethylene glycols are based on extrapolations from measurements of Nelson and Oliver.¹⁸ Measurements of molecular diameters were not available for the glymes but were approximated by assuming the molecular sizes of the hydrated molecules to be the same as those of the parent glycols at the same molecular weight.

Plots of V_i vs. molecular diameter for each of the three series of molecular probes are presented in Figure 1. Each series of solutes should provide similar, but not identical, information on the pore structure of the treated cottons. From the plots in Figure 1 we are able to calculate the internal volume accessible to molecules of specified molecular size. An estimate of internal volume that is accessible to the water molecule (V_2) was obtained from the extrapolated value of V_i at 2 Å. Extrapolation of these least squares lines to $V_i = 0$ gives an estimate of the permeability limit (M_x), which is defined as the minimum size of solute that will be completely excluded from permeating the gel structure. Confidence intervals (95% level) for the pre-

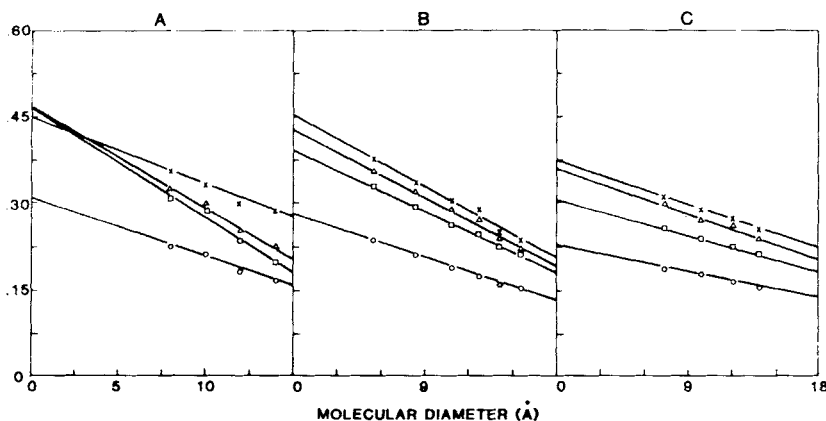


Fig. 1. Internal water (V_i) in purified (○), ammonia-96°C (□), ammonia-25°C (△), and ammonia-water (×) treated cotton battings that is accessible to sugar (A), ethylene glycol (B), and glyme (C) solutes as functions of molecular diameter.

dicted values for V_2 and M_x were estimated by simple linear regression models. Changes in the internal volume accessible to water (V_2) reflect the changes occurring in the small pores. Changes in the value of the permeability limit (M_x), on the other hand, provide a sensitive measure of the extent to which the large pores in the cellulosic composition have been expanded or contracted.

Data for V_2 are summarized in Table II along with values for water of imbibition. Treatment with liquid ammonia increased the water of imbibition of these cotton fibers. The extent of this increase was enhanced by the presence of water during ammonia removal, the greater effect occurring with water in the liquid state. Bredereck and Weckmann⁷ reported the effect of ammonia treatment of cotton printcloth on the water retention values (similar but not identical to water of imbibition). Two of their treatments were similar to those reported here, i.e., water exchange and ambient temperature volatilization. An increase in water retention over the original cellulose is reported for water exchange, in agreement with our results, whereas ambient temperature volatilization gave a value comparable to their starting material. We have found an increase in the latter case as well. Ambient temperature removal of ammonia involves condensation of any water vapor present which induces some water exchange in addition to evaporation. Results would reflect humidity in different geographical locations.

The V_2 values from the three series of molecular probes led to qualitatively similar conclusions albeit numerically different values for the internal volumes accessible to water. V_2 's are extrapolated values which are influenced by the structure and polarity of the specific solute series. V_2 is best described as the internal volume of the water-swollen cellulose available to a sugar (or ethylene glycol or glyme) of a molecular diameter of 2 Å. V_2 's fell in the order sugars > ethylene glycols > glymes. The sugars are relatively stiff and bulky molecules which are similar to cellulose itself in hydrophilicity. It has been postulated¹¹ that the hydrogen bonding power of these sugars is equal to that of the accessible D-glucopyranosyl residues of the cellulose. These solutes can compete successfully with cellulose for bound water within the pores of cotton and find all of the internal water available as solvent.¹¹ In contrast, the ethylene glycols are more flexible, slender molecules containing ether oxygens along with hydroxyl groups. While these molecules might be expected to have greater penetrating power

TABLE II
Internal Volume Accessible to Water as Indicated by Water of Imbibition and Gel Permeation via Various Molecular Probes

Ammonia removal	Water of imbibition	V_2 (mL water/g cotton)		
		Sugars	Ethylene glycols	Glymes
Original batting	0.325 ± 0.004	0.289 ± 0.005	0.265 ± 0.004	0.214 ± 0.005
96°C	0.407 ± 0.003	0.427 ± 0.007	0.367 ± 0.005	0.289 ± 0.008
25°C	0.429 ± 0.002	0.433 ± 0.006	0.400 ± 0.003	0.339 ± 0.004
Water	0.453 ± 0.005	0.426 ± 0.005	0.424 ± 0.004	0.354 ± 0.007

because of their flexibility and capability of tighter coiling, they would compete less successfully for internal bound water and would find a smaller fraction of the internal water available as solvent and a lower V_2 was found. The glymes contain only ether structures, and the V_2 indicated by these solutes is substantially lower than that of the parent ethylene glycols. The internal volume accessible to small molecules is indicated to increase in the order original batting < ammonia-96°C < ammonia-25°C < ammonia-water. The similar values for V_2 as measured by the sugars despite large differences in the overall linear relationships results from steeper slopes for the V_1 /molecular diameter relationships for the ammonia-25°C and ammonia-96°C samples which effects crossover with the ammonia-water cotton at approximately 2.4 Å.

The permeability limits (M_x), the smallest molecules indicated to be excluded from the internal pores of the fibers, are assembled in Table III. Differences among the results for the three series of solutes are substantial and reflect differences in the abilities of these different molecular probes to discriminate among the various pores.

In addition to the numerically different values for M_x the three series of solutes measure different effects from the three liquid ammonia treatments. The M_x values indicated by the ethylene glycols are essentially the same; these solutes show little ability to discriminate among the large pores of the three substrates. Values extrapolated from the glyme data are approximately 30% higher than those from the sugars or ethylene glycols and exhibit greater variability. The glyme data are considered the least reliable because of the molecular diameters of the glymes were extrapolated from data for the parent glycols.¹⁷

M_x values derived from the sugar series indicate that the permeability limit is increased by liquid ammonia treatment followed by water exchange but decreased by volatile removal at either ambient or elevated temperature. A slightly higher values for M_x is observed for the ammonia-25°C than the ammonia-96°C sample. The overall trend for M_x is ammonia-96°C < ammonia-25°C < original batting < ammonia-water. These results generally correlate with the results reported by Brederick and Weckmann,⁷ on the relative dyeability of similarly treated cottons. They report an increase in dye uptake for ammonia treatment followed by water exchange but a decrease for dry volatilization followed by treatment with either steam or hot water.

TABLE III
Permeability Limits (M_x) of Ammonia-Treated Celluloses as Indicated by the Different Molecular Probes

Ammonia removal	M_x , Molecular diameter (Å)		
	Sugars	Ethylene glycols	Glymes
Original batting	30.3 ± 2.0	33.1 ± 2.3	43.8 ± 7.5
96°C	24.2 ± 1.2	32.8 ± 1.8	43.2 ± 9.0
25°C	26.3 ± 1.2	32.2 ± 1.2	40.1 ± 2.8
Water	38.5 ± 2.5	32.8 ± 1.3	43.7 ± 6.2

In a subsequent study with cotton fabric Brederick and Saafan¹⁹ demonstrated that changes in the 20–60 Å diameter pore region correlated directly with dye uptake at equilibrium from aqueous solution. They assessed changes in pore structure via the static exclusion method of Stone and Scallan.¹⁷ A series of carbohydrates including glucose, raffinose, and a series of dextrans with narrow weight ranges were used as the molecular probes. Their results agree with our assessment in this intermediate pore size range. Ammonia treatment followed by water quenching increased the quantity of these larger pores but evaporative removal resulted in a decrease.

The differences in the changes effected in the small and large pore volumes by ammonia volatilization reflect differences in the slopes of the V_i /molecular diameter relationships. Ammonia volatilization, but not water exchange, effected a substantial change in these slopes as measured by the bulky, semirigid sugars but not by the flexible glycols or glymes. The slope differences between water exchange and ammonia volatilization effected crossover of the V_i /molecular diameters lines at approximately 2.4 Å for the sugar series [Fig. 1(a)]. Values for these slopes are assembled in Table IV. Apparently the pores in the ammonia-95°C and ammonia-25°C fibers are less tolerant of the bulky sugars than is the ammonia-water sample or the original batting. The differences between the sugar and glycol series are attributed to the potential changes in the shape as well as the size of the pores in the ammonia/volatilization samples as well as the greater ability of the more flexible oxyethylene chains to conform to the new requirements.

Increased wrinkle recovery in fabrics has been associated with dry volatilization of liquid ammonia.⁶ We associate the loss of large pores with increased resilience. These pores are voids between elementary fibrils or microfibrils and their loss effects closer lateral association between microfibrillar units, i.e., a natural type of crosslinking via lateral hydrogen bonding. Such improvements in resilience are not observed with water exchange where an increase in the large pore volume occurs.

SUMMARY

1. Liquid ammonia treatment of purified cotton batting increased the internal volume that is accessible to very small molecules as indicated by water of imbibition, specific gel volume, total internal water, and the internal volume accessible to a 2-Å-diameter water molecule.

TABLE IV
Slopes of Linear Relationships between V_i and Molecular Diameter of Solutes

Ammonia removal	Sugars	Ethylene glycols	Glymes
	[(mg/g)/Å] × 10 ²		
Original batting	-1.02	-0.85	-0.51
96°C	-1.91	-1.19	-0.71
25°C	-1.78	-1.32	-0.89
Water	-1.17	-1.38	-0.85

2. Values for the internal volume accessible to a 2-Å-diameter molecule were dependent on the structures of the molecular probes and decreased in the order sugars > ethylene glycols > glymes. This order is attributed to the decreasing ability of the solutes to compete successfully with cellulose for bound water within the pores.

3. The extent of the increase in volumes of small pores was related to the presence of water during ammonia removal. The increase was least with ammonia volatilization at elevated temperature, intermediate with ammonia evaporation under ambient conditions, and greatest with water exchange of ammonia. Condensation of water in the cotton fibers during ambient temperature volatilization results in some water exchange in addition to evaporate removal of ammonia.

4. Large pores were decreased by ammonia volatilization at ambient or elevated temperatures but increased by water exchange. This correlates with diminished or enhanced dyeability for volatilization and water exchange of ammonia, respectively. Loss of large pores upon ammonia volatilization is associated with increased resilience attributed to natural crosslinking of cellulosic units via hydrogen bonding.

5. Ammonia volatilization, but not water exchange, effected a substantial change in the slopes of the accessible internal water/molecular diameter linear relationships as measured by the sugar series but not by the flexible glycols or glymes. The pore structures of these ammonia-treated cottons are thus less tolerant of the bulky semirigid sugars than are those of the original batting or the ammonia-treated/water-exchanged sample. Changes in the shape as well as the size of the pores of the ammonia/volatilization samples are indicated.

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