Inverse Gas Chromatography of Wool

J. R. McLAUGHLIN, *Wool Research Organisation of New Zealand (Inc.), Christchurch, New Zealand*, and C. G. POPE, *Department of Chemistry, University of Otago, Dunedin, New Zealand*

Synopsis

The chemical nature of the surface of wool fibers has been examined by inverse gas chromatography. The C_1–C_5 linear alcohols were injected into wool-packed gas chromatography columns and their retention volumes measured. True adsorption studies could be made because the C_2–C_5 alcohols were able to be eluted from the wool columns without absorption into the fibers. Decreases in the retention volume of ethanol during drying of a wool column were interpreted as polar groups at the surface of the wet wool orientating to lie in the bulk of the fiber as the gas phase became less polar. Heats of adsorption for ethanol and propanol on wool were measured. A comparison of both untreated and chlorinated wool columns and columns packed with ion exchange resins showed that the polar sorption sites on wool were of the sulfonic acid type. In contrast, on chlorinated wool, sulfonic groups were not very active in the retention of alcohols.

INTRODUCTION

The properties of the wool surface are of vital importance to the wool industry, affecting such phenomena as dyeing,[1] shrinking,[2] spinning,[3] felting,[4] water repellency,[2] and soiling.[5]

Investigation of the wool surface has been approached in many ways.[1,2,4,6–11] One of the potentially most useful, that of examining gas or vapor adsorption, is hindered in conventional studies by diffusion of adsorbate into the fiber, making it difficult to obtain a clear picture of the wool surface alone.[12] This problem may be overcome by using inverse gas chromatography, where both low, concentration-dependent, diffusion coefficients and relatively rapid flow rates confine the adsorbate molecules to the fiber surface.[13,14]

To use this technique, the wool surface being investigated is made the packing material of a gas chromatography column, and the adsorbing vapor or probe molecule is carried in a series of bands or fronts down the column in an inert gas stream.

Inverse gas chromatography has recently been successfully employed to study collagen,[15] cellulose,[16] and man-made textile fibers,[17,18] but has not previously been applied to wool.

EXPERIMENTAL

The chromatography system was made up of a Shimadzu GC-3BF gas chromatograph and an external injector and column (Fig. 1).

The Shimadzu carrier gas control valve and pressure valve were used to control the flow of carrier gas to the heated injector (150°C). The injector contained a splitting mechanism, the vent of which was connected to a fine needle valve and then a rotameter. A split ratio of 1:10 was maintained at all times. A

Journal of Applied Polymer Science, Vol. 27, 1643–1654 (1982)
 CCC 0021-8995/82/051643-12$02.20

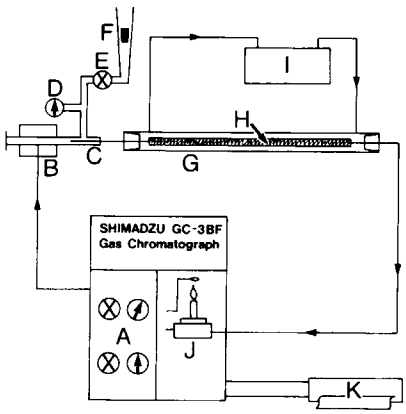

Fig. 1. Schematic diagram of inverse gas chromatograph. (A) Gas chromatograph gas controls; (B) heated injector; (C) splitter; (D) pressure gauge; (E) flow control valve; (F) rotameter; (G) column water jacket; (H) wool-filled glass column; (I) thermostatted water bath; (J) gas chromatograph detector; (K) recorder.

pressure gauge was fitted to the splitter vent near the splitting point, and this was used to measure the pressure difference across the column.

A stainless steel rod was used to pack the wool into 106-cm-long straight glass columns, 0.42 cm internal diameter (i.d.). The columns were joined to the injector and detector via stainless steel swagelok fittings and graphite ferrules, and the whole assembly was contained in a 130 cm × 5 cm perspex tube through which water was continually circulated from a Colora thermostatted water bath. Temperature control was ±0.05°C. Fine stainless steel tubing (0.05 cm i.d.) was used for all connections to minimize dead volume. The outlet from the column passed into the Shimadzu flame ionization detector (maintained at 120°C) and the chromatographs were recorded on a Beckman 10-in. chart recorder.

The carrier gas was either oxygen-free nitrogen, supplied by N.Z. Industrial Gases, or this nitrogen mixed with water vapor to a controlled humidity.

Materials

Wool: fine wool was used in all experiments to maximize the surface area per unit weight. The following columns were used:

Column 1

Undyed merino wool roving, 22.0 μm mean fiber diameter, was washed with nonionic detergent (40°C, 30 min) and then with cold ethanol for a further 10 min.

The wool was packed into the column dampened with ethanol to reduce friction. The ethanol was removed with a nitrogen gas flow at room temperature for 1 day and then at 50°C for 12 h. A distilled water extract of a sample of the wool treated in this way had a pH of 6.61.

Column 2

Merino fleece wool, 23.0 μm mean diameter, had the tips removed to give an average staple length of 6 cm. The fibers were cleaned by Soxhlet extracting for 3 h with 60–80°C boiling petroleum spirit followed by overnight air drying, then a 3-h extraction in distilled water at 55°C followed by air drying. The petroleum spirit and water extractions were repeated at least three times to ensure no cloudiness in the extracting liquids. This was judged to be the most suitable method for cleaning the wool fibers without the introduction of solvents which could react with the wool.[19]

The wool was packed into the column dampened with water, and the water removed by nitrogen flow for 2 days at room temperature, then for 12 h at 50°C and 12 h at 80°C. A distilled water extract of a sample of the wool treated in this way had a pH of 6.90.

Column 3

This wool was identical to that used in column 2 except that the staples were cut to 1 cm.

Column 4

The merino wool, treated as for column 2, was finely dispersed in distilled water at 20°C and at a liquor to wool ratio of 175:1. The pH was brought to 1.5 with HCl and 0.03 g Cl_2/g wool was added. Stirring was carried out during the reaction with chlorine which lasted 8 min, when excess chlorine was neutralised with a 0.1% sodium metabisulphite solution. After washing, the pH of the wool was brought to 7 with a dilute sodium bicarbonate buffer solution. The wool was then rinsed with distilled water for 24 h. The pH of the distilled water extract was 6.22. The wool was packed into the column wet, and the water was removed by nitrogen flow at room temperature for 2 days, then by heating to 50°C for 6 h and 80°C for 12 h.

Ion Exchange Resin Columns

Amberlite IRC-50 (H), a poly(acrylic acid)–divinylbenzene resin, and Dowex 50W-X8 (H), a sulfonate polystyrene–divinylbenzene resin, were purified by distilled water washing. Potassium forms were prepared using Analar potassium bicarbonate and both potassium and hydrogen forms were dried at 70°C and the 40–44 mesh fraction obtained by sieving. Several columns were prepared. For each resin both pure H and K forms were used as well as various mixtures of the H and K forms. The beads were packed into 2.0 mm i.d. stainless steel columns and conditioned at 40°C with nitrogen flowing for 16 h. Chromatography of the alcohols was also carried out at 40°C.

Adsorbates

The C_1–C_5 *n*-alcohols were chosen as probe molecules because of their variations in polarity and molecular volume, and because of the availability of data relating to their sorption by wool.[20–23]

Analar methanol, ethanol, *n*-propanol, and *n*-butanol were used without further purification. Laboratory grade *n*-pentanol was fractionally distilled and the material boiling at 137.0–137.5°C was retained. Experiments showed that drying the alcohols over calcium oxide had no effect on their retention volumes. High purity *n*-octane, used for calibrating the flame ionization detector, was supplied by Sigma Chemical Company.

Method

It was impossible to obtain accurate injections of the very small amounts of alcohols required for this study (<0.3 μL). Accordingly, sample size was obtained from eluted peak areas using relationships between sample size and peak areas which had been determined previously by injecting larger known volumes of the alcohols with the splitter not venting. Curves of retention volume against sample size were then constructed and, for the majority of this work, interpolated at 0.64 μg alcohol/g wool.

All retention volumes given hereafter are specific retention volumes (V_g), i.e., they are corrected for temperature, gas compressibility, weight of wool, and the dead volume of the chromatographic system which was determined by injecting propane.

A glass column packed with 100-mesh glass beads was used to show that adsorption of the alcohols on the glass tubing of the wool columns would not contribute significantly to the measured retention volumes.

Unless otherwise stated the column temperature was 20.00 ± 0.05°C.

RESULTS AND DISCUSSION

In a dynamic system such as a chromatography column the surface coverage decreases from high values at the column inlet to much lower values at the column outlet. However, because of the severe tailing shown by the chromatograms, the alcohols quickly became fairly evenly dispersed over the wool in the column. The average surface coverage when 1 μg alcohol/g wool was injected was about 0.01 monolayer (assuming the alcohol has an adsorption area of 0.20 nm^2 and that the wool fiber is a perfect cylinder), and was clearly in a region where adsorbate-adsorbate interactions are minimal.

Methanol was not eluted from any of the wool columns in measurable time.

The other alcohols gave peaks with severe tailing, although the symmetry of the peaks increased with increasing carbon number. For an individual alcohol, tailing became less with smaller sample sizes and was little affected by gas velocity, implying that the peak asymetry was caused by nonlinear adsorption isotherms rather than by kinetic factors.[24] The retention times of all the alcohols became smaller as the sample size increased implying that the adsorption isotherms of the alcohols on wool are of type I, II, or IV[13] (Fig. 2).

About 90 min was allowed between each injection (2 h in the case of the chlorinated wool column at low flow rates) to allow the previously injected material to be completely eluted. When this was done, the columns behaved in a completely reproducible manner.

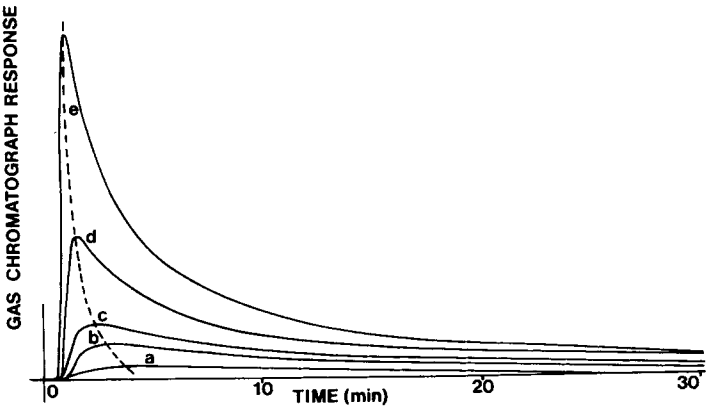

Fig. 2. Typical chromatograms for ethanol on untreated wool (column 1). (a) 1.4, (b) 4.6, (c) 6.8, (d) 10.2, (e) 17.7 μg ethanol. 7.02 g wool, carrier gas flow rate 22 cm^3/min, temp 20.0°C.

Effect of Water on Retention Volumes

Some detailed experiments on the effects of water on retention volume were carried out on column 1, after the column had been dried at 80°C for 5 h in a dry nitrogen stream and had then been partly hydrated by injecting 0.50 cm^3 water onto the column (about 0.07 g water/g wool) (Table I). During subsequent drying the column was periodically removed and weighed to determine the water content.

The drying conditions of (a) and (b) (Table I) did not remove all of the 0.5 g of water injected into the column, and so the very large retention volumes for ethanol could be explained by diffusion of ethanol into the water-swollen wool.[20] After the conditions of (c), however, the amount of water remaining in the column was so slight as to have no appreciable effect on swelling, and so another explanation must be found for the further large decrease in retention volume for treatment (d).

Relative humidities (rh) of 6.2% and 22% in the carrier gas were passed through the column for 16 h for equilibrium to be achieved, and then ethanol was injected (Table I). Surprisingly, and in contrast to our observations when the column was drying out, the retention volumes decreased with increasing water content of the wool, even though there was now significant swelling of the fibers.

TABLE I

Specific Retention Volumes of Ethanol on Column I and Volume Swelling of the Wool Fibers with Different Conditions of Drying and with Humidified Carrier Gas (2.8×10^{-8} mol Ethanol·g^{-1} Wool, Carrier Gas Flow 4.1 cm·s^{-1}) (Column Treatments Sequential)

Conditions	Volume swelling[a] (%)	V_g (cm^3)
(a) Wet column, then dry N_2 flow 48 h, 20°C	6.2	∞
(b) Dry N_2 flow, 12 h, 50°C	1.0	17.4
(c) Dry N_2 flow, 12 h, 50°C	0.3	10.1
(d) Dry N_2 flow, 9 h, 80°C	0.0	2.78
(e) 6.2% rh carrier gas, 16 h	2.8	2.45
(f) 22% rh carrier gas, 16 h	5.5	1.45
(g) Dry N_2 flow, 2 h, 80°C	0.0	2.79

[a] See Ref. 25.

All these results suggest that swelling and increased rates of diffusion of ethanol into the fibers[20] is not the main reason for the observed changes in retention volume with water content.

One explanation of the data in Table I is that with the drying treatment the wool surface is undergoing modification, with the polar groups which are on the surface when the wool is wet turning to lie in the bulk of the wool. In this way the surface becomes more nonpolar, and it is reasonable that the nonpolarity should increase with increasing time and temperature of drying. The elution of ethanol from a nonpolar column will be more rapid than from a polar column. Orientation of surface groups at a keratin surface during wetting or drying has been suggested to explain changes in wettability of human hair.[26] In addition, a recent publication demonstrates how a polypeptide, rich in acidic end groups, can become hydrophobic by surface orientation.[27]

When humidified carrier gas is used, there is a blocking of the adsorption sites for ethanol by the more polar water molecules, a process which would speed up the elution of the alcohol. It seems likely that 22% rh is not a sufficient water content to reverse the inward orientation of the polar surface molecules, and it may be that liquid water, and higher swelling, may be required for this.

Drying the column at 80°C for 2 h restored the sorption characteristics it had before humidified carrier gas was introduced.

The water content of the wool had no effect on the elution rate of *n*-octane, as would be expected for a relatively large nonpolar molecule at low surface coverage.

Wool Pretreatments

Besides the water content, several pretreatments could affect the retention of alcohols in a wool column by modification of the sorption sites. In the following experiments only ethanol was used as adsorbate because the factors that would affect ethanol adsorption would also affect the adsorption of the other alcohols, except perhaps methanol.

The most easily examined factor was staple length, as it was possible that the sorption sites for alcohols were on the relatively polar cut ends of the fibers. Column 3 (1 cm staple) is compared with Column 2 (6 cm staple) in Table II and clearly adsorption on cut ends is not significant, as increasing the number of cut ends six times had very little effect on the retention volumes.

Comparison of the retention volumes of ethanol on column 1 and on columns 2 and 3 (Table II) shows very significant differences. Several factors may be important here.

The wool in column 2 appeared to have more (or stronger) polar surface sorption sites than the wool in column 1. This may have been an intrinsic surface

TABLE II
Specific Retention Volumes of Ethanol on Three Wool Columns after Drying at 80°C, 2 h, Column Temperature 20°C

Ethanol concn (10^{-8} mol·g^{-1} wool)	Retention vol (cm^3)		
	Column 1	Column 2	Column 3
2.8	2.8	16.7	—
4.3	2.4	11.6	12.0

property of the wools but as the wool in column 1 had been carded, gilled, and combed, treatments which would have exposed some of the polar interior of the fibers,[2] it would have been expected that the wool in column 1 would have had the greater number of sorption sites and thus the greater retention volume.

The most probable cause of the difference in ethanol retention between the columns was that some of the polar sites on the column 1 wool had been blocked. The wool in column 1 had been washed in nonionic detergent, which has been shown to sorb strongly at the wool surface,[28] and this may have irreversibly blocked some sites as it would not be removed by the column conditioning.

Differences in the pH of the water extracts of the wools were scarcely significant, and the effect on protonation of the sorption sites (discussed later) would have been very slight.

Retention Volume and Flow Rate

Figure 3 shows the variation of specific retention volume with linear flow rate for untreated and chlorinated wool at 20°C.

On untreated wool the retention volumes of both ethanol and propanol are independent of flow rate between 2.5 and 4.5 $cm \cdot s^{-1}$.

In contrast the retention volume of ethanol on chlorinated wool is much greater at low flow rates but falls rapidly as the flow rate is increased. There is no evidence of a plateau region such as that observed for untreated wool.

The difference between the two wools is easily explained. In chromatography on untreated wool the ethanol is in equilibrium with the surface of the fibers at flow rates between 2.5 and 4.5 $cm \cdot s^{-1}$, and is consequently eluted from the column

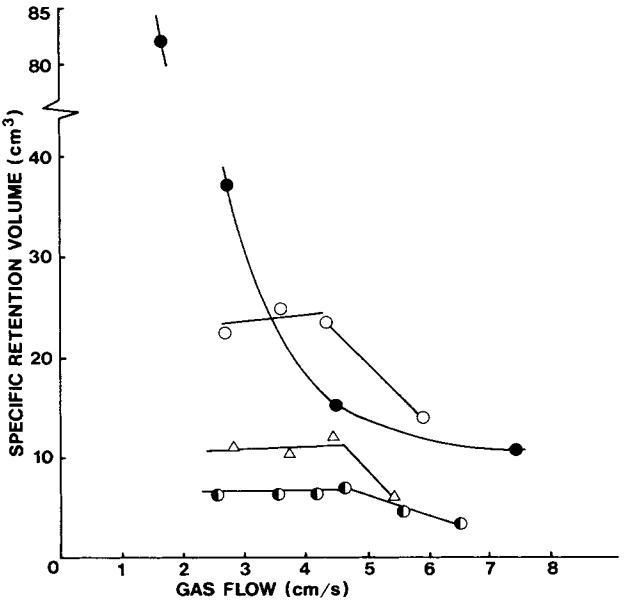

Fig. 3. The effect of linear carrier gas flow rate on specific retention volumes of ethanol and propanol on wool columns at 20.0°C and at 0.64 μg alcohol$\cdot g^{-1}$ wool. (○) Untreated wool, column 2, ethanol; (△) untreated wool, column 2, propanol; (◐) untreated wool, column 1, ethanol; (●) chlorinated wool, column 4, ethanol.

with the same retention volume. At flow rates in excess of 4.5 cm·s^{-1} the ethanol is no longer able to attain equilibrium with the wool surface and is expelled from the column with a reduced retention volume.

On the chlorinated wool column, diffusion of the ethanol into the wool fibers is a predominant factor, and this takes place to an increasing extent as the flow of the ethanol down the column is slowed. At high flow rates a nonequilibrium situation will again exist.[17]

The fact that chlorinated wool shows these effects while untreated wool clearly shows ethanol reacting only with the surface of the fiber means that the chlorination process has removed a barrier to diffusion from the wool surface. An increase in diffusion rates of *n*-propanol with a similar chemical modification has been reported by Bradbury et al.[22] In their study it was found that a potassium permanganate–salt chlorination treatment increased the rate of propanol sorption about 10 times and this was attributed to modification of the cuticle. The chlorination process used in the present work is well known to modify wool cuticle and can, in fact, remove it altogether. [29] In contrast to these results, Leeder and Lipson[23] found that the rate of uptake of liquid ethanol by chlorinated wool was considerably less than its uptake by untreated wool. We are unable to account for this difference.

Heat of Adsorption

Heats of adsorption may be obtained from chromatographic data, provided that the sample has sufficient time to equilibrate with the stationary phase. This is generally assured by using only retention volumes extrapolated to zero flow rates in the calculation, though in fact only small corrections usually arise in this way.[13] This procedure was inappropriate here because extrapolation to zero flow rate would in many cases correspond to a situation in which significant penetration into the fiber had occurred. Accordingly, retention volumes were obtained at a linear carrier gas flow rate of 4.5 cm·s^{-1}, which is slow enough to achieve surface equilibration, but allows little or no penetration (Fig. 3).

For ethanol and propanol on wool, measurements of V_g against sample size were made in the region of 0.7–3 nmol alcohol/g wool and V_g^0, the specific retention volume at zero surface coverage, was found by extrapolation. Values of V_g^0 were obtained at temperatures between 20°C and 40°C and in Figure 4, log V_g^0 is plotted against $1/T$ for both untreated and chlorinated wool. Calculated limiting isosteric heats of adsorption for ethanol and propanol on untreated wool were 35 ± 5 and 50 ± 5 kJ·mol^{-1}, respectively. These heats of adsorption are within the range for physical adsorption, and the similarity of the heats of adsorption of ethanol and propanol on untreated wool to their respective heats of evaporation, 43 and 47 kJ·mol^{-1}, may be taken as evidence that hydrogen bonding is largely responsible for the adsorbent–adsorbate interactions.[30]

On chlorinated wool meaningful heats of adsorption cannot be calculated because of diffusion of the alcohols into the wool fibers. The increase in V_g^0 with temperature which leads to the negative heat of adsorption of ethanol has been observed in other systems, e.g., in semicrystalline polymers above their glass transition temperatures, where diffusion of the sorbate into the polymer increases rapidly with temperature.[14] It is probable that a similar effect also accounts for the low apparent heat of adsorption (about 20 kJ·mol^{-1}) of propanol on chlorinated wool.

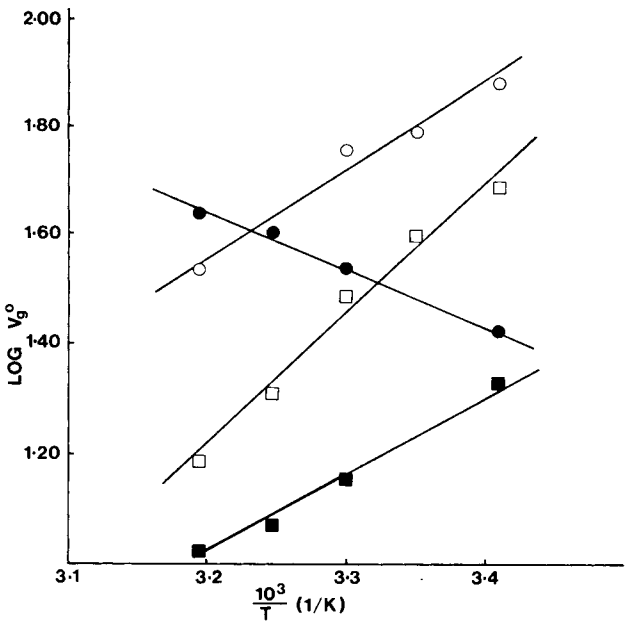

Fig. 4. Variation of logarithm of the limiting specific retention volume with reciprocal absolute temperature for ethanol and propanol on untreated and chlorinated wool at a carrier gas linear flow rate of 4.5 cm·s^{-1}. (○) Untreated wool, ethanol; (□) untreated wool, propanol; (●) chlorinated wool, ethanol; (■) chlorinated wool, propanol.

Retention Volume and Carbon Number

Figure 5(a) shows the variation in log V_g with carbon number (CN) for the *n*-alcohols on untreated (column 2) and chlorinated wool. Methanol retention volumes were all too large to measure, and the retention volume of ethanol on untreated wool was greater than the retention volumes of propanol and butanol. A similar elution pattern was also observed on column I. Nonlinearity of this extent is unusual.

It would be reasonable to argue that retention of the alcohols was diffusion controlled and cite the diffusion coefficients obtained by Watt,[21] which show that the order of the rates of sorption is methanol > ethanol > propanol, were it not for the observation that at the flow rates used in this experiment ethanol (and propanol) have retention volumes independent of flow rate and are thus adsorbed on the fiber surface.

On the other hand, if it could be shown that the sorption sites on untreated wool are very strongly polar, then the observed variation in retention volume with CN could be attributed to bond energies in the order methanol–wool > ethanol–wool > propanol–wool, by virtue of the polarity of the alcohols.[31]

If there were strongly polar sites on the wool surface, these would be expected to be carboxyl and amino groups, although there is a possibility that very polar sulfonic, *S*-sulfonic, or sulfinic groups could also be present. The ion exchange resins Amberlite IRC and Dowex 50W-X8 were therefore used as carboxyl and sulfonic surfaces upon which alcohol elution could be measured to test the effect of polarity.

On the carboxylated Amberlite resin, and in contrast to the wool column [Fig. 5(a)], the retention volumes of the alcohols increased in the order methanol <

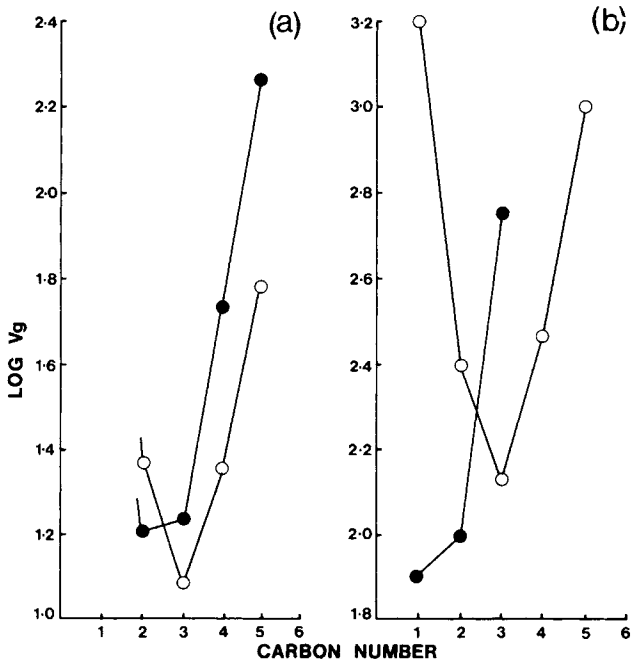

Fig. 5. Variation in logarithm of the specific retention volume with alcohol carbon number for (a): (○) untreated wool; (●) chlorinated wool, at 20.0°C, 4.5 cm·s^{-1} linear carrier gas flow rate and 0.64 μg alcohol·g^{-1} wool; and (b): (○) Dowex 50W-X8 ion exchange resin, 10% H/90% K; and (●) Amberlite-IRC ion exchange resin, 11% H/89% K, at 40.0°C linear carrier gas flow rate 6.5 cm·s^{-1}, 1.64 μg alcohol·g^{-1} resin.

ethanol < propanol, and so it appeared that the strong sorption sites on wool were not carboxyl groups. It was of interest, however, that the retention volumes of the alcohols increased with increased protonation of the Amberlite resin, and a similar effect was observed on the Dowex resin. On the Dowex resin, as in the wool column, the retention volumes of the alcohols decreased in the order methanol > ethanol > propanol [Fig. 5(b)], although only at low sample size on the K form of the resin.

These results give strong evidence that there are very polar groups of the sulfonic type on the wool surface, a finding in agreement with the recent work of Parreira,[32] who has interpreted electrokinetic measurements on human hair as showing the existence of sulfonic acid-type groups at the surface. The presence of strongly polar groups does not mean, of course, that the surface as a whole is polar as these groups were present only at low surface coverages of the order of 0.01 of a monolayer. They may be dispersed over the epicuticle surface (which is cystine rich[7]) or localized, for example, where high sulfur components of the cell membrane complex reach the surface, although simple calculations of the relative areas of cuticular cells and the cell membrane[19] indicate that these sites would not make up 0.01 of a monolayer. The comparison of columns 2 and 3 had showed that the sorption sites were not associated with cut ends. The possibility that the sorption sites were on skin flakes, which can have a high cysteic acid content,[33] was discounted by shaking column-2 wool with 98% formic acid. Only a minute amount of material was released by the wool, probably because the careful washing of the fibers had already removed most of this hy-

drophilic material. In addition, an examination of the literature suggests that wool which has been only commercially scoured has skin flakes with a much higher cysteic acid content[33] than has wool which has been more thoroughly cleaned.[34]

A surprising conclusion that may be drawn from the data of Figure 5(a) is that relating to the retention of alcohols by chlorinated wool. The C_3–C_5 alcohols were retained for longer periods on the chlorinated wool column than on the untreated wool column, and this is entirely in agreement with the well-known more polar nature of chlorinated wool. However, the retention volume of *n*-octane on chlorinated wool was also greater than that on untreated wool, and this implies that chlorination has caused an increase in the wool surface area, probably both by roughening the fiber surface and by extraction of some of the cell membrane complex.

In contrast with the sorption of the C_3–C_5 alcohols, ethanol was retained less on the chlorinated wool than on the untreated wool [Fig. 5(a)] (the carrier gas flow rate was such that diffusion of ethanol into the fiber would be minimal while adsorption equilibrium was still maintained). This can only be explained by the chlorinated wool surface containing less sulfonic groups active in ethanol retention than does untreated wool.

The chlorinated wool could contain less active sulfonic groups than untreated wool because the increase in polarity with chlorination may come more from main-chain scission than from generation of sulfonic groups, although this would seem to be at odds with electrokinetic data.[2] Alternatively the level of chlorination (3%) may have been sufficient to remove all the cystine-rich exocuticle and reveal only the low sulfur endocuticle, which is possible but not very likely in view of the unevenness of a low-pH chlorination treatment.

Another explanation is that there are sulfonic groups on the chlorinated wool surface but that these are not protonated because they have formed salt linkages with relatively labile amino groups produced by main-chain cleavage during the chlorination reaction. The alcohol-retaining part of the chlorinated wool surface would then largely consist of protonated carboxyl groups, and this is consistent with the similarity in alcohol retention of the chlorinated wool and the carboxylated resin (Fig. 5).

The enhanced retention of the alcohols with protonation of the resin surfaces suggests by analogy that wool conditioned at low pH would retain alcohols more strongly that wool conditioned under neutral or basic conditions.

Similarly, other —OH-containing materials, e.g., wool–grease alcohols, nonionic detergents, and some spinning lubricants, may be more strongly sorbed by wool under acid conditions, and this may be one reason why mildly alkaline conditions are favored in the scouring of wool.

CONCLUSIONS

1. Inverse gas chromatography has been used to examine the surface of wool. This technique could be used further on wool, e.g., to obtain information about chemical treatments, surface coatings, mechanical damage, or contaminants.
2. Further evidence has been obtained which suggests macromolecular rearrangements take place at the wool surface on wetting and drying.
3. With chlorinated wool ethanol diffuses into the fiber, showing that the chlorination process removes a surface barrier.

4. There are strongly polar sites, similar in nature to sulfonic groups, on the surface of untreated wool.

The authors would like to thank members of the Textile Chemistry Group of the Wool Research Organisation of New Zealand for many helpful discussions.

References

1. G. M. Hampton and I. D. Rattee, *J. Soc. Dyers Colour.*, **95**(11), 396 (1979).
2. K. R. Makinson, in *Surface Characteristics of Fibers and Textiles, Part I*, M. J. Schick, Ed., Marcel Dekker, New York, 1975, p. 109.
3. G. Mazingue and M. Bauters, *Melliand Textilber., Engl. Ed.*, **9**(4), 504 (1980).
4. D. Stigter, *J. Am. Oil Chem. Soc.*, **48**(7), 340 (1971).
5. A. J. McKinnon and J. R. McLaughlin, *Proc. 6th Quin. Int. Wool Text. Res. Conf.*, **V**, 397 (1980).
6. D. F. G. Orwin, in *Fibrous Proteins: Scientific, Industrial and Medical Aspects*, D. A. D. Parry and L. K. Creamer, Eds., Academic, London, 1979, Vol. 1, p. 271.
7. N. L. R. King and J. H. Bradbury, *Austr. J. Biol. Sci.*, **21**, 375 (1968).
8. B. O. Bateup, J. R. Cook, H. D. Feldtman, and B. E. Fleischfresser, *Text. Res. J.*, **46**, 720 (1976).
9. D. Stigter, *J. Colloid Sci.*, **19**, 268 (1964).
10. B. E. Fleischfresser and G. N. Freeland, *J. Appl. Polym. Sci.*, **20**, 3453 (1976).
11. S. J. Tillin, A. E. Pavlath, S. H. Zeronian, and A. G. Pittman, *Text. Res. J.*, **50**, 724 (1980).
12. J. H. Brooks and J. D. Leeder, *J. Text. Inst.*, **58**, 266 (1967).
13. H. W. Habgood, in *The Solid Gas Interface*, E. A. Flood, Ed., Marcel Dekker, New York, 1967, p. 611.
14. J.-M. Braun and J. E. Guillet, *Adv. Polym. Sci.*, **21**, 107 (1976).
15. U. Coelho, J. Miltz, and S. G. Gilbert, *Macromolecules*, **12**, 284 (1979).
16. G. M. Dorris and D. G. Gray, *J. Colloid Interface Sci.*, **71**, 93 (1979).
17. J. Chauchard, B. Chabert, and G. Edel, *Teintex*, **41**, 299 (1976).
18. B. Miller, H. L. Fredman, and C. H. Meiser, *Text. Res. J.*, **50**, 10 (1980).
19. J. H. Bradbury, *Adv. Protein Chem.*, **27**, 150 (1973).
20. I. C. Watt, *J. Appl. Polym. Sci.*, **8**, 2835 (1964).
21. I. C. Watt, *J. Appl. Polym. Sci.*, **8**, 1737 (1964).
22. J. H. Bradbury, J. D. Leeder, and I. C. Watt, *Appl. Polym. Symp.*, **18**, 227 (1971).
23. J. D. Leeder and M. Lipson, *J. Appl. Polym. Sci.*, **1**, 2053 (1963).
24. J. C. Giddings, *Anal. Chem.*, **35**, 1999 (1963).
25. *Wool Research, Vol. 2. Physical Properties of Wool Fibres and Fabrics*, Wool Industries Research Association, Leeds, 1955, p. 13.
26. Y. K. Kamath, C. J. Dansizer, and H.-D. Weigmann, *J. Soc. Cosmet. Chem.*, **28**, 273 (1977).
27. Y. Nakamura, Y. Hatayama, T. Okazaki, H. Ito, and A. Watanabe, *Proc. 6th Quin. Int. Wool Text. Res. Conf.*, **II**, 273 (1980).
28. C. A. Anderson, R. G. Ganly, and G. F. Wood, *J. Text. Inst.*, **56**, T216 (1965).
29. J. R. McLaughlin and W. S. Simpson, in *Fibrous Proteins: Scientific, Industrial and Medical Aspects*, D. A. D. Parry and L. K. Creamer, Eds., Academic, London, 1980, Vol. 2, p. 213.
30. A. W. Adamson, *Physical Chemistry of Surfaces*, 2nd ed., Wiley-Interscience, New York, 1967, p. 565.
31. L. R. Snyder, *Principles of Adsorption Chromatography*, Marcel Dekker, New York, 1968, Chap. 8.
32. H. C. Parreira, *J. Colloid Interface Sci.*, **75**, 212 (1980).
33. V. G. Kulkarni and H. Baumann, *Text. Res. J.*, **50**, 6 (1980).
34. J. H. Bradbury, G. V. Chapman, and N. L. R. King, *Int. Wool Textile Res. Conf., Proc. 3rd Quim. Int. Wool Text. Res. Conf.*, **I**, 214 (1965).

Received July 29, 1981
Accepted October 26, 1981