Sorption of Liquids by Wool.   Part IV. Sorption of Ethanol by Modified Wool

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INTRODUCTION

The sorption of polar liquids and vapors by proteins is considered to occur initially by hydrogen bonding at polar groups in the protein.[1-7]   These polar sorption sites are mainly side-chain amino, carboxyl, and hydroxyl groups and peptide linkages of the polypeptide chains.   However, there is some doubt as to whether it is side-chain polar groups or peptide links which form the main attractive sites for *initial* sorption.[1-7]

There is some reported research on the effect of side-chain masking on water sorption properties of proteins.   Mellon et al.[5] found that blocking of amino groups of casein by benzoylation decreased the sorption of water vapor.   Modifications of the polar side-chains of wool results in decreased equilibrium sorption of water vapor at low or intermediate vapor pressures[8-11] usually without greatly affecting rate or equilibrium sorption at saturated vapor pressure.   Kanagy and Cassel[12] found that sorption of water vapor by collagen is decreased by deamination, acetylation, and methylation.

With wool, the surface scale structure can be a complicating factor in sorption studies.   Although chemical and physical attack on these surface scales increases the rate of uptake of dyes[13-15] the sorption of water is unaffected.[11,18]

It might also be expected that physical modification of wool would produce changes in sorption behavior due to rearrangement of the polar groups and alterations in accessibility, but it has been found that severe physical changes, including supercontraction, reduction and even complete dissolution and reprecipitation, do not greatly affect the equilibrium sorption of water vapor at relative humidities up to 93%.[16]   Heat denaturation of egg albumin results in very little change in water-sorbing properties, but surprisingly, the sorption of ethanol is greatly decreased.[17]

This can be explained by assuming that because of their small size and high polarity, water molecules are sorbed extremely rapidly, attaching to polar sites with strong hydrogen bonds in such a way that even large changes in the chemical and physical properties of proteins produce little observed effect on the rate of sorption of water.   By using larger and less polar molecules such as alcohols, which are sorbed much more slowly

but to a similar extent,[19,20] effects of chemical and physical modification may become more apparent.

This paper presents results of sorption studies on a variety of modified wools, using liquid ethanol as sorbate. It will be shown that the rate of sorption of ethanol is sensitive to even slight modification.

EXPERIMENTAL

Materials

Wool. The wool used was Merino 64's virgin root wool, cleaned with petroleum ether, warm distilled water, and cold ethanol as previously described.[20]

Ethanol. "Analar" grade ethanol was purified and dried by refluxing with metallic sodium followed by fractional distillation.

Determination of Sorbate Content

The technique of Bradbury and Leeder,[20] using liquified propane gas to wash excess ethanol from the wool, was used in all determinations of sorbate content. All sorption experiments were carried out using liquid ethanol as sorbate at 25°C.

Modification of the Wool

After all treatments except the acidification with HCl, the wool was washed in many changes of distilled water over a period of several days to remove reagents and reaction by-products and to equilibrate the treated wool to the pH of distilled water (pH 5.0–5.5). Weight changes were determined in some instances and are given in the text. The method of obtaining the dry weight of the wool was to immerse it in water for 16 hr., centrifuge, to remove excess water, and dry for 1.5 hr. at 100°C. and 10^{-4} mm. Hg pressure.[21]

(1) Acetylation[22]

In acetylation, 1 part wool was treated at 58°C. for 1 hr. with 1 part acetic anhydride, 4 parts glacial acetic acid, and catalytic amounts of H_2SO_4 and dimethylaniline. Weight increase was 8.0%. A treatment was carried out using ten times the concentration of reagents listed above, resulting in a degraded sample having a weight increase of 7.0%.

(2) Internal Polymerization of Methacrylic Acid[23]

Wool samples (1.3 g.) were heated at 50°C. for (1) 5 min. and (2) 3 hr. in 150 cc. water containing 6 cc. freshly distilled methacrylic acid, 0.5 cc. H_2SO_4, and a trace of H_2O_2. Both samples were pretreated at 25°C. for 1 hr. in 50 cc. of 0.1% aqueous ferrous ammonium sulfate solution. Weight increases were 3% and 127%, respectively.

(3) Acidification

Wool was immersed in approximately $0.01N$ HCl at room temperature for 2 days, centrifuged, and dried without washing to neutrality.

(4) Ninhydrin Treatment[24]

Wool was heated at 100°C. for 15 min. in 1% (0.056M) unbuffered ninhydrin (pH 5.1). Weight increase was 15.3%.

(5) Esterification

(i) **Methanolic-HCl at 20°C.**[25] Wool was immersed in methanol (made $0.1N$ with respect to HCl by addition of concentrated A.R. HCl) for 7 days at 20°C. A control sample was immersed in $0.1N$ aqueous HCl for the same time.

(ii) **Methanolic-HCl at 65°C.**[25] Wool was refluxed for 5 hr. in methanol–$0.1N$ HCl. Weight increase was 2.0%. A control was treated for 5 hr. at 65°C. in $0.1N$ aqueous HCl.

(iii) **Simultaneous Methylation-Acetylation.**[26] A 1-g. sample of wool was immersed in 50 cc. methanol + 5 cc. acetic anhydride at 20°C. for 20 hr. Weight increase was 4.7%. In a control, the acetic anhydride was replaced with an equivalent amount of glacial acetic acid, when some methylation but no acetylation should have occurred.

(iv) **Anhydrous Ethanolic HCl.**[25] Dry wool was refluxed for 5 hr. in dry ethanol made $0.1N$ with respect to HCl with dry HCl gas. Weight increase was 2.7%.

(6) Conversion of Cystine to Lanthionine[27]

Wool was immersed in $0.1N$ aqueous NaOH for (1) 16 hr. and (2) 20 hr., using a liquor ratio of 200:1. Weight decrease for sample (2) was 6.4%.

(7) Reduction and Methylation[28]

Wool was reduced by treatment at 25°C. for 2 days with 0.1M benzyl mercaptan in 20% aqueous n-propanol. The sulfhydryl groups so formed were then blocked by methylation with 0.2M methyl-p-toluene sulfonate in 45% aqueous n-propanol buffered at pH 8. Two samples were prepared. For sample (i) 95% cystine was converted to S-methyl. For sample (ii) 85% cystine was converted to S-methyl, with a weight decrease of 1.6%. (The —S—S— and —SH analyses were done by Dr. J. A. Maclaren using the method of Leach.[55])

(8) Alcoholic Alkali[18]

Wool was treated with 2% KOH in 97% ethanol at 25°C. for 10 min., squeezed, then neutralized in 2% (v/v) H_2SO_4. The same conditions, in the absence of KOH, were used for a control experiment.

(9) Alcoholic Alkali Followed by Supercontraction in LiBr

Wool was treated with alcoholic KOH as above, then heated at 100°C. for 1 hr. in 8M LiBr.

(10) Chlorination[29]

Wool was treated with 2% $KBrO_3$ (on weight of wool) by adding aqueous $KBrO_3$ solution dropwise to the wool immersed in acidified saturated salt solution.

(11) Neutral Permanganate[30]

Wool was treated with 5% $KMnO_4$ in (i) water and (ii) saturated NaCl solution, then cleared in 10% $NaHSO_3$ + 5% CH_3COOH.

(12) Ultrasonic Treatments[31]

(i) Wool, immersed in 98–100% formic acid, was treated for 6 hr. at 20 kcycle/sec. using a probe-type 60-watt M.S.E.–Mullard ultrasonic disintegrator. (ii) Wool, immersed in 98–100% formic acid, was treated for 16 hr. at 40 kcycle/sec. in the tank of a 60-watt Narda Ultrasonics Corporation Sonblaster, series 600.

(13) Ultraviolet Irradiation

Wool was irradiated for 8 hr. in air with occasional mixing to ensure reasonably uniform treatment, using a mercury vapor lamp emitting predominantly 2537 A. light.

(14) Hot Ethanol Extraction

The cold ethanol extraction normally used was replaced by a hot ethanol Soxhlet extraction.

(15) Supercontraction in NaHSO₃

Wool was allowed to supercontract by heating at 100°C. for 1 hr. in 5% aqueous $NaHSO_3$. The wool was degraded by the treatment, as evidenced by its harsh handle and tendency to powder.

(16) Supercontraction in LiBr

Wool was allowed to supercontract by heating at 100°C. for 1 hr. in 8M LiBr.

(17) Crosslinking with Mercuric Acetate[32]

Wool was immersed at 40:1 liquor ratio in 0.1M aqueous mercuric acetate solution, made 0.1N with respect to acetic acid, at 25°C. for 1 hr. Weight increase was 8.0%.

(18) Setting of Wool[33]

Bundles of wool fibers were held at 30% extension (by means of meta stretching frames) for 1 hr. in boiling water, then relaxed for a further hour in the same medium. Average set for a large number of samples was 22%. A control experiment was made by boiling the wool in a relaxed state for 2 hr. in the presence of the metal stretching frames. In each case iron stains were removed by washing in dilute HCl.

(19) Reversible Swelling

Two wool samples were immersed in 98–100% formic acid at 25°C. for (i) 2 min. and (ii) 15 min. The formic acid was then removed by thorough washing in distilled water.

RESULTS AND DISCUSSION

Cassie[3,4] and Windle[34] have applied the B.E.T. theory of multimolecular sorption[35] to the sorption of water vapor by wool, considering that water is sorbed initially by polar sites in the wool. As the polar groups which are accessible to water become saturated, a second layer of water molecules is sorbed on top of the primary water already present. There will not be a sharp change from sorption by primary sites to multimolecular sorption, since some secondary sorption will occur before all primary sites have become accessible as a result of swelling of the wool.

Even at or near saturation sorption, all polar groups present in the wool will not be available as sorption sites due to incomplete accessibility of the crystalline regions.[36]

Progressive sorption of water from dryness to saturation probably occurs firstly onto side-chain NH_2 ($-NH_3^+$) and $-COOH$ ($-COO^-$) groups[36,37] and side-chain hydroxylic groups,[36] then as sorption proceeds swelling of the wool makes available more of these side-chain groups as well as peptide links.[38] The dipole induced in this localized primary layer of water molecules facilitates multimolecular sorption of water (designated intermediate water by Windle[34]). As sorption approaches saturation, loosely bound water analogous to liquid water is taken up. The final amount of sorption is limited by the forces resisting swelling in the fiber network. These forces holding the fiber together are hydrogen bonds (between peptide links in the main polypeptide chains); salt linkages (between free basic and acidic side-chains); and van der Waals' bonds (between hydrophobic groupings in the fiber).

It should be mentioned here that these cohesive forces are considerably weakened by the presence of sorbate, i.e., salt links and hydrogen bonds are broken and polar groups forced apart by sorption and swelling. Thus Speakman found that wool immersed in water or alcohol is less resistant to extension than dry wool[39] and that the presence of water decreased the rigidity of wool fibers.[40]

The view that initial sorption by dry wool is mainly onto side-chain polar groups is supported by comparing activation energies of diffusion[10,41] and heats of hydration[7] for the wool–water system with the values obtained for the individual polar groups.   It is found that the forces of sorption at low relative humidities are approximately what would be expected if the side-chain polar groups participated in the initial sorption of water by wool.

In the following discussion of the sorption of ethanol by wool it is assumed that the mechanism of sorption is similar to that for water, [1,20,42] i.e., sorption takes place mainly by means of hydrogen bonding.   However, the possibility that a slightly different mechanism is operative for alcohol sorption should not be discounted, in view of some of the unexpected results obtained.

Results in Tables I–V are for sorption of ethanol (in grams/100 g. dry wool) in 1 hr. at 25°C.   These results, as will be shown later, (Figs. 1 and 2) provide a good indication of the initial rate of sorption.   The treated wools have been grouped in tables according to the main effect considered to result from the modification.   Since very few reactions for wool are completely specific, side-effects will sometimes partially contribute to the observed change in sorption properties.

The foregoing theory indicates that if the highly polar primary sorption sites are removed, blocked or inactivated, a decrease in the rate and quantity of sorption would be expected.   Table I shows that blocking of basic groups substantially reduces the rate of sorption of ethanol.   As mentioned earlier, modifications to the amino groups of proteins slightly decreases the equilibrium sorption of water at low or intermediate vapor pressures, apparently without affecting the rate of sorption, although a slight change in the rate of desorption of water from acetylated wool has been reported.[10] Nicholls and Speakman[43] found that acid present in wool decreased the sorption of water, particularly at intermediate relative humidities.   They state that conversion of —COO⁻ to —COOH accounts for only a slight decrease, so the result in Table I for wool containing HCl is considered to be due to blocking of —NH₃⁺ groups with Cl⁻ ions.   Part of the change in ethanol sorption rate with ninhydrin-treated wool is probably due to increased crosslinking (see Table V).

TABLE I

Effect of Amino Group Modification on the Sorption of Liquid Ethanol in 1 hr. at 25°C.

Pretreatment	Ethanol sorbed by treated wool, %[a]
Untreated	14.0
Acetylation	1.8
Acidification with HCl	6.9
Ninhydrin treatment	7.3
Acetylation (overtreatment)	8.8

[a] Corrections have not been made for the weight of added reagents, since in most cases the correction factors are small and do not alter the conclusions of the paper.

TABLE II
Effect of Carboxyl Group Modification on the Sorption of Liquid Ethanol in 1 hr. at 25°C.

Pretreatment	Ethanol sorbed by treated wool, %
Untreated	14.0
Methanolic HCl at 20°C.	23.2
Control[a]	14.8
Methanolic HCl at 65°C.	23.7
Control[a]	22.1
Methylation-acetylation	24.7
Control[a]	17.6
Anhydrous ethanolic HCl	26.9

[a] See text.

With amino group modification, the decreased rate of sorption is probably mainly due to the decreased number of highly polar sorption sites.

With carboxyl group modification (Table II) a decrease in the sorption rate would also be expected, but the reverse is the case.   The possibility that main-chain hydrolysis by the HCl catalyst used in the esterifications is responsible for the observed increase was checked by control experiments, since it was found that degradation by an acetylation overtreatment gave a considerably higher rate of sorption than normal acetylation (Table I).   Thus the effect due to methylation at 65°C., without using specially dried reagents, was found to be mainly the result of degradation of the wool. However, with low temperature methylation and anhydrous ethylation, very little main-chain hydrolysis should have occurred[25,44] so that esterification of —COOH groups definitely increases the sorption rate of ethanol. Considering that the esterifications resulted in reaction with 55–67% of COOH groups,[25] i.e., probably with most of the —COOH groups which are normally accessible to ethanol, the effect on the sorption rate is particularly striking.

Valentine[36] has calculated that at 65% R.H., amino groups of wool are approximately three times more hygroscopic than acidic groups, and Speakman[7] has found that the heat of hydration (and therefore presumably the energy of sorption) for —COOH groups is much lower than that for —NH$_2$ groups.   Thus, masking of amino groups would be expected to have a greater effect on sorption properties than an equimolar masking of carboxyl groups.   A possible explanation for the increased sorption rate is that masking of the accessible carboxyl groups would leave the amino groups more readily available as primary sorption sites, resulting in easier and faster penetration of sorbate molecules.

Opening of the wool structure by esterification may contribute to the increase in sorption rate, but this should also apply to acetylation and other treatments where no increases in sorption rate were found.   However, this possibility is supported by density measurements.   The density of ethylated wool (1.297 g./cm.^{3}) was found to be slightly lower than untreated

wool (1.299 g./cm.^{3}), whereas the density of acetylated wool (1.339 g./cm.^{3}) was considerably higher.[11]   Baker and Fuller found that esterification of the amide groups of nylon increased the vapor state sorption of water by opening up the structure,[45] but the effect should not be as great with wool due to its lower degree of crystallinity.

Another possibility is that the methoxyl or ethoxyl groups present after esterification contribute to sorption of ethanol by van der Waals' bonding with the hydrocarbon ends of ethanol molecules.   This is supported by the results in Table II, where the greatest increase in rate was obtained by esterification with ethanol, the —OC$_2$H$_5$ group being more hydrophobic than the —OCH$_3$ group.

The great increase in sorption rate found with wool which had been simultaneously methylated and acetylated appears to be an anomalous case, since the increase was greater than for the control sample, which was only methylated.   This may also be the result of a change in density, since the methylated-acetylated wool had a lower density than untreated wool.

TABLE III

Effect of Disulfide Bond Modification on the Sorption of Liquid Ethanol in 1 hr. at 25°C.

Pretreatment	Ethanol sorbed by treated wool, %
Untreated	14.0
Cystine → lanthionine (i)	24.1
Cystine → lanthionine (ii)	20.7
Reduction and methylation (i)	26.1
Reduction and methylation (ii)	22.4
Ultraviolet irradiation	18.1

Reactions designed to modify the disulfide bonds of wool greatly increase the rate of uptake of ethanol (Table IV).   It is assumed that cystine does not bind sorbate molecules at the —S—S— position[16,36] so another explanation must be sought for this effect.

With the reduced and methylated wool, where the disulfide crosslinks have been almost completely removed, the wool will have less resistance to swelling, and this could explain the increased sorption.   A consequence of this hypothesis is that initially inaccessible polar groups would be more readily available as sorption sites due to the increased ease of swelling. That the wool fibers are in a more open condition is supported by density measurements;[11] it has been found that the density of reduced and methylated wool sample (ii) is 1.286 g./cm.^{3}, which is significantly less than that of untreated wool.

The above explanation does not appear to hold for the 0.1N aqueous NaOH treated wool, where approximately 50% of cystine was converted to lanthionine.[26]   The density of the treated wool was 1.310 g./cm.^{3}.   It is possible that the higher density results from closer alignment of polypeptide

chains due to the shorter length of lanthionine bonds (R—S—R) compared to disulfide bonds (R—S—S—R). However, this would suggest a decrease in rate instead of the observed increase. The weight loss of 6.4% following reaction with alkali suggests that as well as —S—S— breakage, hydrolysis and degradation has taken place, with —NH$_2$ and —COOH terminal groups being formed by peptide bond hydrolysis.

Ultraviolet irradiation results in attack on cystine, with the formation of polar degradation products,[46] which would account for the increased rate of sorption.

TABLE IV

Effect of Surface Modification on the Sorption of Liquid Ethanol in 1 hr. at 25°C

Pretreatment	Ethanol sorbed by treated wool, %
Untreated	14.0
Alcoholic KOH	0.9
Control (without KOH)	15.2
Alcoholic KOH + supercontraction	1.8
Chlorination	4.2
Permanganate-water	4.5
Permanganate-saturated salt	6.6
Ultrasonics (i)	9.0
Ultrasonics (ii)	10.3
Hot ethanol extraction	19.5

Most of the treatments in Table IV were expected to produce an increase in the initial rate of sorption of ethanol due to removal or disruption of a "surface barrier to diffusion."[13,47–49] Extraction of the wool with hot ethanol was the only treatment which had this effect, probably due to the solvent action of the ethanol, which "cleans" the fiber surface without chemical attack.

Wool subjected to shrinkproofing treatments (alcoholic KOH, chlorination and neutral permanganate) is wetted by water more rapidly than untreated wool and usually shows an increased rate of uptake of acid dyes.[13–15] This suggests that the polar nature of the wool fiber surface is altered. Thus Bradbury[50] has found that oxidative shrinkproofing treatments convert cystine to cysteic acid, mainly near the surface of the fiber, thus giving increased polarity. These treatments would therefore be expected to increase the initial rate of sorption, which is not the case.

A possible explanation is that the configuration and polar nature of the surface is altered such that the "holes" in the surface are changed and slow down the penetration of ethanol.

With ultrasonic treatment, mechanical disruption of the scale layer, without chemical damage,[31] would not be expected to show the observed decrease in sorption rate. This cannot at present be explained.

The whole fiber treatments listed in Table V show decreases in initial sorption rate, which can be explained by configurational and steric changes.

TABLE V

Effect of Whole-fiber Chemical and Physical Modification on the Sorption of Liquid Ethanol in 1 hr. at 25°C.

Pretreatment	Ethanol sorbed by treated wool, %
Untreated	14.0
Supercontraction in NaHSO₃	1.7
Alcoholic KOH + supercontraction in LiBr	1.8
Supercontraction in LiBr	2.8
127% Polymethacrylic acid	3.8
Ninhydrin treatment	7.3
Mercuric acetate crosslinking	8.3
Permanent setting	12.0
3% polymethacrylic acid	12.7
Reversible swelling (i)	13.7
Reversible swelling (ii)	13.7

Supercontraction in LiBr and NaHSO₃ decreases the sorption rate partly because the supercontracted wool has greater density (probably due to more economical packing of bulky side-chains[61]) and partly because supercontraction gives a decrease in surface area and therefore a decrease in sorption rate. The different conformation of the supercontracted wool may also affect the accessibility of polar groups.

Compared with water, the lower polarity of ethanol molecules would result in lower forces of attraction, which, coupled with their larger size, may magnify the effect of conformational changes. In this connection it has been found[17] that heat denaturation of egg albumin results in a decreased rate of sorption of ethanol with very little change in the water-sorbing properties.

Conformational changes would also account for the lower sorption rate of set wool, any possible increase in rate due to greater surface area being outweighed by these factors.

The effect obtained with ninhydrin treatment and internal polymerization of methacrylic acid may be due to steric blocking of sorption sites and increased resistance to swelling. Thus it was expected that mercuric acetate crosslinking would give the effect observed. Also mercuric acetate may form crosslinks with amino groups,[32,52] thus decreasing the number of primary sorption sites.

Immersion of wool in formic acid, which gives reversible swelling, caused no changes in subsequent sorption properties because there was no permanent change in conformation.

Figures 1 and 2 contain more complete sorption data on several of the modified wools already discussed. It can be seen that the general shape of the graphs of sorption vs. time are not greatly altered by the modifications used. Thus the general conclusions in this paper can be arrived at without determining the full graph of sorption vs. time.
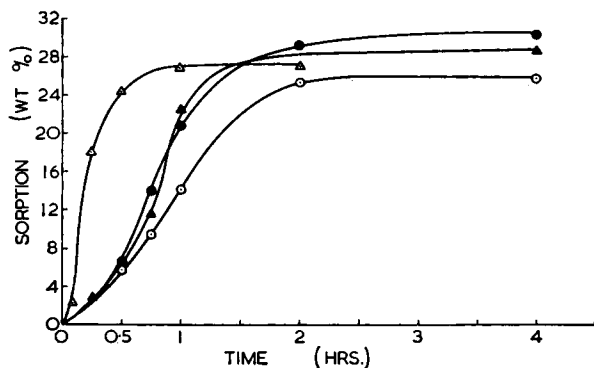
Fig. 1. Rate of sorption of liquid ethanol at 25° by (○) untreated wool; (△) anhydrous ethylated wool; (▲) reduced and methylated wool; (●) wool treated with aqueous alkali.
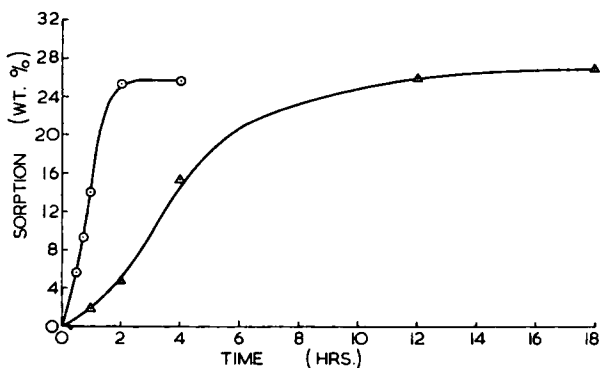

Fig. 2. Rate of sorption of liquid ethanol at 25° by (○) untreated wool; (△) acetylated wool.

Saturation sorption values were obtained on several samples by immersing the wool in ethanol under vacuum for 6–20 weeks in a water bath at 25°C.[20] Results are listed in Table VI.

TABLE VI

Saturation Equilibrium Sorption of Liquid Ethanol by Modified Wools at 25°C.

Pretreatment	Ethanol sorbed by treated wool, %
Untreated	28.0
Permanent setting	28.6
Anhydrous ethylation	28.6
Acetylation	29.8
Supercontraction in LiBr	30.2
Ultraviolet irradiation	31.4
Cystine → lanthionine	32.1
Reduction and methylation	32.5

Although chemical and physical modification of wool produces large changes in rate of sorption of ethanol, the saturation sorption figures are not greatly changed by the treatments.

The maximum amount of sorbate taken up by wool is determined, not by the total number of sorption sites or their accessibility, but by the number and strength of cohesive bonds in the wool. When these cohesive forces are equalized by the swelling force of sorbate inside the fibers, sorption will cease. When formic acid is used as the swelling agent, much greater swelling occurs due to the greater hydrogen bond breaking power of formic acid.[53] In fact, Watt[54] has found an abnormal degree of swelling and sorption by reduced and methylated wool using formic acid vapor as sorbate.

Thus acetylation, esterification, supercontraction, and setting do not greatly affect the saturation sorption of ethanol because these treatments do not permanently break the disulfide or hydrogen bonds which stabilize the fiber structure.

The higher saturation sorption value for reduced and methylated wool and ultraviolet-irradiated wool is due to removal of cystine crosslinks, resulting in a lower resistance to swelling. However, it would seem that the disulfide bonds do not confer great stability on the intact wool fiber, since permanent disruption of 85% of these bonds by reduction and methylation did not increase the saturation sorption figure as much as might be expected.

The higher saturation value obtained when 50% cystine is converted to lanthionine is further evidence for severe attack on the fiber by aqueous alkali.

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Synopsis

Experimental results for the sorption of liquid ethanol by a variety of modified wools are described. Even slight changes in the chemical and physical structure of wool produced large changes in ethanol sorption rate. Blocking of amino groups decreased the sorption rate due to removal of primary sorption sites, but, surprisingly, carboxyl group modification greatly increased the rate. Modification of disulfide crosslinks increased the rate, while in most cases surface modification decreased it, which is contrary to expectation if a surface barrier to diffusion of penetrants is assumed. Theories are advanced for the observed changes in sorption properties and for the small changes found when water if used as sorbate. Saturation sorption values showed only slight changes from that for untreated wool. The largest increases resulted from disulfide

bond modification, which is explained as due to lower resistance of the treated wool to swelling forces, allowing greater swelling and sorption.

Résumé

Les résultats expérimentaux de la sorption de l'éthanol liquide par diverses laines modifiées sont décrits. Des modifications de structure chimique et physique de la laine parfois faibles provoquent des variations importantes de la vitesse de sorption de l'éthanol. Le blocage des groupes aminés élimine la vitesse de sorption en raison d'une dispartition des sites primaires de sorption. Il est surprenant, par contre, que la modification des groupes carboxyles augmente considérablement la vitesse, tandis que dans la plupart des cas des modifications de surface provoquent une diminution. Ceci est contraire aux prévisions si l'on admet l'existence d'une barrière à la surface pour la diffusion de substances. Des théories sont proposées pour expliquer les variations des propriétés de sorption observées et les faibles modifications trouvées lors de l'empvi de l'eau comme substance absorbée. Les valeurs de la sorption à la saturation ne présentent que des variations faibles par rapport aux valeurs obtenues pour la laine nontraitée. Les augmentations les plus importantes résultent d'une modification des points disulfurés. Ceci peut etre intérprété par une résistance plus faible aux forces de gonflement de la laine nontraîtée permettant un gonflement et une sorption plus importantes.

Zusammenfassung

Versuchsergebnisse für die Sorption von flüssigem Äthanol durch eine Anzahl modifizierter Wollproben werden mitgeteilt. Schon recht kleine Veränderungen des chemischen und physikalischen Aufbaus von Wolle erzeugten grosse Änderungen der Sorptionsgeschwindigkeit des Äthanols. Blockierung der Aminogruppen führte infolge der Entfernung primärer Sorptionsstellen zu einer Abnahme der Sorptionsgeshwindigkeit, eine Modifizierung der Karboxylgruppe erhöhte jedoch überraschenderweise die Geschwindigkeit stark. Modifizierung der Disulfidvernetzungen führte zu einer Erhöhung der Geschwindigkeit, während eine Oberflächenmodifizierung in den meisten Fällen zu einer Herabsetzung führte, was im Widerspruch zur Erwartung steht, wenn eine Oberflächenbarriere für die Diffusion angenommen wird. Theoretische Vorstellungen für die beobachteten Änderungen des Sorptionsverhaltens und für die kleinen Änderungen bei Anwendung von Wasser als Sorbat werden entwickelt. Die Sättigungswerte für die Sorption zeigen gengenüber unbehandelter Wolle nur schwache Änderungen. Die grösste Zunahme wurde durch Modifizierung der Disulfidbindung erreicht, was durch die geringere Beständigkeit der behandelten Wolle gegen Quellungseinflüsse erklärt wird, die eine grössere Quellung und Sorption ermöglicht.