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Sorption of Liquids by Wool. Part III. Accessibility of Wool to Sorbates

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INTRODUCTION

The sorption method for measuring accessibility gives unequivocal results in cases where sorption is so extremely slow (as in the case of *n*-pentane on wool[1]) that for all practical purposes one can assume that the sorbent is inaccessible. However, when there is an appreciable amount of sorption the situation becomes complex, as shown by the behavior of cellulose. With a number of different celluloses there is a direct relation between the percentage sorption of water at 58% R.H. and the accessibility to D_2O of the cellulose[2,3] Unfortunately, this correlation between sorption and accessibility cannot be extended to anhydrous formic acid, since in it cellulose swells about twice as much as in D_2O, although the accessibility of cellulose toward both reagents is about the same.[4]

On sorption of water and some primary alcohols by wool it was found that the molar amount of sorption (at a particular relative humidity) decreased as the size of the molecule increased.[5] By application of the Hailwood-Horrobin isotherm[6] to the results it was concluded that the accessibility of wool to water and primary alcohols decreased as the size of the molecule increased. However reevaluation of the results showed that approximately the same volume of sorbate was sorbed at saturation by the wool in all cases,[7] and the results have now been confirmed and extended to isopropanol and *n*-butanol. These observations, together with the fact that there is about the same volume contraction on sorption of the various sorbates by wool,[7,8] was interpreted as indicating that wool is equally accessible to each of these sorbates. This paper describes a quantitative approach to the phenomenon of volume contraction on sorption and correlates the results with other evidence on the accessibility of wool to sorbates obtained from chemical, mechanical, x-ray, and infrared studies.

DERIVATION OF EQUATIONS

The specific volume v_D of a dry sample of wool measured in a nonpenetrating liquid such as *n*-hexane[8] is equal to the sum of the constitutive

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volume of the amino acid residues in the wool, v_{AA}, and the volume of pores in the dry wool. The evidence for the occurrence of the latter is summarized in Part II.[8] Thus

$$\text{Pore volume in dry wool} = v_D - v_{AA} \quad (1)$$

When a liquid is used which penetrates wool, the eqs. (2)–(4) are applicable at all stages of sorption:

$$v_C = v_E + v_{NP} + \text{volume pores accessible to sorbate} \quad (2)$$

$$\text{Pore volume in dry wool} = \text{volume pores accessible to sorbate} + \text{volume pores inaccessible to sorbate} \quad (3)$$

$$\phi = v_D - v_C \quad (4)$$

where v_C is the total volume contraction/g. dry wool, v_E is the volume contraction/g. dry wool due to orientation and close packing around charged groups (i.e., electrostriction), v_{NP} is the volume contraction/g. dry wool due to structural changes in the sorbate in the vicinity of nonpolar side chains, and ϕ is the apparent specific volume. The volume of pores inaccessible to sorbate, eq. (3), is called the excluded volume in the field of soluble proteins.[9,10] Combination of eqs. (1)–(4) gives

$$\phi = v_{AA} + \text{volume pores inaccessible to sorbate} - v_E - v_{NP} \quad (5)$$

At saturation $\phi = \bar{v}_{sat}$,[8] the partial specific volume of wool at saturation, hence

$$\bar{v}_{sat} = v_{AA} + \text{volume pores inaccessible to sorbate} - v_E - v_{NP} \quad (6)$$

Equation (6) expresses quantitatively current ideas.[11]

CALCULATIONS AND RESULTS

Constitutive Volume, v_{AA}

This quantity was calculated by McMeekin and Marshall[12] to be 0.712 by the summation of the contribution of each amino acid.[13] Using the same method and the mean of the most recent analytical figures for Merino wool[14,15] one obtains the value 0.715.

Electrostriction, v_E

The volume contraction v_E/g. dry wool, due to orientation of sorbate molecules around charged groups in the protein is dependent on the number of charged groups in the wool, their accessibility to sorbate and the sorbate used. The results of the calculations are given in Table I, from which it is noted that the volume contraction per charged group is much larger for the alcohols than for water. In aqueous HCl at pH 2 the carboxyl groups are uncharged, hence leaving the positively charged basic groups as the sole contributors to electrostriction.[10,18]

TABLE I
Data Used in Calculation of Electrostriction of Wool at Saturation

Sorbate	Electrostriction, cm.³/mole charged groups	Charged groups, mole/g. dry wool	v_E, cm.³/g. dry wool[a]
Water	10.5[b,c,d]	0.00158	0.017
Aqueous HCl, pH 2	10.5	0.00086	0.009
Ethanol	28.6[b]	0.00158	0.044
n-Propanol	30.9[b]	0.00158	0.047

[a] Calculated on the assumption that all charged groups are accessible to sorbate at saturation. This is valid for water but may be in error for the alcohols, because it is well known that all charged groups can be titrated with acid or base in aqueous solution but there is no information regarding titrations in alcohol.

[b] Data of Vosburgh et al.[16]

[c] Data of Edsall.[17]

[d] Data of Kauzmann.[11]

Volume Contraction of Sorbate Due to Nonpolar Side Chains, v_{NP}

It has been found that the partial molal volumes of methane and ethane in *n*-hexane are 60.0 and 69.3,[19] whereas in water they are only 37.3 and 51.2,[20] respectively. Kauzmann[11] has reviewed the evidence, from which it is concluded that this volume decrease of about 20 cm.³/mole in the passage of the hydrocarbon from a nonpolar to an aqueous environment is due to the formation of icebergs[21] of water surrounding each hydrocarbon molecule. The structure of the water in these icebergs is very different from that in ice, since formation of the latter would be accompanied by an increase of volume, rather than the decrease which is actually observed. Nevertheless, Masterton[20] postulated an increase in volume in order to explain the effect of temperature on partial molal volume of methane and ethane in water, and Klotz[22] subsequently supported this view, but it is clearly at variance with the experimental results.

The sorption of water around nonpolar groups in wool can be considered to occur in two stages, the first of which involves the formation of icebergs of water around each separate nonpolar side chain, assuming 100% accessibility to water. This is followed by the formation of hydrophobic bonds[11,23] between various separate nonpolar side chains with the formation of small micelles or hydrophobic areas. This second stage of the process is favored by the increase of entropy due to the breakdown of the iceberg structure surrounding each nonpolar side chain and reformation of a less extensive iceberg structure around the hydrophobic area.[11]

An approximate measure of the volume decrease accompanying the first stage is obtained by assuming a volume decrease of 20 cm.³/mole of aliphatic nonpolar side chains (from alanine, isoleucine, leucine, and valine) and a decrease of 6 cm.³/mole of aromatic side chains of phenylalanine.[11] On the assumption of 100% accessibility to water, the volume decrease amounts to 0.038 cm.³/g. dry wool. The second stage, that of formation of hydrophobic areas with consequent decrease of the extent of the iceberg

structure, is accompanied by an increase of volume. Unfortunately, insufficient is known about the extent of hydrophobic bonding in wool or the accessibility of hydrophobic areas to water to be able to make even a reasonable guess of the value of v_{NP}. One can only define its limits as being between 0 and 0.038 cm.^{3}/g. dry wool. In view of this indefiniteness, together with the fact that previous workers[9,10,17] in the field of soluble proteins have not considered this effect, it is proposed to assume $v_{NP} = 0$ for sorption of water, in the knowledge that the results may require revision at some later date. Also $v_{NP} = 0$ for sorption of alcohols by wool, since it is unlikely that hydrophobic bonding can occur in this case.

Accessibility of Pores in Wool to Sorbate

The relevant experimental information required for the calculation of the volume of pores accessible to sorbate and the pore volume of wool is given in Table II. The pore volume in dry wool recorded in Table III is calculated by eq. (1), for a value of $v_{AA} = 0.715$ in all cases. The volume of

TABLE II
Partial Specific Volume at Saturation $\bar{v}_{sat}$ and Specific Volume of Wool at 25°C.

Sample of wool	Sorbate	Specific volume in nonpenetrating liquid v_D, cm.^{3}/g.	$\bar{v}_{sat}$, cm.^{3}/g.
Merino 64's virgin root wool[b]	*n*-Hexane	0.770[a]	—
	Water	—	0.724
	Aqueous HCl, pH 2	—	0.718
	Ethanol	—	0.723
	n-Propanol	—	0.725
	Acetone	—	0.720
	n-Butanol (wool sat. at 80°C.)	—	0.740
Merino 64's super-contracted in LiBr[b]	*n*-Hexane	0.766	—
	Water	—	0.718
Cape wool[c]	Benzene	0.767	—
	Helium	—	0.754
	Water	—	0.723

[a] Values of the densities of native keratins, including various grades of wool in non-penetrating liquids, are summarized by Fraser and Macrae,[24] who obtained a value of $v_D = 0.768$ for Merino 64's.

[b] Data of Bradbury and Leeder.[8]

[c] Data of Heertjes.[25]

pores inaccessible to solvent is calculated by eq. (6) for $v_{NP} = 0$ and on substitution of the appropriate values of v_E and $\bar{v}_{sat}$ from Tables I and II, respectively. The volume of pores accessible to sorbate is calculated by eq. (3).

TABLE III
Accessibility of Pores in Wool to Sorbate at 25°C.

Sample of wool	Sorbate	Pore volume in dry wool, cm.³/g.	Volume of pores inaccessible to sorbate, cm.³/g.[a]	Volume of pores accessible to sorbate, cm.³/g.	Volume of pores accessible to sorbate, %
Merino 64's virgin wool	Water	0.055	0.025	0.030	55
	Aqueous HCl, pH 2	0.055	0.012	0.043	78
	Ethanol	0.055	0.053	0.002	4[b]
	n-Propanol	0.055	0.055	0.000	0[b]
Merino 64's supercontracted in LiBr	Water	0.051	0.019	0.032	63
Cape wool	Water[c]	0.052	0.024	0.028	54
	Helium[d]	0.052	0.039	0.013	25

[a] Called "excluded volume" in soluble protein work.

[b] If only 50% of the charged groups are accessible to ethanol and *n*-propanol then v_E is 0.023, and the pore volume accessible to solvent is 43%. It seems likely that the true value lies between 0 and 43%, since values much in excess of 43% would mean that the per cent of pores accessible to sorbate would be greater than the per cent of charged groups accessible to sorbate. By analogy with the situation with water this seems unlikely.

[c] Since the amino acid composition of Cape wool is unlikely to be very different from that of Merino 64's, the values of v_{AA} and v_E calculated for the latter is used in this calculation.

[d] $v_E = 0$ in this case.

DISCUSSION

It is seen in Tables II and III that there is reasonable agreement between the results obtained for Merino 64's and Cape wool. Also, there is very little difference between the densities of different grades of wool measured in a nonpenetrating liquid.[24] It is therefore concluded that the specific volume, partial specific volume in water, and the pore volume of wool are only slightly dependent on the grade of wool used. However, coarse wool fibers containing large amounts of medulla may give much greater values for the pore volume.

The volume of pores accessible to helium gas is only about half that accessible to water. This is due to the fact that the helium atom, although much smaller than the water molecule, is unable to penetrate the fiber by breaking hydrogen bonds. Similarly, it is found that alcohols penetrate the fiber much more rapidly than hydrocarbons of smaller size.[1] Because of the lack of penetration of the fiber by helium, many pores of diameter greater than that of the helium atom (1.78 A.)[26] are probably inaccessible to it.

The titration of the carboxylate ion with HCl causes a decrease in the electrostriction of water molecules and a considerable increase in the volume of pores accessible to water. This is probably due to a reversible change in the fiber by which water is able to penetrate more readily the formerly inaccessible pores, some of which are located in the crystalline region. A similar reversible phenomenon is observed with the serum albumins.[9,18] This process may account for the decrease in the work to stretch fibers 30% in water as the pH is decreased,[27] although other factors such as the removal of salt links and increased swelling at low pH may also be important (reviewed by Alexander and Hudson[28]).

It is rather extraordinary that the percentage of pores of virgin wool accessible at pH 2 is greater than that available to water with supercontracted wool. Of greater significance are the results in Table II, which show that both v_D and $\bar{v}_{sat}$ (water) are decreased by supercontraction in LiBr. Thus supercontraction produces a decrease in the pore volume and a considerable decrease in the volume of pores inaccessible to water as shown in Table III. Since supercontraction is a disordering process[29] which is analogous to denaturation of soluble proteins, it is worthwhile examining the volume changes which occur during denaturation.

Linderstrøm-Lang[30] found that there was a large initial decrease of volume on the breakdown of β-lactoglobulin and other proteins with trypsin, from which he concluded that the denatured form of the protein is probably more compact than the native form. The reversible denaturation of the albumins at low pH[9,18] is due to a partial transition from the α-helical to the random coil form,[18] and this is accompanied by a decrease of the partial specific volume in water and of the volume of pores inaccessible to water. In addition, Charlwood[9] has noted that gelatin, which behaves in many ways like a random coil in solution,[31] has only a very small volume of pores inaccessible to water compared with the albumins investigated. The reversible denaturation of rabbit and pinna tropomyosin in urea is also accompanied by a decrease in v and in the volume of pores inaccessible to solvent,[10] and various physical measurements have shown that this denaturation is a transition from α-helix to random coil.[32,33] All the evidence points to the conclusion that the transition from the α-helical to the random coil form characteristic of denaturation of soluble proteins, is accompanied by a decrease of $\bar{v}$ and a decrease of the volume of pores inaccessible to the solvent.

This conclusion accords well with the decrease in v_D, $\bar{v}_{sat}$ (water), pore volume, and volume of pores inaccessible to water which accompanies removal of the crystalline phase[29] on supercontraction of wool. Furthermore, wool supercontracted in steam has a slightly higher density (smaller value of v_D) than virgin wool.[34] Also it is found[34] that the wool fiber cuticle, which is known to consist of amorphous material, is denser than cortical cells which contain the crystalline component of the fiber. However, it may be that the cuticle contains material of a higher density present as a contaminant[35] and/or as an integral part of it, although the latter

seems to be unlikely.[36] Finally, it is found that there is a qualitative correlation between the definition of the x-ray diffraction pattern and the density of the α-keratin. For example, quill tip gives a better defined x-ray pattern and is denser than cow hoof.[24] This is the only result which appears to contradict the large amount of evidence already given. However there may be an alternative explanation of the apparently anomalous result, such as a difference in amino acid content between different α-keratins.

It is therefore porposed that the α-helical regions in proteins are less dense than the random coil regions. Thus in wool, the crystalline regions consist of an arrangement of α-helices surrounded by a matrix protein which consists largely of random coils. Although the details of the structure are still speculative,[37] it is known that supercontraction disorders the structure (i.e., removes the crystalline α-helical regions) and, it is postulated, thereby increases the density of the fiber.

It is pertinent to consider the origin of the proposed less dense α-helical regions as compared with the random coil regions. The constitutive volume of the polypeptide chain is calculated by summation of the contributions of each amino acid residue (see above) and is therefore independent of the conformation of the chain. Also it is known that the α-helix is a tight helix with van der Waal's contact of atoms close to the helical axis, such that there is no hole down the center of the helix.[38] The relative openness of the α-helical regions would therefore seen to reside in the packing together of the α-helices. Waugh[39,40] has shown that it is not possible to obtain close packing of the diverse side chains which project from the α-helices of the protein. It seems likely that the side-chain packing is poorer in crystalline, α-helical regions than in the amorphous, random coil regions, since in the latter the chains can readily bend to accommodate bulky side chains. This would mean that the volume of pores per gram of crystalline region is greater than the volume of pores per gram of amorphous region.

In contrast to this, it is found that with cellulose and synthetic polymers the crystalline are denser than the amorphous regions.[2,3,41] For example, the threefold helix of polypropylene produces a crystalline polymer of greater density than that from the random coil form.[41] The only exception known to the author is the α-form of poly-γ-methyl-L-glutamate in which the density of the crystalline form, calculated from x-ray diffraction measurements of the unit cell, is less than the observed density of the polymer.[42,43] In these cases there is not the diversity of side chains which is found in proteins, hence it is possible for close packing of the side chains to occur in the crystalline material, with a consequent increase in density over that of the amorphous material.

The data on the accessibility of wool to various sorbates have been collected from all sources and are summarized in Table IV. Additional information is given as follows. First, x-ray studies have shown that the microfibril lattice expands by about the same amount as the fiber during

sorption of water to saturation, but the interchain distance within the microfibrils expands by only about 5%.[50] Very recent x-ray results[51] indicate that the interchain distance within the microfibrils expands by a greater amount on sorption of methanol, ethanol, and *n*-propanol. There is therefore a limited amount of penetration of the microfibrils by water and the lower alcohols, as compared with no appreciable amount of penetration of the crystalline region of cellulose, nylon, and silk by water.[3,52] This is consistent with H–D exchange experiments on wool, where it is found that about 20–30% of the peptide bond hydrogen atoms are not exchanged after treatment at 30°C. for 1000 hr.[53,54] The latter are located in the microfibrils. All the amide side chain hydrogens are readily exchanged under these conditions,[55] thus giving reasonable agreement between results of the infrared method and the less specific, gravimetric method of estimation of per cent exchange.[56] On supercontraction in LiBr, the x-ray pattern is destroyed,[29] and the exchange of amide hydrogen by deuterium goes to completion.[57]

It is clear from Table IV that the volume sorption at saturation is approximately constant for nearly all the sorbates, and so is the volume contraction at saturation. This shows that the volume swelling at sat-

TABLE IV
Summary of Accessibility Data on Wool

Sorbate	Saturation sorption, cm.³/g.	Saturation volume contraction v_C[a] cm.³/g.	Volume of pores accessible to sorbate, %	Work to stretch fiber 30%, g./cm.² initial area × 10^{-5}	Esterification in alcohol, %	Iodination of tyrosine, %
Water	0.333	0.046	55	1.43	—	—
Methanol	0.371	—	—	1.72	67	100
Ethanol	0.349	0.047	4–43	2.44	56	93
n-Propanol	0.329	0.045	0–43	4.43	54	40
Iso-propanol	0.323	—	—	—	15	—
Acetone	0.234	0.050	—	4.17	—	—
n-Butanol	0.342	0.030	—	5.01[b]	39	0.5[c]
n-Pentanol	—	—	—	5.02[b]	21	0.3[c]
Experimental conditions	Merino 64's at 25°C.	Merino 64's at 25°C. *n*-Butanol at 80°C.	Merino 64's at 25°C.	Cotswold wool, dry = 5.37	Merino fabric, b.p. or 100°C. in 0.1*N* HCl	Romney and Lincoln wool I_2 in alcohol, 22.2°C.

[a] Calculated by the equation $v_C = v_D - \bar{v}_{sat}$ (see above) using values from Table II.

[b] Since the fibers used in these experiments were equilibrated with the sorbate for 24 hr., only a small amount of sorption has occurred.[1]

[c] Experiments continued for 28 days, during which time sorption of *n*-butanol for Merino wool amounts to only about 2.4%; this would be less for the larger diameter Romney and Lincoln fibers, and the sorption of *n*-pentanol would be less again.

uration is approximately constant for all sorbates except acetone [by eq. (2)],[8] and was previously interpreted[7] as indicating that wool is equally accessible to all these sorbates. This conclusion is consistent with the recent x-ray diffraction results,[51] but appears to be contradicted by the results in the last four columns of Table IV.

It is seen that the percentage volume of pores accessible to water is apparently greater than for ethanol and *n*-propanol. However the value for water is uncertain, since it was calculated on the assumption that $v_{NP} = 0$. If v_{NP} is assigned the not unreasonable figure of 0.019 cm.^{3}/g. dry wool (see above), then the calculated percentage volume of pores accessible to water is decreased to 18%. Hence no firm conclusions can be drawn from these results.

The interesting pioneering studies of Speakman[44-46] on the work required to stretch fibers 30% in various sorbates, lead him to conclude that molecules of size greater than *n*-propanol cannot penetrate the wool fiber. This is now known to be incorrect.[1] If one ignores the results for *n*-butanol and *n*-pentanol, since only slight penetration of the fiber was possible in the 24 hr. allowed for equilibration (14 days were allowed for *n*-propanol[46]), it is clear that there is a steady decrease in the amount of weakening of the fiber per gram sorbate in going from water to *n*-propanol. However, the weakening of the fiber per molecule of sorbate increases from water through to ethanol and decreases again with *n*-propanol to a lower value than with water. This weakening is produced by fission of hydrogen and other types of bonds within the wool structure, a process which is dependent not only on the weight of sorbate but more fundamentally on the actual number of sorbate molecules present. Thus, the lower alcohols are at least as effective molecule for molecule as water in breaking bonds, but do not produce as great a weakening effect as water because of their larger size rather than their inferior ability to penetrate the fiber. According to this interpretation,* the results in Table IV, column 5, indicate approximately equal accessibility of wool towards water and the lower alcohols.

The results in Table IV show that there is a decrease in the amount of esterification of carboxyl groups at elevated temperature in 0.1*N* HCl as the size of the alcohol increases, with the exception of isopropanol. This may be due to decreasing accessibility of carboxyl groups to larger alcohols, but could possibly be due to other factors. Finally, the decrease in the amount of iodination of tyrosine by iodine in the series methanol, ethanol, and and *n*-propanol has been interpreted[48] as indicative of decreasing accessibility of wool towards the alcohols in this series. However, these results should be treated with some reserve because it has been found recently that the iodination of *N*-acetyltyrosine ethyl ester occurs to a much greater extent in ethanol than in *n*-propanol and not at all in *n*-butanol.[58] X-ray examination of wool iodinated in ethanol and *n*-propanol shows that some tyrosine in the microfibrils react in ethanol but not in *n*-propanol.[49] This

* Suggested by Mr. M. Feughelman, who has kindly agreed to its reproduction here.

indicates that ethanol penetrates the microfibrils and *n*-propanol does not, but once again the reactivity of iodine in the sorbate may be an important factor.

The weight of evidence suggests that wool is approximately equally accessible to water and the lower alcohols. This problem will probably be finally resolved by application of those methods which allow differentiation between the crystalline and amorphous regions, viz., x-ray diffraction, infrared dichroism, electron microscopy, and mechanical property measurements.

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Synopsis

Equations are derived which relate the pore volume and the volume of pores accessible to sorbate with the constitutive volume v_{AA}, the electrostriction of sorbate by the charged groups of wool v_E, and the volume contraction of sorbate in the neighborhood of nonpolar side chains v_{NP}. The pore volume and the volume of pores accessible to sorbate are calculated by use of values of v_{AA} and v_E estimated from theory and assuming $v_{NP} = 0$. The percentage of pores accessible to water increases from 55 to 78 as the pH is decreased from 7 to 2, due to a reversible change which is probably analogous to the reversible unfolding of the serum albumins. Supercontraction in LiBr produces a decrease in the specific volume of wool in *n*-hexane, the partial specific volume in water, the pore volume, and the volume of pores inaccessible to water. Since analogous changes occur on denaturation of soluble proteins it is proposed that the crystalline regions (containing α-helices) are less dense than the amorphous regions (containing random coils). This is probably due to poorer packing of the diverse side chains in the crystalline regions than in the amorphous regions, since in the latter the chains should be able to bend to accommodate bulky side chains. All evidence available on the accessibility of wool to various sorbates is summarized. Although it is not yet possible to be dogmatic, it is clear that the weight of evidence suggests that wool is approximately equally accessible to water and the lower alcohols.

Résumé

On a dérivé des équations qui relient le volume des pores et les volumes des pores accessibles au produit adsorbé avec le volume constitutif v_{AA}, l'électrostriction du produit adsorbé par les groupes chargés de la laine v_E, et la contraction de volume du produit adsorbé au voisinage des chaînes latérales non polaires v_{NP}. Le volume des pores et le

volume des pores accessibles au produit adsorbé est calculé à partir des valeurs de v_{AA} et v_E déduites de la théorie, et en posant que $v_{NP} = 0$. Le pourcentage des pores accessibles à l'eau croît de 55 à 78% quand le pH décroît de 7 à 2, ceci est causé par une modification réversible qui est probablement analogue au déroulement réversible des sérums albumines. La supercontraction dans LiBr produit une diminution du volume spécifique de la laine dans le *n*-hexane, du volume spécifique partiel dans l'eau et du volume de la pore et des pores inaccessibles à l'eau. Vu que des variations analogues se passent lors de la dénaturation des protéines solubles, on propose que les régions cristallines (comportant des hélices α) sont moins denses que les régions amorphes (contenant des pelotes statistiques). Ceci est probablement dû à l'entassement plus lâche des diverses chaînes latérales dans les régions cristallines que dans les régions amorphes, vu que dans ces dernières les chaînes pourraient être capables de se courber pour accomoder les groupes latéraux volumineux. On résume tous les faits utiles quant à l'accessibilité de la laine au différents produits adsorbés. Quoiqu'il ne soit pas encore possible d'être formel, il est clair que les faits suggèrent que la laine est environ également accessible à l'eau et aux alcools inférieurs.

Zusammenfassung

Es werden Beziehungen zwischen dem Porenvolumen und dem dem Sorbat zugänglichen Porenvolumen einerseits und dem konstitutiven Volumen v_{AA}, der Elektrostriktion des Sorbats durch die geladenen Gruppen der Wolle v_E und der Volumskontraktion des Sorbats in der Nachbarschaft nichtpolarer Seitenketten v_{NP} andererseits abgeleitet. Das Porenvolumen und das dem Sorbat zugängliche Porenvolumen werden unter Verwendung theoretisch erhaltener Werte für v_{AA} und v_E und unter der Annahme $v_{NP} = 0$ berechnet. Der Prozentsatz der für Wasser zugänglichen Poren steigt bei Herabsetzung des pH von 7 auf 2 von 55 auf 78, was auf eine reversible, wahrscheinlich der reversiblen Auffaltung der Serumalbumine analoge Umlagerung zurückzuführen ist. Superkontraktion in LiBr führt zu einer Abnahme des spezifischen Volumens der Wolle in *n*-Hexan, des partiellen spezifischen Volumens in Wasser, des Porenvolumens und des für Wasser nicht zugänglichen Porenvolumens. Da bei der Denaturierung löslicher Proteine analoge Veränderungen auftreten, wird angenommen, dass die kristallinen Bereiche (α-Helices) weniger dicht als die amorphen (statistische Knäuel) sind. Dies ist wahrscheinlich durch eine schlechtere Packung der verschiedenen Seitenketten in den kristallinen Bereichen als in den amorphen bedingt, da sich in den letzteren grosse Seitenketten durch Verbiegung der Ketten leichter unterbringen lassen. Alles verfübare Material über die Zugänglichkeit der Wolle für verschiedene Sorbate wird zusammengefasst. Obwohl man noch nichts Endgültiges aussagen kann, ist es klar, dass überwiegende Hinweise auf eine gleiche Aufnahmsfähigkeit der Wolle für Wasser und die niedrigen Alkohole bestehen.

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