HPLC Determination of the Pore Distribution and Chromatographic Properties of Cellulosic Textile Materials

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Synopsis

HPLC columns packed with cellulosic textile materials as stationary phase were examined with respect to their chromatographic parameters. The interaction of the stationary phase with water-soluble substances (mainly textile chemicals) was also studied. The size-exclusion effects of the porous material were measured for molecules with MW 20–2 × 10^6, thus giving further information concerning structural changes during the pretreatment of textile materials. Electrostatic and sorptive interactions were detected simultaneously, but found to exert a minor influence. Using a recently developed mathematical model, the pore volume distribution of swollen celluose could be determined from the size-exclusion data without the introduction of empirical factors. The applied HPLC method of characterizing cellulosic materials offers an alternative to the previously utilized static and chromatographic methods, especially for studies on pretreated textile materials.

INTRODUCTION

Characterizing textile materials with respect to their chemical and structural attributes is of essential importance for pretreatment, dyeing, and finishing. For the determination of the internal structure (pores, hollow chambers), liquid chromatographic methods are utilized as well as static procedures. An additional advantage of the first mentioned methods is that they can be used to study interactions of the solutes with the surface of fibrous materials. According to static exclusion experiments, where the size of the internal hollow space in a cellulosic material was determined by measuring the dilution of a stock solution of standard substances with different molecular weights, caused by mixing with accessible internal water, Stone and Scallan developed a model with "lamellae" as a substructure of pine-Kraft fibers.[1] Similar experiments with pretreated cellulose showed the change in internal structure of textile materials, especially the increase in pore volume caused by the mercerization process.[2-4] It was also possible to estimate the range of pore sizes, but exact knowledge about the pore size distribution was not gained, except by introducing different calculation coefficients, depending on the chosen pore model, to correlate data with other porosity experiments. Furthermore, no investigations were made to date at elevated temperatures, such as occur during dyeing and finishing processes.

Size-exclusion chromatography of ball-milled decrystallized cotton in water-swollen form, as a gel-like stationary phase, was applied for the first

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time by Martin and Rowland.[5] Apart from the static exclusion method, which is very susceptible to disturbances, the above-mentioned procedure shows the only way to characterize pore structure under aqueous conditions. With classical methods, such as adsorption of gases or mercury porosimetry, the portion of pores created by swelling cannot be determined.[6]

Using the size-exclusion method, the changes in structure caused by crosslinking with formaldehyde[7-9] and by mercerization[9,10] were investigated; the exclusion limits and internal solvent volumina were only determined by extreme extrapolation of the measured curves. By correlating the results with those obtained from dyeing experiments, the dye uptake of cotton was satisfactorily explained.[11] Interactions of textile chemicals in aqueous solution with cellulosic materials were studied by analyzing the retention of homologous series with different functional groups.[12,13] In addition to the classical methods of packing gel permeation chromatography columns, Rowland et al. utilized die-cut pieces of fabric for filling their columns, with which they achieved reproducible results; the columns, however, were applicable only for a few experiments due to the formation of microscopic channels.[10]

In the present work a similar method to that described in Ref. 10 was applied using a 250 × 4 mm stainless steel column, which allows a tighter packing of material by putting on higher pressures. These columns can be installed in an HPLC-column oven, and therefore experiments at temperatures up to 90°C can be carried out; furthermore, only very small amounts of sample and textile material are required. In the following paragraphs, the chromatographic characteristics of the columns and their behavior towards a spectrum of substances are reported. Among these compounds, frequently used textile chemicals were employed as well as substances, which served as test molecules for characterizing the structure and chemistry of the packing. Data obtained from differently pretreated cotton textiles are compared with those from a column of Sephadex G-25 (fine). Employing recently developed mathematical models for the determination of pore distributions,[14,15] the results are interpreted with respect to former research on adsorption and other molecular interactions.[16]

EXPERIMENTAL

HPLC System

The HPLC apparatus consisted of a Beckman Solvent Delivery Mode 112 with sample injector (20 μL), an RP-C-18 precolumn for achieving a higher and more constant back pressure, an adjustable column oven (Shimadzu CT0-2A), a Knauer Dual Detector (RI/UV 254 nm), and a Spectra Physics integrator SP 4270.

Stationary Phase

The stationary phase for each column was prepared from a cotton sheeting (137 g/m^2) by one of the following treatments:

Desizing. The fabric was enzymatically desized with 5 g/L Rapidase 1800 (Gist Brocades), 3 g/L NaCl at pH 6.5 and 70°C (fabric–liquor ratio 1 : 40), scoured in hot and cold water, and dried at 110°C.

Bleaching. The fabric was bleached with 5 mL/L H_2O_2 (35%), 0.5 mL/L Tinoclarit G (Ciba-Geigy), 1 g/L NaOH, 1 g/L Leonil DB (Hoechst) at pH 5–12 and 80–95°C (fabric–liquor ratio 1 : 30), neutralized, scoured with hot and cold water, and dried at 110°C.

Mercerization. A tensionless mercerization procedure (2.5 min) was carried out at room temperature using 272 g/L NaOH and 6 g/L Mercerol SAW (Sandoz). After scouring with cold water and neutralizing with 3% acetic acid, the fabric was scoured once more and dried.

The dressed fabric was a pretreated, synthetic resin finished cotton cloth (easy care finish with Knittex FA conc (BASF); 108 g/m^2). The Viscose fabric (192 g/m^2) was from normal yarn, pretreated, and washed.

Preparation of Chromatographic Columns

With a die, stacks of four to seven pieces were cut out of the fabric and filled into the columns (250 × 4 mm stainless steel) by pressing manually with a suitable piston. After closing the columns, the textile material was penetrated with distilled, filtered water, increasing the flow linearily. This swelling procedure was continued for 12–18 h.

Two grams Sephadex G-25 fine (Pharmacia) were suspended in 10 mL of distilled water, degassed, and left to swell for 3 h. After pouring the suspension into the column, it was allowed to settle for 20 min and scoured with distilled water. The column was closed, and the flow was continuously increased up to 0.2 cm/s.

All textile columns were emptied after use, and the dry weight of the solid phase was determined.

Test Substances

As test molecules, several inorganic salts and low-chain alcohols (Merck, p.a.), 1-naphthol, 3,4-dihydroxybenzaldehyde, mono-, di-, and triethylene glycol, poly(ethylene glycol)s (PEG, 200–35,000, Loba Chemie), mono- and oligosaccharides (Merck, Serva Feinbiochemica) and dextran fractions (Serva Feinbiochemica, Pharmacia), poly(propylene glycol)s (Pluronic-products, Serva Feinbiochemica), nonylphenol poly(ethylene glycol)s (Arkopal N-products, Hoechst), poly(vinyl alcohol)s (15,000–100,000, Fluka), Na-*n*-alkyl sulfonates (Fluka), and deuterated water (Merck) were used. The concentration of test substances was chosen according to their solubility and the signal height of the detector signal in the range 0.2–1% (w/w).

The elution volume of each test molecule was determined three times. Several analysis series were repeated after some days on the same column. From the bleached fabric a second column was filled to control the reproducibility.

RESULTS AND DISCUSSION

Chromatographic Characterization

As parameters for the HPLC system, the height equivalent h of a theoretical plate, the ratio h/u, where u is the linear liquor velocity, and the resolution R, calculated from the relation between the elution volume of a

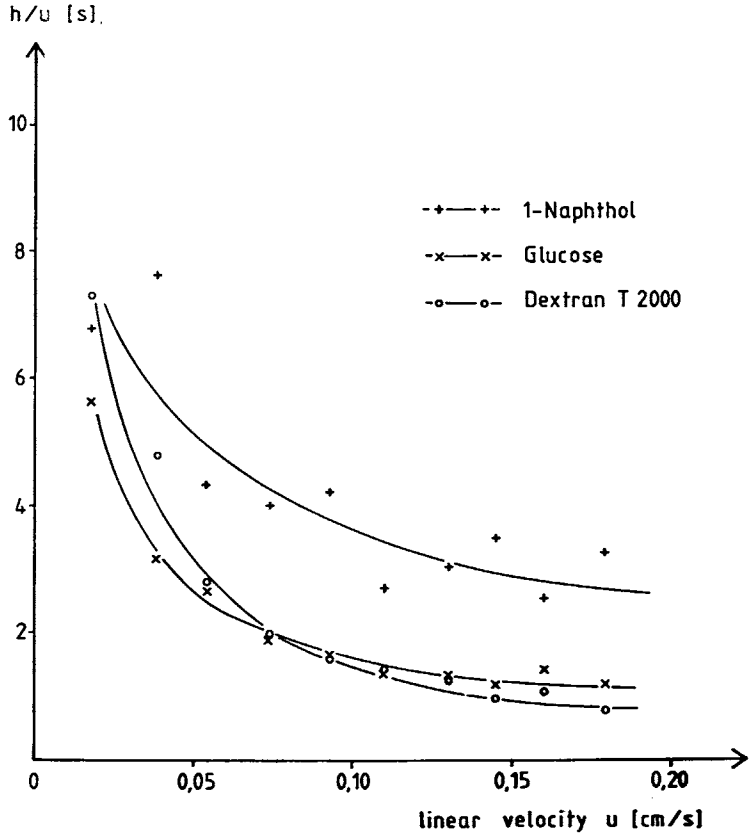

Fig. 1. h/u plot for optimization of the linear velocity u (stationary phase: cotton desized, mobile phase: water, $T = 40°C$).

substance V_{el} and its peak width in the chromatogram, were determined in dependence of the linear velocity u. Figure 1 shows the typical h/u curve for a chromatographic system with a relatively steep increase below 0.05 cm/s; Figure 2 demonstrates a general distinct increase in resolution (calculated for different pairs of substances) with decreasing velocity. The optimal conditions were found at 0.02 cm/s; nevertheless, for keeping the flow at a more constant rate and for obtaining quicker and more reproducible results, further investigations were made at 0.07 cm/s. The values for the number of theoretical plates in a 250 × 4 mm column with regard to the chosen conditions were nearly the same for the differently treated cotton and viscose materials; only Sephadex, a well-defined reference material for size-exclusion determinations, gave higher values (Table I).

In the swollen state, the columns were stable for 1–2 months, whereby the elution volume of a reference molecule [poly(ethylene glycol) 35,000 or NaCl] was measured daily for control, so that some small deviations could be corrected. Over the period mentioned, no deviations greater than 3–5% of the absolute value were observed. Two columns showed an effect of channeling after a short time, which was detected by the typical "pretailing" of the peaks. In this case, the results were no longer reproducible, and the analysis

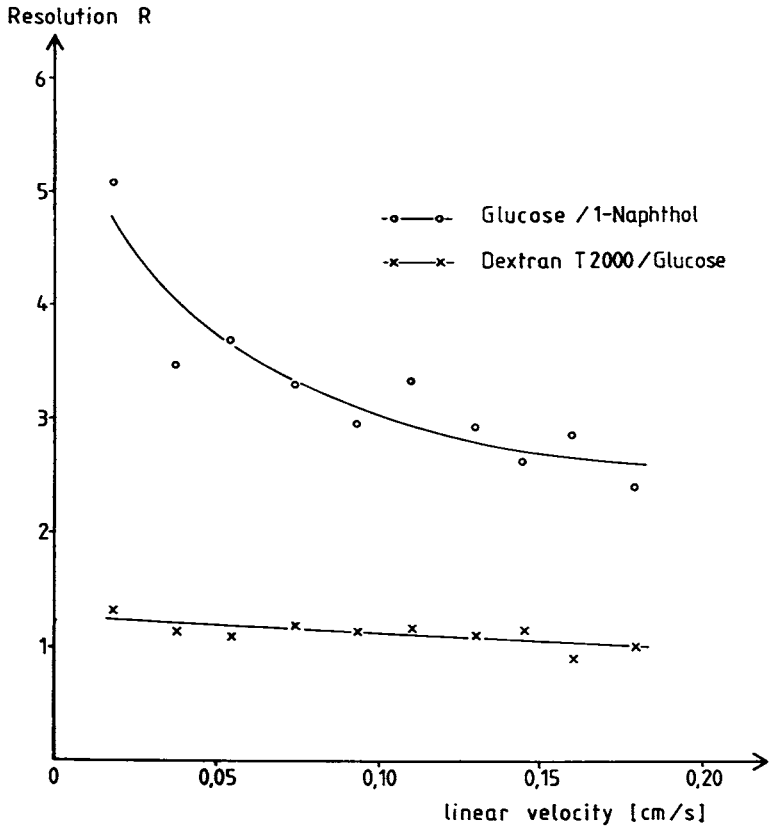

Fig. 2. Dependence of the chromatographic resolution R on the linear velocity for pairs of test substances (stationary phase: cotton desized; mobile phase: water; T = 40°C).

TABLE I
Characteristic Data of the Packing Materials and Chromatographic Columns (250 × 4 mm Stainless Steel)[a]

	Mass per unit area (g/m^2)	Number of theoretical plates (1-Naphthol)	Dry weight (g)
Cotton (sheeting)	137		
Desized	—	83	2.265
Bleached	150	77	1.917
Mercerized	207	71	2.265
Cotton finished	108	60	2.295
Viscose	192	73	2.178
Sephadex G-25 fine	—	158	—

[a] Temperature of the column oven, T = 40°C; linear velocity, 0.07 cm/s.

was repeated with new columns. At temperatures up to 90°C, no significant changes of the packing materials occurred.

For elimination of the unequal density of the packings caused by the filling procedure, the measured elution volumina V_{el} were related to the elution volume V_0 of an excluded molecule (Dextran T 2000, average molecular weight 2,000,000) and the dry weight m of the column packing, defining a relative elution volume V_{rel} by the following equation:

$$V_{rel} = (V_{el} - V_0)/m \tag{1}$$

Application of this correcting procedure had led to comparable results in previous works,[7,8,11,12,13] and allowed the linear parts of the exclusion curves to be brought to coincidence, which also confirmed the accuracy of the measurements.

The V_{rel} values of small molecules approaching the molecular weight of water correspond to the "accessible pore volume" or "internal solvent volume" with good approximation, if the specific molecule is eluted only according to its size, and if it does not interact with the stationary phase. The term "accessible pore volume" is equivalent to the maximum volume of solvent (nonbound) water, leaving out the immobilized water bound to the stationary phase.

Data Discussion

Solutions of Polymer Molecules

The analysis of polymer fractions of different molecular weight and various functional groups gave the expected typical curves of size exclusion, when V_{rel} was plotted against the logarithm of the molecular weight. Previous work had only covered small sections of these curves,[7-13] and therefore authors had to extrapolate their measured data to a large extent. In this work, the exclusion behavior for a variety of substances with a molecular weight in the full range from 20 to 2×10^6 was investigated for the first time (Fig. 3).

The curvature of the plots for all cellulosic materials is very similar to that shown in Figure 3; the differences appear according to the slope of the linear part and to the exclusion limit MW_{ex}, which is defined as the molecular weight at the upper break point of the curve. Because of their smaller hydrodynamic radius, sugar and dextran molecules can penetrate the pore system better than poly(ethylene glycol)s with the same molecular weight. Macromolecular poly(vinyl alcohol)s with molecular weights in the range 10^5–10^6, which are frequently used as sizing agents (preparation for the weaving process), are totally excluded from the pore system. As was expected, the different shape of the curves depends mainly on steric effects; deviations from occurring interactions are described later.

By completing the exclusion curves at the lower end with elution data of chemically similar small molecules (methanol, ethanol), the internal accessible water volume V_i may be calculated from the V_{rel} value at molecular weight 18 (water molecule). This assumption is confirmed by the fact that in this region the extrapolated curves of the poly(ethylene glycol)s and the sugars/dextrans

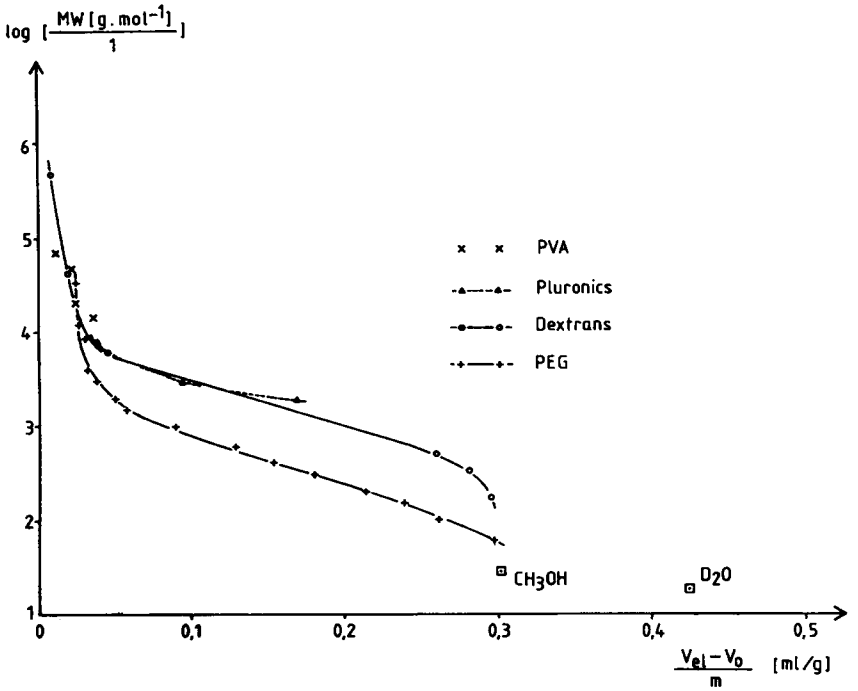

Fig. 3. Exclusion curves of poly(ethylene glycol)s, dextran fractions/sugars, poly(propylene glycol)s and poly(vinyl alcohol)s (stationary phase: cotton bleached; mobile phase: water; linear velocity: 0.07 cm/s; T = 40°C).

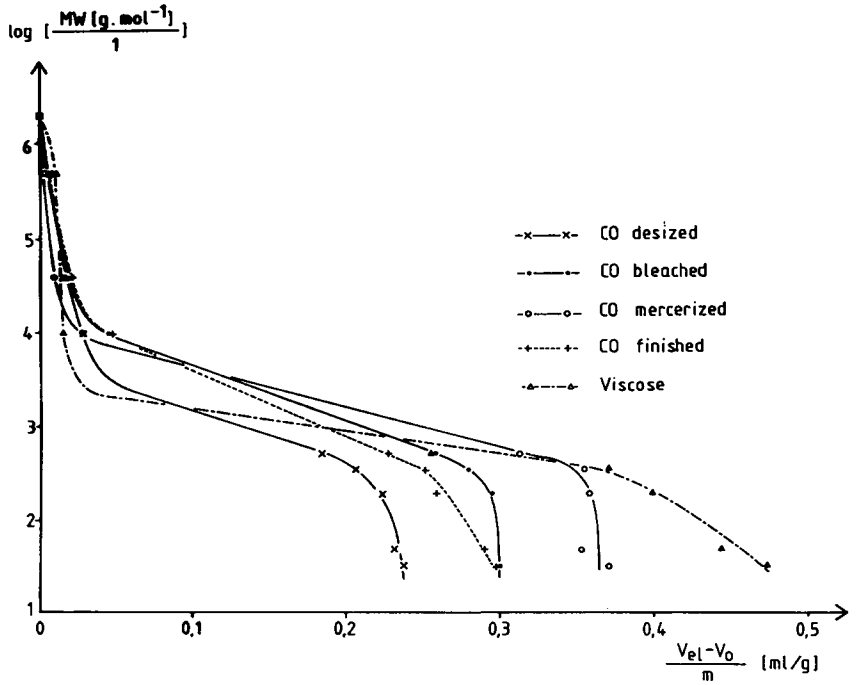

Fig. 4. Comparison of the exclusion curves for dextran fractions/sugars, studied on different stationary phases (mobile phase: water; linear velocity: 0.07 cm/s; T = 40°C).

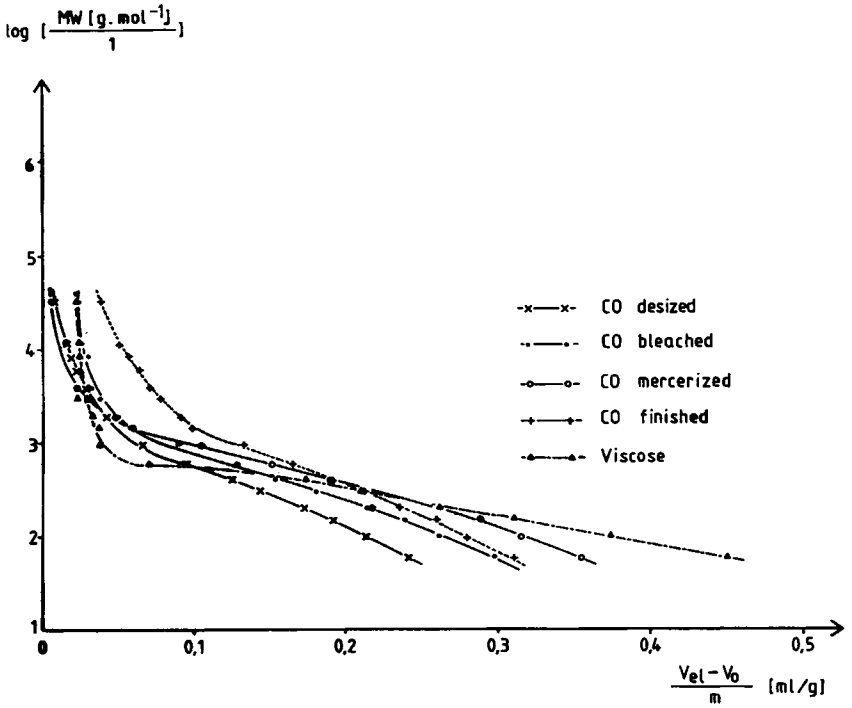

Fig. 5. Comparison of the exclusion curves for poly(ethylene glycol)s, studied on different stationary phases (mobile phase: water; linear velocity: 0.07 cm/s; $T = 40°C$).

almost intersect (Fig. 3). The elution volume of D_2O would indicate a higher value for the internal accessible volume, but this contradiction can be explained by OH—/OD— interchange reactions.[10]

A comparison of the dextran elution curves for differently treated cotton materials shows the changes of the pore structure during the pretreatment processes with a sharp increase in internal volume for mercerized cotton, but only slight changes in the range of the pore dimensions (Fig. 4). Viscose shows a well-defined pore structure with a high internal volume and a low exclusion limit. The same fact can also be concluded from the poly(ethylene glycol) curves (Fig. 5), with the only difference that the curves (and therefore the exclusion limits) are shifted towards lower molecular weights. This fact is of importance for many textile treating processes, as the penetration of cotton by surfactants or dyes with long linear chains is described by evaluating Figure 5 rather than by Figure 4. The exclusion ranges of the man-made fiber viscose and the reference material Sephadex, measured for poly(ethylene glycol)s and dextrans, indicate a narrow pore size distribution, contrasting to the values for the pretreated materials from natural fibres, where the exclusion mechanism works for a widespread variety of molecule sizes (Table II).

Table III gives a survey of the changes in internal accessible volume during the pretreatment processes with a significant increase after the mercerization. Additional finishing procedures may diminish again the accessible pore volume. As shown by the exclusion curves in Figures 4 and 5, viscose has the greatest amount of internal cavities. In general, the values calculated by static

TABLE II
Exclusion Ranges of the Cellulosic Materials

	Exclusion range (MW)	
	PEG	Dextrans
Cotton		
Desized	20–2000	300–10,000
Bleached	20–2500	300–12,000
Mercerized	20–2500	300–12,000
Finished	20–3000	300–12,000
Viscose	20–1000	300–2000
Sephadex G-25	20–1500	300–5000

TABLE III
Internal Accessible Water Volume V_i (mL/g)

	V_i (mL/g)		
	This work	Ref. 9	Ref. 3
Cotton			
Desized	0.26	0.29	0.44[a]
Bleached	0.31	—	—
Mercerized	0.38	0.45	0.60
Finished	0.30	—	—
Viscose	0.47	—	0.70

[a] Cotton dewaxed.

experiments[3] are higher than those from the chromatographic investigations (Ref. 9 and this work). This may be due to the evaluation of the dilution experiments, where the accessible water volume is calculated from the difference between the final water volume after dilution and the total water contents of the fibrous material, which contains also immobilized bound water.

As the interaction and temperature effects, which are discussed in the following chapters, are very similar for all investigated materials, only the data for desized cotton will be presented.

Substances with Interactions by Sorption or Electrostatic Repulsion/Attraction

Studies of homologous compounds with the same functional group demonstrated some significant deviations from the pure steric exclusion mechanism. For example, alcohols show positive sorption by hydrophobic interactions with increasing influence of the alkyl group, and they are retarded more than expected from their molecular weight (Fig. 6), which has been observed in a similar manner for *n*-alkyl carbamates.[13] The same effect occurs for the nonionic nonylphenol poly(ethylene glycol ether)s (Arkopal N), which behave like the normal poly(ethylene glycol)s of the same molecular weight only when they contain more than 10 ethoxyl groups. With a shorter ethylene glycol chain, the interactions of the hydrophobic part are dominant and cause higher

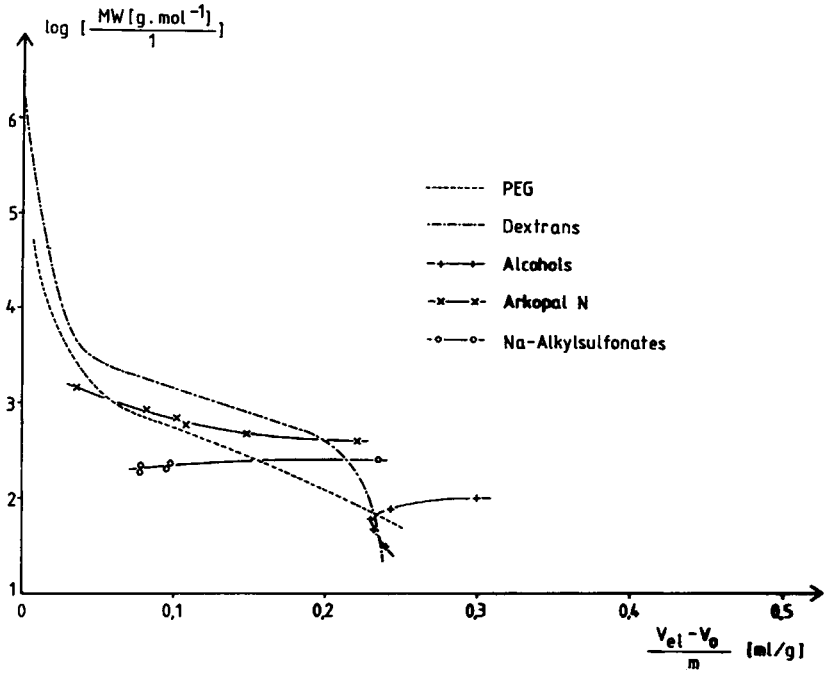

Fig. 6. Deviation from the steric exclusion behavior according to different interactions: alcohols, nonylphenol poly(ethylene glycol)s, and Na-*n*-alkylsulfonates compared with the exclusion curves of poly(ethylene glycol)s and dextrans (stationary phase: cotton desized; mobile phase: water; linear velocity: 0.07 cm/s; T = 40°C).

retention. An effect of electrostatic repulsion of negative end groups by dissociated hydroxyl groups of the cellulosic matrix is noticed with anionic tensides (Na-*n*-alkylsulfonates), similar to the behavior of compounds with carboxyl groups described in Ref. 12. But with increasing length of the alkyl chain, the hydrophobic part dominates and causes higher retention (Fig. 6). In Table IV the measured elution volumes V_{rel} are compared with the theoreti-

TABLE IV
Elution Data of the Substances with Interaction[a]

	MW (g/mol)	V_{rel} (mL/g)	V_{calc} (mL/g)	V_{rel}/V_{calc}
Methanol	32	0.24	0.24	1.00
Ethanol	46	0.23	0.23	1.00
Propanol	60	0.23	0.23	1.00
Butanol	74	0.24	0.23	1.04
Cyclohexanol	100	0.30	0.23	1.30
Arkopal N 040	396	0.22	0.12	1.83
Arkopal N 060	484	0.17	0.11	1.54
Arkopal N 090	616	0.11	0.09	1.22
Arkopal N 110	704	0.10	0.09	1.11
Arkopal N 150	880	0.08	0.08	1.00
Arkopal N 300	1440	0.04	0.05	0.80

[a]Stationary phase: cotton desized; mobile phase: water; linear velocity: 0.07 cm/s; T = 40°C.

cally expected values V_{calc}, calculated from the calibration curves in Figures 3 and 6. The quotient V_{rel}/V_{calc} gives evidence about strength and type of interactions with the stationary phase: Values greater than 1 indicate positive sorption; values smaller than 1 indicate negative sorption or electrostatic repulsion. For a very strongly adsorbed molecule (1-naphthol, base compound for the naphthol dyes, which are very important in textile technology), the enthalpy of adsorption can be determined by experiments at elevated temperatures, which are described in the next chapter. This value can serve as a measure for the different strength of hydrophobic interactions with the cellulosic materials.

Experiments at Elevated Temperatures

Various authors, who studied the exclusion behavior at room temperature, also tried to describe quantitatively the dyeing behavior at temperatures up to 95°C.[3,4,11] With cotton materials, good agreement was obtained between dye uptake and values of the internal accessible volume and the internal surface, determined by exclusion experiments. This was ascribed to the constance of the pore structure even at high dyeing temperatures. But with viscose materials, no correlation was detected, and Bredereck and Schick assumed changes in the internal structure at high temperatures.[17]

In this work, elution data of poly(ethylene glycol)s and dextrans, determined at 90°C with bleached cotton and viscose column packings, indicate almost undetectable changes of the pore structure apart from some insignificant deviations in the MW range 600–2000. This confirms the transferability of pore structure data obtained at room temperature, but also indicates the absence of interactions other than that of the steric effects for the class of dextrans and poly(ethylene glycol)s. In the literature, such weak but measurable interactions are mentioned,[12,13] but could not be verified in this work.

The cellulosic materials do not show any significant changes of the internal volume in the temperature range 25–90°C, as can be seen by measuring elution volumes of glucose and dextran T 2000 (Fig. 7). Measurable effects occur for the adsorbed molecules (3,4-dihydroxybenzaldehyde and 1-naphthol). By analyzing the temperature dependence of the elution volumes, the enthalpy of interaction or enthalpy of adsorption ΔH may be calculated from the exclusion coefficient K according to Ref. 16:

$$\frac{d \ln K}{dT} = \frac{d \ln[(V_{el} - V_0)/(V_t - V_0)]}{dT} = \frac{\Delta H}{RT^2} \tag{2}$$

where V_t is the total internal solvent volume. By indefinite integration and addition of the term $(V_t - V_0)$ to the integrating constant, ΔH can be directly calculated from the following equation:

$$\ln(V_{el} - V_0) = -\frac{\Delta H}{R} \cdot \frac{1}{T} + \text{const} \tag{3}$$

by determining the slope of the straight lines, as shown in Figure 8. The ΔH values of the pretreated cotton materials decrease continuously from the desized to the mercerized state (Table V), which can be explained by an

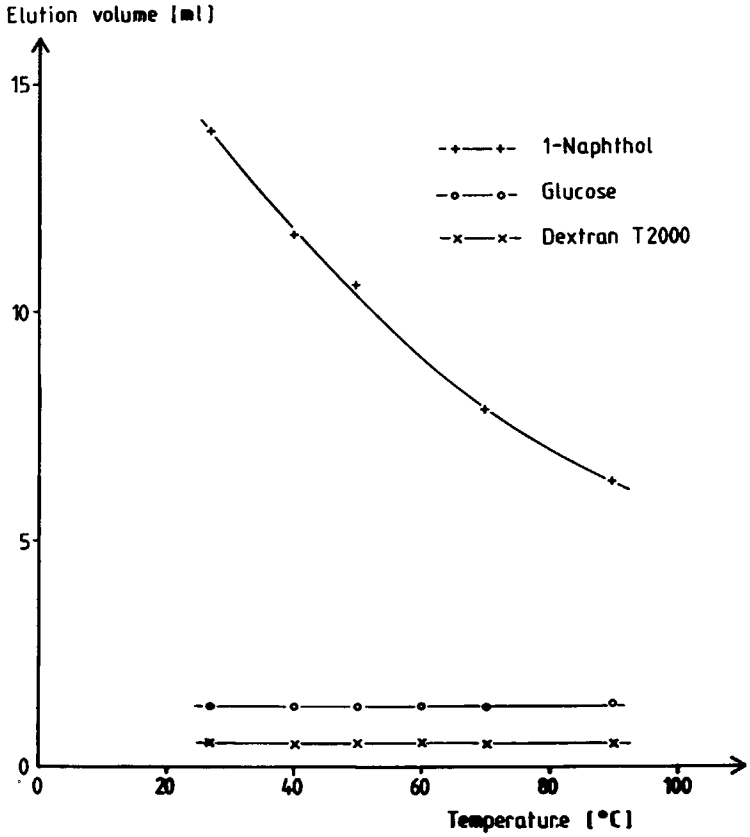

Fig. 7. Elution volume depending on the temperature for the test molecules dextran T 2000, glucose and 1-naphthol (stationary phase: viscose; mobile phase: water; linear velocity: 0.07 cm/s).

increasing hydrophilization through removal of accompanying apolar substances (waxes etc.). The enthalpy for the finished substrate is due to the kind of user adapted quality of the fabric (easy care, no iron finish). For viscose and Sephadex, the "reversed phase" mechanism in the system water/ 1-naphthol/ cellulosic substrate is considerably reduced, as can be seen from the low ΔH values.

Experiments with Electrolyte Solutions as the Mobile Phase

Changes in the influence of electrostatic interactions can be detected by using 0.1% and 1% Na_2SO_4 in distilled water as the mobile phase. While the elution curves for the dextrans and the poly(ethylene glycol)s are not shifted, the anionic tensides are no longer repulsed because of removal of the electrostatic interactions. Apart from the pore mechanism, positive adsorption by hydrophobic interactions of the alkyl chain and decreased solubility by the high electrolyte concentration are the dominant effects (Table VI).

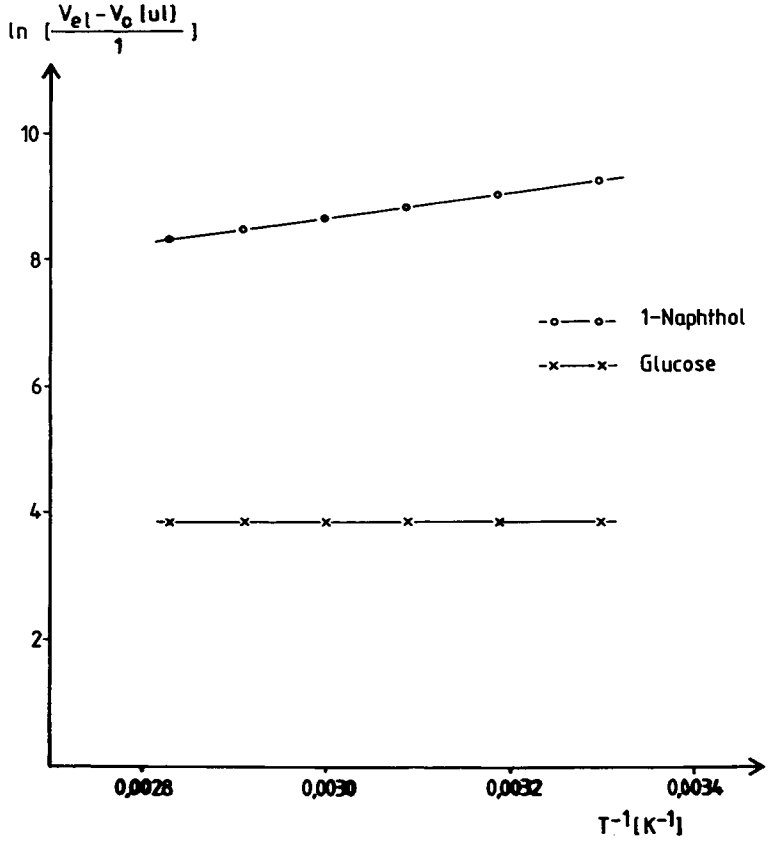

Fig. 8. Calculation of the adsorption enthalpy ΔH from the plot $\ln(V_{el} - V_0)$ vs. T^{-1} (stationary phase: cotton desized; mobile phase: water; linear velocity: 0.07 cm/s).

TABLE V
Enthalpy of Adsorption ΔH of 1-Naphthol on the Cellulosic Materials

	$-\Delta H$ (kJ/mol)
Cotton	
Desized	16.2
Bleached	14.9
Mercerized	14.6
Finished	14.1
Viscose	11.7
Sephadex G-25 fine	9.9

Pore Distribution

Various authors considered exclusion curves as a direct image of the pore distribution,[6,18] i.e., molecules with a certain radius were thought to penetrate totally pores with the same radius. But the results of experiments with materials of which the pore distribution was known from porosimetric investigations, showed a shift of the exclusion curve vs. the pore distribution curve

TABLE VI
Changes in Elution Data with Electrolyte Solutions as Mobile Phase[a]

	$V_{el} - V_0$ (mL)	
	Dist. water	1% Na_2SO_4
PEG 200	0.62	0.64
PEG 1000	0.37	0.37
PEG 35000	0.05	0.08
Na-pentanesulfonate	0.43	0.72
Na-hexanesulfonate	0.45	0.72
Na-heptanesulfonate	0.48	0.72
Na-octanesulfonate	0.51	0.85
Na-decanesulfonate	0.75	1.68

[a]Stationary phase: cotton bleached; mobile phase: 1% Na_2SO_4 in distilled water; linear velocity: 0.07 cm/s; $T = 40°C$.

when plotted in the same figure; furthermore, the slopes were not identical.[17,19] The model of total penetration of a pore for molecules with radius r smaller than the pore radius R had to be revised in favor of a description considering a gradual increase of penetration with decreasing pore radius.

Due to these facts, a mathematical model based upon geometric considerations for spherical molecules and cylindrical pores was developed by Knox and Scott. As a main improvement, the exclusion coefficient $K(r)$ for a molecule with radius r was not simply defined as the ratio of accessible pore volume to total pore volume, but it was calculated in the form of an integral summing up the contributions of pore volume fractions with different r/R ratios. In this way, the condition of the observed gradual rather than abrupt increase of penetration with decreasing molecular radius is fulfilled. By differentiating the sum integral expression for $K(r)$ three times, the pore volume distribution $g(R)$ was directly obtained from the exclusion curve $K(r)$ and its first and second derivative.[14] Nikolov extended this model for any pore geometry and calculated the pore size distribution from the pore volume distribution data.[15]

In this work, data were treated according to the mathematically simpler Knox–Scott model, and its improvements are discussed here. First of all, the exclusion curve for the sugars and dextrans given by the variable hydrodynamic molecular radius was plotted in the frequently used logarithmic form, with ln r as the variable:

$$K(\ln r) = \frac{V_{el}(\ln r) - V_0}{V_m - V_0} \tag{4}$$

where $V_{el}(\ln r)$ is the elution volume of the molecule with hydrodynamic radius ln r, V_0 the elution volume of dextran T 2000, and V_m the elution volume of methanol, which gives a good approach for the total accessible pore volume. The definition of $K(\ln r)$ follows the example of the K_{av} value commonly utilized in size exclusion chromatography, with the difference that the total accessible pore volume is inserted instead of the total gel volume. Using $K(\ln r)$, the exclusion curve is automatically normalized to a zero value for total exclusion and to the value of 1 for total penetration. The values for

the hydrodynamic radii r were calculated from diffusion data and published by Stone and Scallan.[1] The first and second derivatives of $K(\ln r)$ were determined graphically and by curve approximation using the function $K(\ln r) = a * \exp[b * (\ln r + c)^2]$. The parameter c was found by empirical optimization of the position of the maximum; the constants a and b were calculated from the slope of the plot ln K vs. ln r. The pore volume distribution $g(\ln R)$ for pores with radius R was then calculated from the following formula derived by Knox and Scott:

$$g(\ln R) = K(\ln r)_{r=R} - 1.5 * \left.\frac{dK}{d(\ln r)}\right|_{r=R} + 0.5 * \left.\frac{d^2K}{d(\ln r)^2}\right|_{r=R} \quad (5)$$

Figure 9 shows the comparison of the measured exclusion curve $K(\ln r)$ with the calculated pore volume distribution $g(\ln R)$. The steeper slope of $g(\ln R)$ and the shift of about 2.5–3 units (in logarithmic scale 0.9–1) vs. $K(\ln r)$ is clearly distinguishable and explains the former discrepancies between exclusion experiments and porosimetric studies (see Ref. 17). The average pore radius of the volume distribution (pore radius for 50% accessibility), obtained from the curve point $g(\ln R) = 0.5$, lies in the same range as

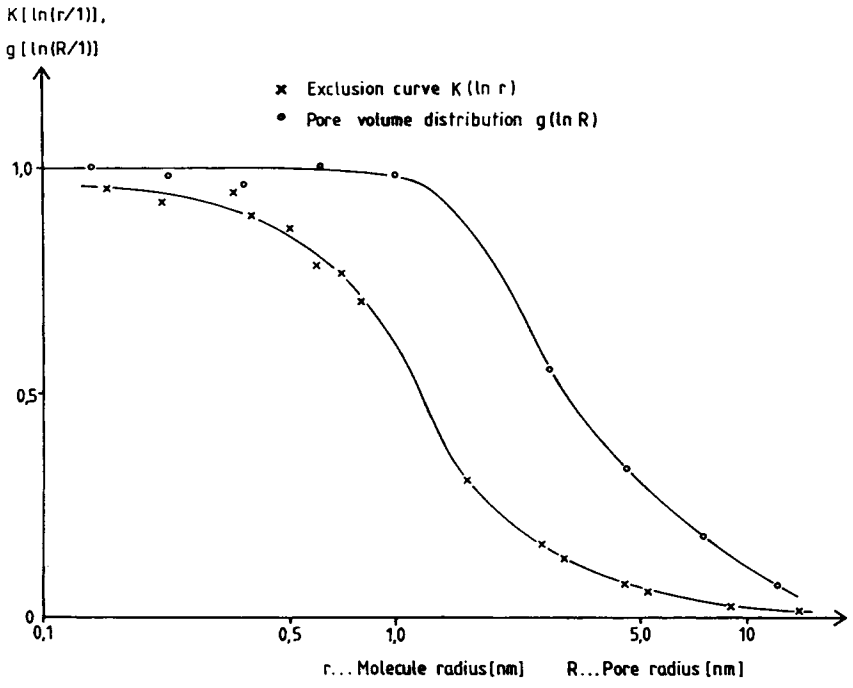

Fig. 9. Comparison of the exclusion curve $K(\ln r)$ for dextran fractions/sugars with the calculated pore volume distribution $g(\ln R)$ (stationary phase: cotton finished; mobile phase: water; linear velocity: 0.07 cm/s; T = 40°C).

TABLE VII
Average Pore Radius $R_{0.5}$, Upper Limit R_{max}, and Lower Limit R_{min} of the Pore Volume Distribution of the Cellulosic Materials (nm)

	R_{min}	R_{max}	$R_{0.5}$	
			This work	Ref. 17
Cotton				
Desized	0.8	16	2.5	3.1
Bleached	0.8	13	2.5	—
Mercerized	1.0	9	2.8	2.8
Finished	0.6	12	3.0	—
Viscose	0.8	4	1.3	2.4

Bredereck's values, calculated by introducing empirical correcting factors (Table VII). Nevertheless, full accordance is not achieved due to the different slopes of the distribution curves. The average pore radius $R_{0.5}$ and the lower limit of the pore volume distribution R_{min} [defined at $g(R) = 0.95$] is almost the same for the pretreated cotton materials; but for the mercerized fabric, the pore distribution is smaller and the upper limit of the pore range R_{max} [at $g(R) = 0.05$] is significantly shifted towards smaller R values. Present investigations, whereby other geometric models (slit pores) are applied, aim at further improved results.

CONCLUSIONS

From the present studies, the following facts are concluded:

1. Using mechanically packed columns containing cellulosic materials, especially textile substrates, for an HPLC study, reproducible results concerning the characteristics of the packing materials and their interactions with water-soluble substances (textile chemicals) were obtained. The columns were usable for 1–2 months; in a few cases, a "channeling effect" occurred.
2. By extensive studies, the molecular exclusion behavior for compounds of different shape and chain length, which plays an important role for dyeing and finishing, was determined for differently treated cotton materials and, for comparison, for a man-made fiber packing (viscose) and Sephadex G-25 fine, a commonly used reference material for exclusion experiments. Significant changes of the pore structure were observed especially in the mercerization process (increase of the internal volume). The man-made fiber viscose showed a higher pore volume and a more homogeneous pore distribution.
3. By further mathematical treatment of the exclusion data with a recently developed model, the pore volume distribution was reconstructed without introduction of empirical correcting factors. An improvement of the model seems to be possible by application of iteration procedures for describing the pore geometry.
4. Electrostatic interactions as well as positive and negative sorption were found to influence the retention of some test molecules, thus giving information about changes in the chemical properties of the packings. From

temperature experiments, the strength of sorptive interactions was calculated; hence there are only slight alterations concerning the chemical characteristics of differently pretreated cotton materials. Although viscose and Sephadex showed lower values for the enthalpy of adsorption, the nature of interactions with the test molecules, which can be briefly characterized as "reversed phase behavior," was similar to that of the cotton materials.

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