Sorption of Liquids by Wool.   Part I.   Determination of the Sorbate Content by a New Technique

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INTRODUCTION

McLaren and Rowen[1] have reviewed the gravimetric and volumetric methods used for the determination of the sorption of vapors by polymers and proteins.   A Vibroscope method has been used for fibers[2] and a new method developed which allowed the direct measurement of the concentration of diffusing vapor at any point through a film.[3-5]

Sorption by polymers or proteins of a second component from aqueous or organic solution can be followed by measurement of the concentration of the residual solution[6,7] or of the concentration of solute in the solid material.[8]   In the latter method it is necessary to remove the excess solute from the surface without removing solute from inside the solid. This difficulty is accentuated when one considers the measurement of the sorption of pure liquids by polymers and proteins.   With relatively large, uniform pieces of polymer it is possible to remove surface sorbate with blotting paper,[9,10] but with textile fibers and proteins this is not possible.   It was generally considered that centrifugation gave incomplete removal of surface liquid,[11,12] but recently Brown[13] has used a slightly modified method which removes almost all the surface water from wool, Terylene and glass fibers.   This paper describes a washing technique involving the use of liquid propane at −78°C. which removes organic liquids from the surface without affecting the liquid sorbed by the wool.

Various methods have been used which do not measure sorption directly, but rather some other property of the fiber, from which it is sometimes possible to draw inferences with regard to sorption.   One such method is the microscopic examination of single fibers during sorption, when it is possible to measure the rate of movement of the penetrating front of solvent and the rate of swelling of the fiber.[14-17]   Another method involves the measurement of the work required to stretch dry wool fibers 30% of their length in air and in various liquids.[18,19]   It was found that the work was lowest in water and increased with the size of the primary alcohol, tending to a limiting value with n-butanol and n-pentanol which was less than that

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for dry air.   From these data Speakman[18,19] concluded that the pores of the dry wool fiber through which sorbate enters are of the same order as the length of the n-propanol molecule, and that dry wool fibers are inaccessible to molecules of size greater than that of n-propanol.   A third indirect method is to react a specific group in the wool molecule with a reagent until equilibrium is attained.   Thus Alexander et al.[20] esterified the carboxyl groups of wool using various alcohols at the boiling point with HCl as catalyst and obtained some esterification, even with n-pentanol and cetyl alcohol in xylene.   They therefore questioned the validity of Speakman's conclusions, but the latter appear to be confirmed by recent results obtained from the iodination of the tyrosine groups of wool.[21]   However, it has been found subsequently that the iodination of N-acetyl tyrosine ethyl ester occurs to a much greater extent in ethanol than in n-propanol and not at all in n-butanol.[22]

It is therefore necessary to use extreme caution in drawing conclusions with regard to sorption from this type of indirect experiment.   The work described in this paper was undertaken in order to resolve the above difficulties by direct determination of the rate of sorption of organic liquids by wool.

EXPERIMENTAL

Materials

Wool.   A sample of Merino 64's virgin root wool was extracted in a Soxhlet apparatus with petroleum ether (Shell X222 solvent) for 5 hr., dried, and washed five times with distilled water at 50°C.   The wool was dried, extracted continuously with ethanol at room temperature for 5 hr., and washed in two changes of distilled water for 24 hr. to remove any ethanol which remained inside the fiber.   Excess water was removed by centrifugation and the wool was stored at 65% R.H. and 20°C.

Organic Liquids.   Analar grade ethanol, n-butanol, and benzene and reagent-grade n-propanol, isopropanol, n-pentanol, and n-hexanol were purified by refluxing over sodium followed by fractional distillation.   Analar acetone was dried for 16 hr. over anhydrous $CaSO_4$ and fractionally distilled.[23]   n-Pentane, kindly supplied by Vacuum Oil Co., was refluxed over P_2O_5 and then fractionally distilled, a fraction of b.p. 35.8–36.2°C. being collected.

Procedure

Wool (1.5 g.) at 65% R.H. and 20°C. was immersed in distilled water for 16 hr.,[24] centrifuged to remove excess water, and then dried for 1.5 hr. at 100°C. and 10^{-4} mm. Hg pressure to obtain an accurate dry weight. (Test experiments showed that constant weight was obtained after heating for 1 hr.)   The wool was transferred to a large test tube fitted with a B29 cone, the tube constricted, and the wool dried at 100°C. in vacuo.   A first
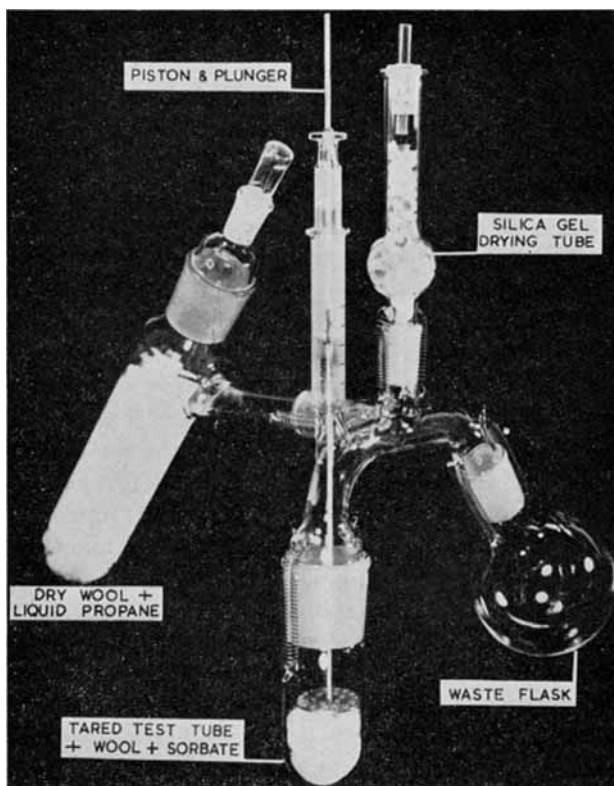
Fig. 1. Apparatus for propane washing of wool.

fraction was then distilled from the purified organic liquid into the liquid oxygen trap and then 40–60 ml. into the tube containing the wool. This was sealed off *in vacuo* and the tube transferred to a thermostat bath. After the required time had elapsed, the tube was opened and a density measurement carried out on the wool as described elsewhere.[25] Most of the excess liquid was rapidly squeezed from the wool using a metal plunger and it was transferred to a tared, short, test tube which was closed with a B34 stopper.

In the meantime, about 350 ml. of liquid propane was condensed from a cylinder of commercial propane gas into a 500-ml. capacity tube fitted with a silica gel drying tube and cooled by liquid oxygen. A forerun was allowed to escape through the drying tube and the middle fraction, about 200 ml., was distilled into a 250-ml. capacity tube fitted with a side arm and drying tube and containing about 10 g. of dry Merino 64's wool. The distillation removed some of the odoriferous impurities in the commercial propane and the remainder were adsorbed by the wool. The tube containing wool and propane was then immersed in a Dry Ice–alcohol mixture. To the side arm was connected a fitting with three outlets as shown in Figure 1. To one outlet was connected the B34 tube containing the sample of wool

described in the preceding paragraph, to another a 150-ml. capacity flask, and to the third outlet a drying tube. The ground glass connections were held firmly in place by metal springs. A stainless steel plunger, cemented through the piston of a glass syringe, was also fitted inside the B34 tube in such a way that by movement of the syringe the wool could be squeezed and moved around in the tube.

Liquid propane at −78°C. was then poured slowly over into the B34 tube (cooled in Dry Ice–alcohol) until the wool was covered. Care was necessary at this stage because of the large volume of propane gas produced by the rapid evaporation of the propane (BP − 42°) during cooling of the apparatus. The wool was agitated for 2 min. by means of the plunger, which had two small lugs projecting from its base to catch in the wool. The apparatus was then twisted at the central glass joint so that the liquid propane plus organic liquid from the surface of the wool passed over into the waste flask. The wool was squeezed by the plunger to remove as much liquid as possible. A second portion of liquid propane was then run onto the wool, which was agitated by the plunger and allowed to stand for 10 min. before being poured into the waste flask. This latter washing was repeated three times, making a total of five washings.

The 250-ml. capacity reservoir of propane was then immersed in liquid oxygen, and the propane from the surface of the wool in the B34 tube allowed to distil into the reservoir. After 1 hr. the B34 tube was disconnected from the apparatus, quickly stoppered, and weighed (x_1 g.). The evaporation and weighing cycle was repeated over three successive 1-hr. intervals, giving weights x_2, x_3, and x_4, respectively. It was found that after distillation for 1 hr. nearly all the propane was removed but there were further small decreases of weight due to slow removal of the organic liquid from inside the wool. The weight x_0 of tube plus wool plus sorbed liquid (in the absence of propane) at zero time is then given by the equation

$$x_0 = x_2 + (x_2 - x_4)$$

The largest value of $(x_2 - x_4)$ amounted to 5% of the total sorption and was obtained for acetone and ethanol, the most volatile sorbates. The least volatile sorbate, n-hexanol, gave a slightly negative value (1%), due presumably to sorption of water during the short time the B34 tube was open to the atmosphere.

This washing technique was sufficient to remove all surface liquid from the wool, since the latter could always be detected, even if present in small amounts, by the appearance of small droplets on the inside of the B34 tube. However there was still the possibility that some of the sorbate would be removed from the inside of the wool by the propane washing or that an impurity from the propane would be sorbed by the wool. This was checked in every experiment by repeating the washing and distillation procedure once more when a new value of x_0, viz. x'_0, was obtained. This was subtracted from the weight of bottle, wool and sorbate at the beginning of the check experiment to give the washing correction. This amounted

to 5% of the amount of sorption for ethanol but was usually much less and sometimes slightly negative. The washing correction was added to the value of x_0 obtained from the first washing procedure to give the corrected weight of bottle plus wool plus sorbate. The per cent sorption was then calculated by the equation

$$\% \text{ sorption} = 100 \times \text{wt. sorbate/wt. dry wool}$$

The initial dry weight of wool was used, but a final weight was also sometimes obtained by immersing the wool in several changes of distilled water over about five days and drying at 100°C. *in vacuo*. A loss of weight of 2–4 mg. was obtained, showing that there was no appreciable degradation of the wool during sorption. In determinations of saturation sorption values it was usual to treat one sample for about 4–5 times as long as appeared (from the graph) to be necessary for saturation to be achieved.

Accuracy and Applicability of the Method

A test of the accuracy of the method was made by obtaining dry weights on two samples of wool and then allowing them to sorb ethanol vapor *in vacuo*. The exact amount of sorption was obtained by weighing, and then both samples were subjected to the washing procedure and the per cent sorption calculated as described above. The results obtained by weighing and by washing for sample 1 were 17.6 and 17.3% and for sample 2, 17.1 and 16.9%, respectively. The reproducibility of the method is shown by the standard errors of various duplicate determinations given in Table II. The accuracy of the method is therefore about ±2%.

The method should be applicable to all textile fibers for measurement of the sorption of organic liquids which are miscible with propane and have a melting point less than −42°C. Thus it is not possible to remove surface benzene from wool by washing with propane because the benzene freezes. However *n*-butane, (b.p. 1°C.) obtained commercially and purified in the same way as propane, works quite well in this case, but there is more difficulty in removing the *n*-butane afterwards by distillation. The miscibility requirement between propane and the liquid introduces a second limitation on the applicability of the method and precluded experiments with water and methanol.

RESULTS

In Figures 2–4 are shown the rate curves for sorption of various liquids by wool including, for purposes of comparison, two vapor-state sorption curves obtained by King.[26,27] When graphs of per cent sorption versus square root of time are constructed, it is found that they are inflected near the origin as found by Watt[28] for the sorption of water by wool. The sorption is therefore non-Fickian or anomalous[4,5] and cannot be interpreted in terms of a diffusion coefficient, although this has been attempted in the past for vapor sorptions.[26,27] However, the initial rates of sorption are
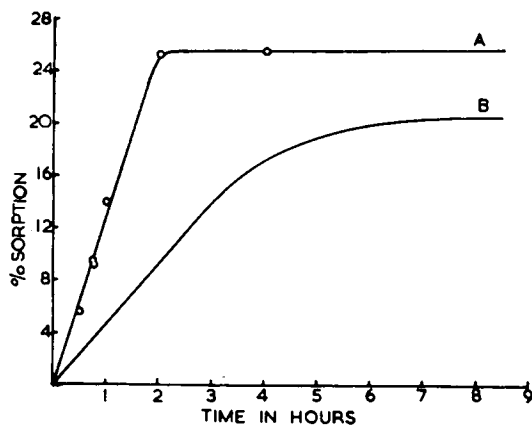
Fig. 2. Rate of sorption of ethanol on wool at 25°C.: (A) in the liquid state; (B) in the vapor state (data of King[26]).
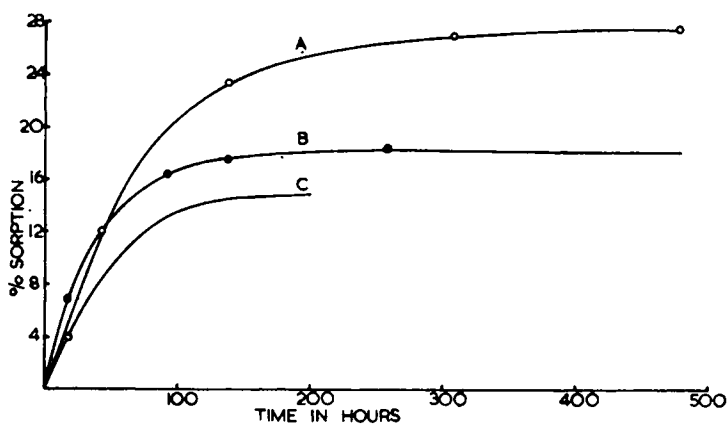

Fig. 3. Rate of sorption on wool at 25°C. of (A) n-propanol and (B) acetone in the liquid state and (C) n-propanol and acetone in the vapor state (data of King[27]).
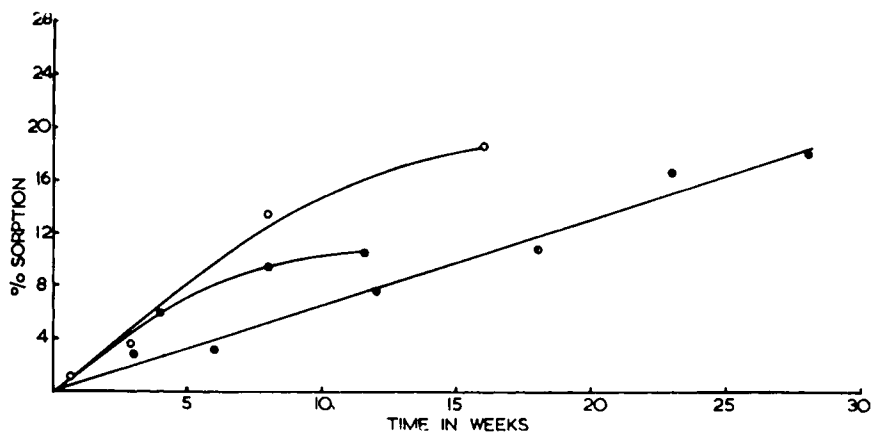

Fig. 4. Rate of sorption on wool of (O) isopropanol at 25°C.; (⊙) n-butanol at 25°C.; (●) n-hexanol at 80°C.

TABLE I
Sorption Rates Obtained from Initial Slope of Curve

Sorbate	V_m ml./ g. mole at 25°C.	Rate of liquid sorption, g./100 g. dry wool/hr.			Rate of vapor sorption at 25°C.[a] g./100 g. dry wool/hr.
		At 25°C.	At 40°C.	At 80°C.	
Methanol	41	—	—	—	81
Ethanol	59	12.8	—	—	4.6
n-Propanol	75	0.26	—	—	0.22
Isopropanol	77	9.2×10^{-3}	—	—	—
Acetone	74	0.37	—	—	0.22
n-Butanol	92	3.9×10^{-3}	—	—	—
n-Pentanol	110	3.8×10^{-4b}	—	—	—
n-Hexanol	126	2.0×10^{-4b}	—	8.8×10^{-3}	—
n-Pentane	116	—	1.4×10^{-4b}	—	—
Benzene	90	—	8.3×10^{-4b}	—	—
Ethanol[c]	59	3.8^b			
n-Butanol[d]	92	5.3×10^{-3b}			

[a] Data of King.[26,27]

[b] These results are open to considerable error since they are calculated from the following experimental results: n-pentanol 1.9% sorbed in 30 weeks, n-hexanol 0.9% in 27 weeks, n-pentane 1.2% in 51 weeks, benzene 2.5%, and 3.7% in 16 and 30 weeks, respectively, ethanol (denatured wool) 3.0% in 0.8 hr., and n-butanol (wool previously treated in n-butanol) 20.5% in 23 weeks.

[c] Wool denatured by treatment for 1 hr. at 100°C. in 8M LiBr.

[d] Wool was discolored by a previous sorption experiment in n-butanol at 80°C. for 23 weeks.

TABLE II
Saturation Sorption Values on Wool from Liquid and Vapor States

Sorbate	Saturation sorption from vapor state at 25°C., g./100 g.[a]	Saturation sorption from liquid state, g./100 g.			Saturation sorption at 25°C., cm.³/100 g.	
		At 25°C.	At 20°C.	At 80°C.	From vapor	From liquid
Water	33.2	—	—	—	33.3	—
Methanol	29.2	—	—	—	37.1	—
Ethanol	26.1	28.3 ± 0.4^b	27.5 ± 0.2	23.0	33.8	36.0
n-Propanol	25.0	27.5 ± 0.2	—	—	31.3	34.4
Isopropanol	—	25.2^c	—	20.5	—	32.3
Acetone	—	18.3 ± 0.1	—	—	—	23.4
n-Butanol	—	27.6^c	—	22.4	—	34.2
Ethanol[d]	—	30.2	—	—	—	38.4

[a] Data of Bradbury.[29]

[b] Standard error which equals standard deviation of the mean.

[c] These values were calculated from the experimental results at 80°C. using the ratio for saturation at 25°C. as compared with saturation at 80°C. obtained with ethanol.

[d] Wool was denatured by treatment for 1 hr. at 100°C. in 8M LiBr prior to sorption.

determined in each case from the gradient of the graph of per cent sorption versus time at zero time, and are given in Table I together with approximate values obtained in some cases. In Table II are collected the saturation values for sorption of liquids and vapors[29] by wool at various temperatures.

DISCUSSION

In comparing the sorption of vapor and liquid by wool it is seen that the rate of sorption by a liquid is greater than that of its saturated vapor (Figs. 2 and 3). However, the results in Table I show that there is considerable variation between the ratios of the initial rates of liquid and vapor sorption for ethanol (2.8), n-propanol (1.2), and acetone (1.7). The greater rate in the liquid state is due to the greater concentration of sorbate at the solid surface, which results in an increased rate of diffusion of sorbate over that in the vapor state. Similarly, it has been observed that the rate of deuteration of cellulose is greater in liquid D_2O than in the saturated vapor.[30] The saturation sorption results in Table II are lower for the vapor than for the liquid. This is probably due to the difficulty of obtaining 100% saturation in vapor-state experiments, particularly when very long times of equilibration are involved.[31] However, there is still the possibility that more sorption occurs from the liquid than from the vapor phase, in view of Mann and Marrinan's observation that the amount of deuteration of cellulose from the liquid phase is greater than from the vapor phase.[30]

The increase in the rate of sorption which is produced by increasing the temperature was used to facilitate the attainment of saturation with slowly penetrating molecules. In agreement with work on the sorption of water vapor on wool[32] and egg albumin,[33] it is found that the saturation sorption decreases with increase of temperature. The decrease observed for ethanol has been used to obtain approximate values of the saturation sorption of isopropanol and n-butanol at 25°C. from the figures given at 80°C., as shown in Table II.

Speakman[18,19] considered that the sorbate enters the fiber through pores which are of about the same size as the length of the n-propanol molecule. This conclusion is based on the premise that the wool fiber cannot sorb n-butanol or larger molecules (which appears to be supported by the results of Giles et al.[6,34]), but the results in Table I show that even molecules as large as n-hexanol can be sorbed at 25°C. If Speakman's theory is correct in essence, i.e., if there are pores of a finite size through which sorbate molecules of smaller size can penetrate but not molecules of larger size, then it is clear that the limiting size has not been reached with n-hexanol. However it seems more likely that a modification of Eyring's hole theory of diffusion is applicable.[35,36] Accordingly, it is considered that wool contains holes or pores* of various sizes, some of which are present initially in its

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* The word "pore" is used in preference to "hole" for consistency with modern terminology.[37,38]

structure,[25,39] others being produced by movements of atoms and groups within the fibers. This movement may be the result of both thermal fluctuations and interactions with sorbate molecules. The concentration of pores of a particular size which are present at any one time decreases rapidly with increasing size of the pore. Diffusion occurs by movement of the sorbate molecule from its current position into the pore, a process which may require several jumps. Nevertheless, in the application of this theory to wool it is important to remember that the fiber is heterogeneous. Thus, sorption of dyes occurs most rapidly at the distal edges of the scales,[40] and reagents such as $KMnO_4$, which react with the fiber, do not penetrate the fiber evenly.[41]

One consequence of this theory is that the rate of sorption decreases with increasing size of the sorbate molecule but would not suddenly become zero as predicted by Speakman's theory. Thus quite large molecules should be able to penetrate the fiber if given sufficient time. The large decrease in the rate of sorption which occurs in passing from n-propanol to isopropanol, which has the same volume but is less elongated, is due to the increased cross-sectional area of the pore required for the latter. The shape of the sorbate molecule is also an important factor in controlling the rate of sorption of organic vapors by synthetic polymers.[36,42] A second consequence is that long molecules, such as n-hexanol, would diffuse almost entirely along their long axis. The decrease in rate which is observed in the ascending series of normal alcohols in Table I would then be due to the need for correct orientation of the larger molecules and for a pore of larger volume (produced by several jumps of the sorbate molecule) rather than larger cross-sectional area.

According to the theory, sorbate molecules may also participate in the formation of pores by breaking hydrogen[43] and van der Waal's bonds which stabilize the protein structure. Thus, the hydroxyl group of the alcohol molecule can form a hydrogen bond with the protein, while its hydrophobic end may also be able to interact with a hydrophobic part of the protein. The alcohols can therefore penetrate the fiber much more rapidly than hydrocarbons, which can only form van der Waal's bonds. For example, it is found that n-pentane, which has a similar shape to, but smaller volume than, n-hexanol is sorbed more slowly at 40°C. than is n-hexanol at 25°.

The sorption of acetone is much faster than that of isopropanol, but reaches a lower saturation value. Since both molecules have the same volume and shape, the observed differences must reside in the different properties of the carbonyl as compared with the hydroxyl group. The rate of sorption of ethanol by wool super-contracted in LiBr is about one-third that of virgin wool, but the saturation value is probably slightly greater (see Table II). However, the saturation sorption of water is less with supercontracted wool[44] and denatured egg albumin[43] than with the corresponding native proteins. The decreased rate on supercontraction is due to the considerable increase in diameter of the fiber and proportional decrease in the surface area through which diffusion occurs. Another

contributing factor may be the decrease in the volume of pores present in super-contracted wool.[39] Wool used in a previous sorption experiment at 80°C. showed an increased rate of sorption of n-butanol over that of virgin wool; hence apparently small alterations of the structure of the fiber can affect greatly its sorption properties.

It was found previously[29] that the volume sorption at saturation for water, methanol, ethanol and n-propanol vapors is constant within experimental error. As shown in Table II, these values agree with the saturation figures obtained for liquid sorption of ethanol, n-propanol, isopropanol, and n-butanol, giving a mean of 8 values of 34.1 ± 0.7 cm.^{3}/100 g. The significance of this is discussed in Part III of this series.[39]

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Synopsis

When liquids are sorbed by wool or other textile fibers it is necessary to distinguish between sorbed liquid and liquid held mechanically on the surface and in the interstices between fibers. A method is described by which the latter can be removed by washing the fibers under anhydrous conditions with liquid propane at −78°C. The propane is subsequently distilled off at room temperature leaving the sample of wool containing sorbate. Small corrections are made for loss of sorbate during washing and distillation. The method is accurate to about ±2%. Sorption curves and saturation values are recorded for ethanol, n-propanol, isopropanol, acetone, and n-butanol and initial rates of sorption for n-pentanol, n-hexanol, n-pentane, and benzene. A theory is proposed in which it is postulated that holes of various sizes can be produced by thermal fluctuations and also interactions with the sorbate. A consequence of the theory is that even large molecules can penetrate the fiber if given sufficient time. The experimental values of the initial rate of sorption are interpreted in terms of the volume, shape and ability to form hydrogen bonds of the sorbate molecule. The rate of sorption is very sensitive to quite small modification of the wool fiber. The volume sorption at saturation is found to be constant for water, methanol, ethanol, n-propanol, isopropanol, and n-butanol with a mean value of 34.1 ± 0.7 cm.³/100 g.

Résumé

Quand des liquides sont adsorbés sur la chaîne ou sur d'autres fibres textiles, il est nécessaire de faire une distinction entre le liquide absorbé et le liquide retenu mécaniquement sur la surface et dans les interstices entre les fibres. On a décrit une méthode par laquelle se dernier peut-être éliminé par lavage des fibres dans des conditions anhydres, avec du propane par distillation à température de chambre et on obtient l'échantillon de laine contenant le produit adsorbé. On apporte de légères corrections pour la perte de produit adsorbé pendant le lavage et la distillation. Cette méthode est valable dans une limite de ±2%. On trace des courbes d'adsorption et on note les valeurs de saturation pour l'éthanol, le n-propanol, l'isopropanol, l'acétone et le n-butanol ainsi que les vitesses initiales d'adsorption du n-pentanol, n-hexanol, n-pentane et benzène. On propose une théorie dans laquelle on postule que des cavités de dimensions diverses peuvent se produire par des fluctutions thermiques, ainsi que par des interactions avec le produit adsorbé. Une conséquence de la théorie est, que même de grandes molécules peuvent pénétrer dans la fibre, si on leur laisse assez de temps. On interprète les valeurs expérimentales de la vitesse initiale d'adsorption en fonction du volume, de la dimension et de la capacité à former des liaisons hydrogène de la molecule du produit adsorbé. La vitesse d'adsorption est très sensible à de très légères modifications de la fibre de laine. On a trouvé que le volume de l'adsorption, à saturation, est constant pour l'eau, le

méthanol, l'éthanol, le n-propanol, l'isopropanol et le n-butanol, avec une valeur moyenne de 34,1 ± 0,7 cm³/100 g.

Zusammenfassung

Bei Sorption von Flüssigkeiten durch Wolle oder andere Textilfasern muss nan zwischen sorbierter Flüssigkeit und der mechanisch an der Oberfläche oder in den Zwischenräumen zwischen den Fasern festgehaltenen Flüssigkeit unterscheiden. Es wird eine Methode beschrieben, mit der man letztere durch Waschen der Fasern unter Wasserausschluss mit flüssigem Propan bei −78°C entfernen kann. Das Propen wird anschliessend bei Zimmertemperatur abdestilliert und es bleibt die das Sorbat enthaltende Wollprobe zurück. Geringe Korrekturen wurden für Verlust an Sorbat während des Waschens und der Destillation angebracht. Die Methode besitzt eine Genauigkeit von etwa ±2%. Sorptionskurven und Sättigungswerte werden für n-Propanol, Äthanol, Isopropanol, Azeton und n-Butanol angegeben, die Anfangsgeschwindigkeit der Sorption wird für n-Pentanol, n-Hexanol, n-Pentan und Benzol bestimmt. Eine Theorie wird aufgestellt, die auf der Annahme beruht, dass durch die thermische Bewegung und auch durch die Wechselwirkungen mit dem Sorbat Löcher von verschiedener Grösse erzeugt werden können. Aus dieser Theorie folgt, dass auch grosse Moleküle nach genügend langer Zeit in die Faser eindringen können. Die experimentellen Werte für die Anfangsgeschwindigkeit der Sorption werden mit dem Volumen, der Gestalt und der Fähigkeit dur Wasserstoffbindungsbildung der sorbierten Moleküle in Zusammenhang gebracht. Die Sorptionsgeschwindigkeit ist gegen sehr kleine Modifizierungen der Wollfaser sehr empfindlich. Das Sorptionsvolumen bei Sättigung ist für Wasser, Methanol, Äthanol, n-Propanol, Isopropanol und n-Butanol konstant und beträgt im Mittel 34,1 ± 0,7 cm³/100 g.