Sorption of Organic Vapors by Wool Keratin

I. C. WATT, *Wool Research Laboratories, Division of Textile Physics, C.S.I.R.O., Ryde, Sydney, Australia*

Synopsis

The absorption and desorption behavior of organic vapors and wool keratin has been investigated.   At low relative vapor pressures sorption is Fickian and the rate of diffusion is determined by the size and configuration of the sorbate molecule.   For absorption to saturation vapor pressure a second absorption mechanism is involved, depending on the ease with which the sorbate can disrupt the keratin network structure.   This mechanism is superimposed on the Fickian mechanism, and the uptake shows non-Fickian anomalies. On desorption there is an initial rapid removal of sorbate before the rate of removal becomes extremely slow.   The amount of retained sorbate in the region of slow removal is dependent on the temperature, the size, and the configuration of the sorbate molecules and has been qualitatively related to the measured diffusion coefficients at low relative vapor pressures.

The important role of water vapor in wool technology has ensured that wool–water vapor sorption behavior has been studied extensively. Studies made with other penetrants from the vapor phase have been much more limited in scope.   However, because of the opportunities of comparing and contrasting the behavior of related molecules, the sorption behavior of organic vapors can be extremely rewarding.

More extensive investigations of the sorption behavior of organic penetrants from the liquid phase have been made because of the many practical implications.   A recent technique of measuring liquid absorption, developed by Bradbury and Leeder,[1] has been applied to the absorption of alcohols and acetone.   However, no information as to the desorption of the penetrants has been obtained by this technique.

The aliphatic alcohols form a series of penetrants of which the sorption behavior can yield much information as to the role of penetrant size and configuration.   The absorption of these molecules has been studied by King[2,3] and by Speakman and co-workers.[4,5]   King showed that for the absorption of methanol, ethanol, and propanol by wool at 20 and 25 °C. the rate of uptake and the amount absorbed decrease as the size of the sorbate molecule increases.   Bradbury and Leeder have pointed out that the volume of each sorbate taken up is approximately the same.   Similar behavior has been observed in the present study in which the measurements have been carried over the temperature range of 20–50 °C.

The aliphatic acids form another homologous series of which the lower

members are capable of being absorbed by dry wool. Comparative data are presented for the sorption behavior of members of this series. In addition to the variations in the size of the sorbate molecule while retaining the same functional group, it is also of interest to compare the sorption behavior of molecules of similar size but with a different functional group. Comparisons of the sorption behavior, under similar conditions, of such molecules have been made in the present study. The desorption behavior of each penetrant has been described in more detail than previously and is shown to be dependent on the size and shape of the sorbate molecules. For the latter stages of desorption when the wool is not in a highly swollen state, the course of desorption can be correlated with the absorption at low relative pressures.

It became evident during the course of this work that with the larger sorbate molecules there is some variation in quantitative values of rates and sorbate contents according to the keratin and even between wools of the same type. However for a particular keratin the relation between the sorption behavior of the various sorbates appeared the same. Accordingly a Merino wool was chosen as representative of keratin, and all the measurements were made on samples from the same source.

EXPERIMENTAL

Methods

Sorption measurements were carried out by a gravimetric technique with the use of a quartz spiral spring sorption balance mounted in a vacuum system, the whole apparatus being enclosed in an air thermostat. The apparatus used and experimental procedure have been described fully elsewhere.[6] The average dry diameter of the fibers was measured with a vibroscope and found to be 20 μ.

Purification of Reagents

Wool. Measurements were made with a Merino pen-grown wool. The greasy wool was cleaned prior to use by repeated washings with cold petroleum ether, two washings with cold ethanol followed by thorough rinsing with cold distilled water until the pH of the wash water was unaltered by contact with the wool.

Acetone. Analar grade acetone was further purified by shaking with Drierite ($CaSO_4$) and vacuum distillation prior to use.

Acrylonitrile. Acrylonitrile was washed with successive portions of dilute sulfuric acid, dilute sodium hydroxide, and saturated sodium sulfate, dried over anhydrous potassium carbonate, and fractionally distilled. The first fraction containing the residual water as an azeotrope with acrylonitrile was rejected, and the middle fraction was refractionated and stored under vacuum.

Alcohols. Methyl and ethyl alcohol were purified by refluxing over a Grignard reagent formed by adding iodine and magnesium to the alcohol, fractionally distilling and collecting the middle range which distilled at a constant temperature. Propyl alcohol, *n*-butyl alcohol, and isopropyl alcohol were refluxed over metallic sodium prior to fractional distillation. Analar grade *sec*-butyl alcohol and *tert*-butyl alcohol were used without further purification. The alcohols were stored over Drierite until transferred to the vacuum line.

Aliphatic Acids. Analar grade acids were further purified by drying over an appropriate desiccant and distilling on the vacuum line.

RESULTS

Absorption of Alcohols at Saturation Vapor Pressure

The uptake of alcohol for dry wool exposed to saturation vapor pressure of alcohol is illustrated by the curves of Figures 1, 2, and 3. The curves are plotted as a function of the square root of time and show the uptake of methanol, ethanol, and propanol, respectively at 20, 35, and 50°C. By plotting the graphs as a function of (time)$^{1/2}$ it is possible to produce the three uptake curves on the one graph and at the same time demonstrates the departure from the initially linear uptake expected for Fickian diffusion. The corresponding desorption curves at 35°C. are given in each figure and the uptake of isopropyl alcohol at 35°C. is included in Figure 3.
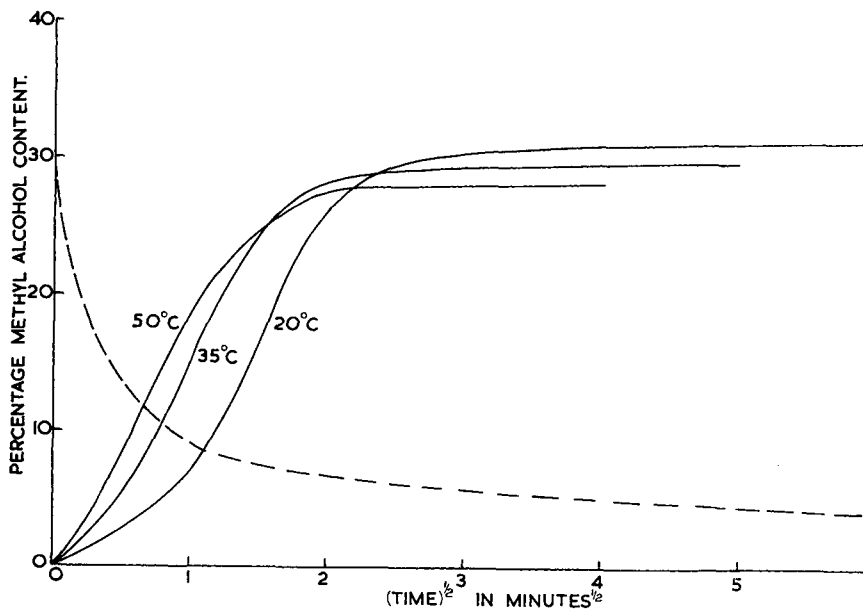

Fig. 1. Uptake curves of methyl alcohol by dry wool at 20°C., 35°C., and 50°C. after exposure to saturation vapor pressure of the alcohol. Desorption of methyl alcohol at 35°C.
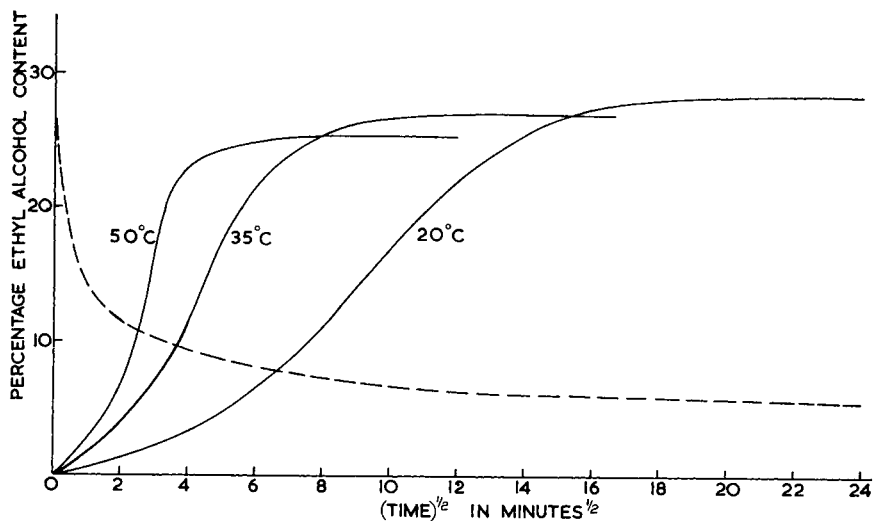
Fig. 2. Uptake curves of ethyl alcohol by dry wool at 20°C., 35°C., and 50°C. after exposure to saturation vapor pressure of the alcohol.   Desorption of ethyl alcohol at 35°C.
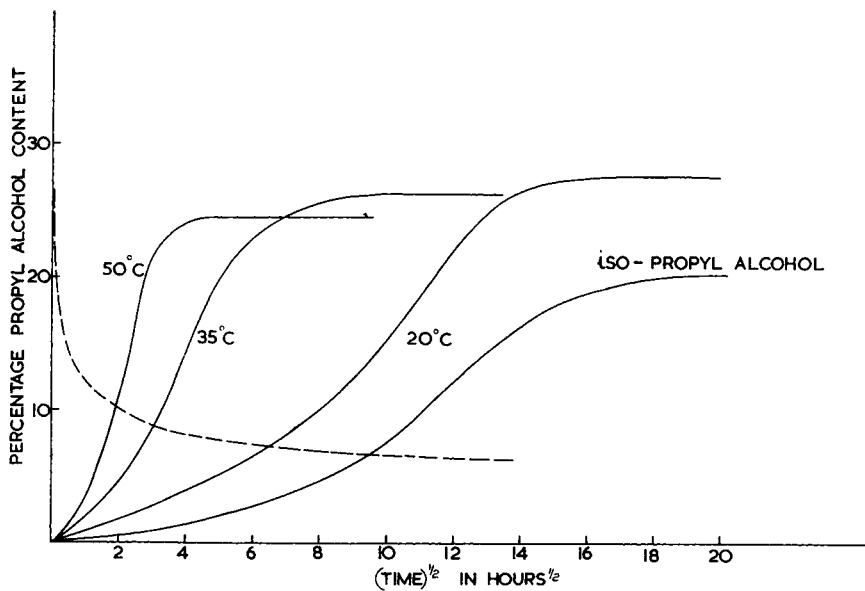

Fig. 3. Uptake curves of n-propyl alcohol by dry wool at 20°C., 35°C., and 50°C., and isopropyl alcohol at 35°C., after exposure to saturation vapor pressure of the alcohol. Desorption of n-propyl alcohol at 35°C.

All uptake curves have a sigmoidal shape, and the initial rate of desorption is faster than the initial rate of absorption in each case.   These are characteristics of anomalous sorption behavior.   As has been reported previously the rate of uptake is reduced with each succeeding penetrant in the

homologous series, and the weight uptake of penetrant at equilibrium decreases with the increasing size of the penetrant molecule.   This of course means that the number of penetrant molecules is substantially reduced with each increase of molecular size.

It is immediately apparent that the overall rate of uptake of the larger molecules shows greater temperature dependence.   The shape of the uptake curve is changed so that for the lower temperature and the bigger sorbate molecule a more marked sigmoidal uptake curve is obtained. This indicates that the initial rate of uptake is markedly affected by conditions such as temperature and size of the sorbate molecule.   Although the higher temperature means an increased rate of absorption, the equilibrium weight of alcohol decreases.   This is in line with the sorption behavior exhibited with water.

It is noticeable that the vapor phase uptake of ethanol and propanol at 20°C. are in good agreement with the liquid phase uptakes reported by Bradbury and Leeder[1] but are more rapid and reach a higher equilibrium value than the vapor phase uptake reported at 25°C. by King.[2,3]

When wool is exposed to the mixed vapors of alcohol and water then the weight uptake at equilibrium is higher than for either the alcohol or the water vapor alone.   For instance the weight uptake at 35°C. of propyl alcohol and water vapors each at 50% relative pressure, was 39.5%.   This is in agreement with the finding of Atkinson, Filson, and Speakman[7] that wool immersed in a mixed alcohol–water medium swells to a greater extent than in water or alcohol alone.

Desorption of Alcohols

The desorption of an alcohol from wool is initially very rapid, irrespective of the size of the sorbate molecule.   It has been reported by King[2] and Speakman,[4] however, that up to 6% of methyl alcohol and ethyl alcohol is retained by the wool and is not removed by evacuation.   We have found that following the initial rapid desorption of alcohol there is a slow removal of alcohol which continues over many days without reaching an equilibrium value.   The amount of alcohol retained after the initial rapid desorption varies with the size and shape of the alcohol molecule and the temperature of desorption.   A convenient comparison of the later stages of desorption of the various penetrants is given by the amount retained after a sufficient period of time such that the rate of removal of the alcohol is very slow.

In Table I the weight of the various alcohols retained are given at each temperature.   The amounts retained at 35°C. are also expressed as moles of alcohol/100 g. of wool and the volume of liquid alcohol.   As the variation in the densities of the alcohols is small the volumes show the same pattern of variation as the weights.   Butyl alcohols are included in the series although the rate of uptake at 35°C. is slow.   For the branched-chain butyl alcohols the wool was immersed in an aqueous–alcohol solution for several weeks prior to desorption at 35°C.   Although it has been

shown that an alcohol–water mixture absorbs to a greater extent than the alcohol or water alone, the relative contribution of each has not been established. However, on desorption the latter part of the desorption curve follows the same path as the desorption of the particular alcohol and gives the same value of retained sorbate.

TABLE I
Amounts of Retained Alcohol on Desorption

	Percentage weight of sorbate retained after 17 hr.			Retained sorbate/100 g. of wool at 35°C.	
Sorbate	At 20°C.	At 35°C.	At 50°C.	Number moles × 10²	Volume of liquid, cc.
Methyl alcohol	2.9	1.7	0.6	5.3	2.15
Ethyl alcohol	6.2	5.1	3.9	11.1	6.5
n-Propyl alcohol	11.7	8.1	5.6	13.5	10.1
Isopropyl alcohol	—	9.2	—	15.3	11.7
n-Butyl alcohol	—	10.2	—	13.8	12.6
sec-Butyl alcohol	—	11.6	—	15.7	14.5
tert-Butyl alcohol	—	13.2	—	17.8	16.9

The increased weight of alcohol retained as the molecular size is increased also represents an increased number of sorbate molecules, as least as far as n-propyl alcohol.

The original weight of wool was obtained by vacuum desorption of wool which had been wet with water. It has been established that residual water remains in the wool,[8] some of which can be subsequently removed by raising the temperature. The amount of alcohol retained also decreases with increasing temperature. However in the case of water, an equilibrium weight was established at each temperature, whereas here the alcohol is still being slowly removed from the wool for a period of weeks. At 80°C. methyl alcohol but not the higher alcohols can be completely removed from the wool in the 17-hr. period.

The retained alcohol can be removed by exposing the wool to saturation vapor pressure of water vapor and desorbing. The exposure time required at 35°C. for the lower alcohols is no longer than 10 min. for Merino wool showing that the alcohol can diffuse out of the swollen fibers with great rapidity. Much of the retained higher alcohols were also removed by 10 min. exposure to water vapor but periods up to 1 hr. were required to establish equilibrium.

The Aliphatic Acid Series

The very rapid absorption of formic acid vapor has been noted by King.[9] The uptake of formic acid at saturation vapor pressure is shown in Figure 4. However, the accompanying liberation of heat would make
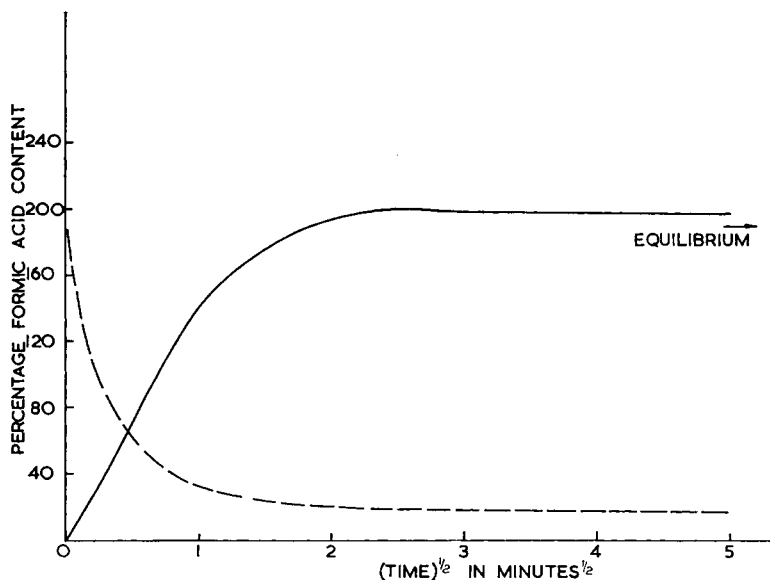
Fig. 4. Uptake curve of formic acid by dry wool after exposure to saturation vapor pressure of the acid at 35°C. and the corresponding desorption curve.
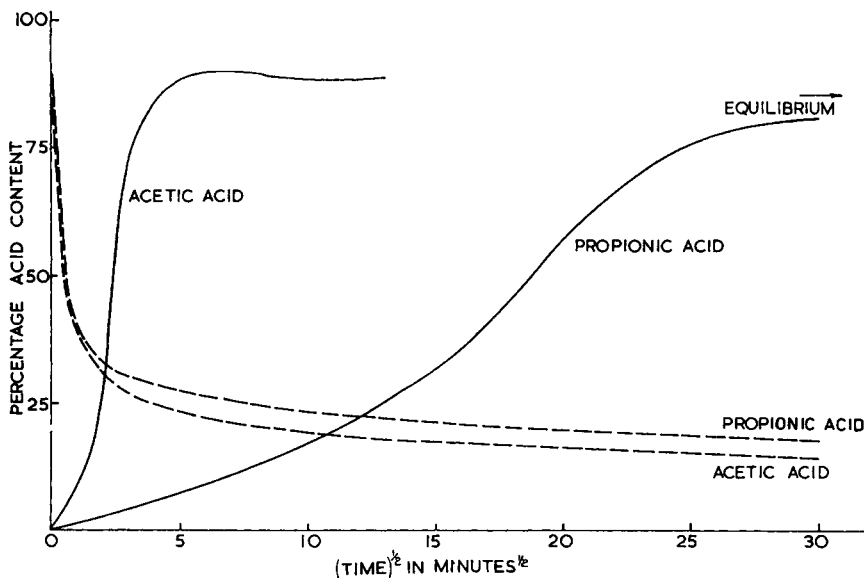
Fig. 5. Uptake curves of acetic acid and propionic acid by dry wool after exposure to saturation vapor pressure of the acid at 35°C. and the corresponding desorption curves.

the control of temperature around the sample difficult. That is, the temperature of the wool could rise and the relative vapor pressure of the formic acid around the wool would be less than saturation until the liberated heat could be carried away. It is possible therefore that the uptake

TABLE II

Desorption of Aliphatic Acid Vapors

Sorbate	Percentage weight of sorbate			Volume of liquid equivalent to retained sorbate, cc./100 g.
	Equilibrium at saturation vapor pressure	Retained after 17 hr.	Retained following leaching with water vapor	
Formic acid	187	8.9	5.4	7.3
Acetic acid	89	12.5	1.8	11.9
Propionic acid	85	16.1	1.3	16.1

of formic acid vapor would be even more rapid than shown by Figure 4. The corresponding desorption curve on evacuation is shown as the dotted curve of Figure 4. With the slower rate of uptake of acetic acid and propionic acid no such temperature effects would be evident. The uptake and desorption curves of the larger aliphatic acid molecules of acetic acid and propionic acid between zero and saturation vapor pressure are shown in Figure 5. The uptake of butyric acid at 35°C. is very slow, and only 5% was absorbed in one week.

The uptake curve of formic acid shows an overshoot of the equilibrium formic acid content similar to the overshoots which have been reported for the uptake of water vapor.[6] The overshoot is not apparent in the propionic acid uptake curve and is only small in the acetic acid uptake curve. A pronounced sigmoidal shape of the uptake curve is apparent for the higher acids, even more pronounced than for the alcohols of comparable size. The variation between the equilibrium acid content reached by formic acid compared with acetic acid and propionic acid is quite marked. On desorption all three acids are initially removed extremely rapidly in the first minute but thereafter desorb at a much slower rate. In Table II the acid content of the wool samples at saturation vapor pressure and the acid content of the wool after desorption for 17 hr. are given for the three acids. The wool had been exposed to the acid vapor for 24 hr. prior to desorption.

We have found that there is much more difficulty in leaching out retained acid, particularly formic acid, than for the alcohols. The weight of acid retained after saturation of the sorption chamber with water vapor for 1 hr. and desorption for 17 hr. is also given in Table II. Successive treatments or longer exposure to the water vapor (24 hr.) brought the formic acid content down by a further 1.3%. On the other hand, if the wool had contained the formic acid for a longer period then more formic acid was retained in the wool fibers after similar desorption treatment. After saturation with formic acid vapor for five days the amount of acid retained after water vapor saturation rose by 1.0%. That is there is an affinity of the acids for the wool which is dependent on the acid and the

sorption history of the wool–acid system.   It has been noted during the course of this work that there is considerable variation in both the formic acid vapor absorbed and the amount retained according to the source of the wool sample.

Absorption at Low Relative Pressures

For all the sorbates studied it was found that for absorptions with low final sorbate contents, the sigmoidal shape of the uptake curve as a function of $(time)^{1/2}$ was no longer evident, and the initial rate of desorption was not greater than the initial rate of absorption.   The uptakes conformed to the mathematical model of uptake predicted assuming Fickian diffusion of the sorbate into a cylindrical sorbent if the final sorbate content was within the range of 0–3%.   An average diffusion coefficient $\bar{D}$, for absorption to 3% equilibrium sorbate content was determined for the smaller alcohols and acids and are tabulated in Table III.

TABLE III
Diffusion Coefficients at 35°C.

Sorbate	$\bar{D}$, cm.²/sec.
Methyl alcohol	$4.5 \pm 0.5 \times 10^{-12}$
Formic acid	$5.3 \pm 0.7 \times 10^{-13}$
Ethyl alcohol	$5.0 \pm 0.7 \times 10^{-13}$
n-Propyl alcohol[a]	$5.0 \pm 1.0 \times 10^{-14}$
Acetic acid[a]	$2.5 \pm 1.0 \times 10^{-14}$

[a] For these slow absorptions over a period of many weeks, only the initial portion of the uptake curve was measured experimentally.   For purpose of calculation of diffusion coefficients the equilibrium content of n-propyl alcohol was taken as equivalent to the equilibrium content of ethyl alcohol at the same relative pressure.   For acetic acid it was assumed that the curve would follow the course predicted by Fickion diffusion.

Acetone and Acrylonitrile

Much useful information as to the nature of the sorption process can be obtained by using sorbate molecules of similar size but different functional groups.   The uptake and desorption curves between zero and saturation vapor pressure for acetone and acrylonitrile are shown in Figure 6.   The molecular weights of these molecules are between those of ethyl alcohol and propyl alcohol.   The behavior might be expected to be similar to propyl alcohol as the molecules have a 3-C chain as for propyl alcohol.   In each case the initial uptake occurs more rapidly than for propyl alcohol and in each case the equilibrium amount absorbed is less than for propyl alcohol, being 18% for acetone and 14% for acrylonitrile.   The uptake curves show very little inflection.

In Table IV are tabulated the amounts of sorbate retained after desorption for the standard period of 17 hr., the equivalent volume of liquid sorbate and the average diffusion coefficients $\bar{D}$ obtained for absorption to 3% equilibrium sorbate content at 35°C.
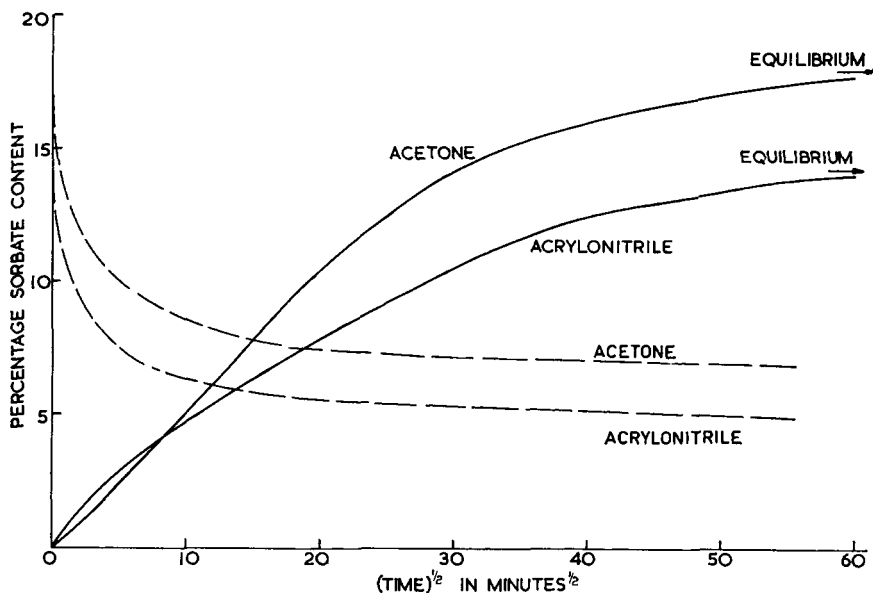
Fig. 6. Uptake curves of acetone and acrylonitrile by dry wool after exposure to saturation vapor pressure of the sorbate at 35°C. and the corresponding desorption curves.

TABLE IV
Comparison of Retained Sorbate and Diffusion Coefficients

Sorbate	Percentage sorbate retained after 17 hr.	Volume of liquid equivalent to retained sorbate, cc./100 g.	Average diffusion coefficient $\bar{D}$, cm.^{2}/sec.
Acrylo-nitrile	5.3	6.6	$3.0 \pm 0.7 \times 10^{-13}$
Acetone	7.0	7.5	$2.5 \pm 0.7 \times 10^{-13}$

DISCUSSION

A feature of the absorption results is the very close agreement between the saturation vapor pressure uptakes of the alcohols and acetone and the uptake from the liquid phase of the corresponding sorbates obtained by Bradbury and Leeder.[1] Similarly the rate of absorption from the vapor phase of ethyl alcohol and n-propyl alcohol at 20°C. is only slightly slower than the rates of absorption of the same sorbates from the liquid phase at 25°C. obtained by Bradbury and Leeder. The fact that they obtained higher equilibrium uptakes in a shorter period than previously published values for alcohol absorption[2,3] from the vapor phase led Bradbury and Leeder to propose that an increased rate of uptake resulted from the greater concentration of sorbate molecules at the fibre surfaces. On the

present results such a proposal is no longer necessary, especially as the concentration of sorbate molecules at the surface is many times greater than the amount absorbed.

Bradbury and Leeder commented on the possibility of less than 100% relative vapor pressure around the wool being obtained in previously published vapor state experiments. Another possible cause of variation in published results is the pretreatment of the wool. Leeder and Lipson[10] have recently shown wide variations in the rate of ethyl alcohol absorption according to a series of modifications carried out on the wool. It may be significant that the wools used by Bradbury and Leeder and in the present study were taken from the same source, given similar cleaning procedures, and vacuum-dried immediately prior to the alcohol absorption. Thus it would appear that vapor phase and liquid phase absorption of the alcohols are in close agreement when conditions are standardized, and it is justifiable to consider the liquid phase as the limiting case of vapor absorption, i.e. saturation vapor pressure.

Sorption at Low Relative Vapor Pressures

In agreement with the wool–water system, the absorption experiments carried out at low relative pressures showed characteristics of Fickian diffusion. It is apparent that molecular size is the dominant factor controlling the rate of diffusion at low relative pressures. It is of particular interest that the rate of uptake of vapors of formic acid and ethyl alcohol were comparable in this region, but greatly different when taken to high sorbate contents.

The desorption data obtained by evacuation (i.e., zero relative pressure) give another method of determining the comparative ability of a sorbate to diffuse through the wool. Much of the sorbate is removed very quickly from saturated fibers, but the concentration of sorbate reaches a level after which further desorption proceeds very slowly and evacuation over a period of weeks fails to remove all the sorbate. The wool is not undergoing dimensional changes, and it is the slow rate of diffusion at the particular level of swelling of the wool which causes the retention of the sorbate. In the absence of measured values of the swelling due to each retained sorbate the volume of an equivalent amount of liquid sorbate may be taken as a guide. There is usually a total volume contraction accompanying absorption, and this may differ from sorbate to sorbate. Such differences are not thought to be great, especially for similar molecules.[11] The swelling measurements made by King[9] show good agreement between the ratio of the observed swelling for a particular weight of water and formic acid and the ratios of the volumes occupied by the liquid sorbates. Then the equivalent volume of retained sorbate is a qualitative measure of the amount of swelling required for each sorbate before rapid transfer through the wool is possible.

Comparison of the measured diffusion coefficients and the level of retained sorbate shows that, in general, an increased level of retained sorbate

indicates a lower diffusion coefficient. The level of retained sorbate seems a little higher with the acids than would be expected from the corresponding diffusion coefficients. It is possible that this is due to the affinity of the acid for the wool. Estimates may be made by this method of the rate of diffusion of sorbates which absorb so slowly that a period of weeks is necessary to complete an absorption step at low relative pressures. The sorbate may be taken into the wool rapidly at saturation vapor pressure or by preswelling the wool with water and the amount of retained sorbate determined by evacuation for less than one day.

For the aliphatic alcohol series, the number of moles retained increases with molecular size of the straight chain molecules. The introduction of branching into the hydrocarbon chain also increases the amount retained over that retained for the corresponding straight-chain molecule. This would indicate a slower rate of diffusion for the branched molecule at low relative pressures, as found by Prager and Long[12] for the Fickian diffusion of hydrocarbons in polyisobutylene. Both of these facts show that the retention of alcohol is not merely the substitution of one molecule for another at specific sorption sites but structural impedance to diffusion.

The amount of sorbate retained is reduced by raising the temperature. Part of this reduction would represent an increased rate of desorption, but mostly it represents less sorbate retained, presumably because of a more open structure of the wool due to thermal agitation.

Absorption at Saturation Vapor Pressure

For all the sorbates considered here, sorption to saturation vapor pressure has shown typical anomalous kinetic behavior.

Anomalous sorption in a number of polymer penetrant systems has been shown to be the result of more than one mechanism of sorption being operative. This has been demonstrated for the wool–water system,[13,14] in which part of the uptake occurred by a mechanism of sorption involving configurational changes within the fibers and part of the uptake followed Fick's laws of diffusion.

It is not possible from sorption data alone to detail the factors contributing to swelling. However, for a polar sorbent such as wool and the polar sorbates considered here, the swelling is usually highly exothermic and involves the rupture of hydrogen bonds. If we assume that this is a more important cause of swelling than random mixing in the present systems, then the high rate of uptake of formic acid at saturation vapor pressure compared with the rate of uptake of methyl alcohol is brought about by the ability of formic acid to break hydrogen bonds and so allow the network to swell. Acetic acid and propionic acid are not as effective as formic acid in breaking hydrogen bonds and so reach a lower equilibrium content at saturation.

The alcohols have similar ability to break hydrogen bonds and so swell the wool fibers and it has been shown[1,15] that the volume uptake is similar for a number of alcohols. The slower rate of uptake observed for the

larger molecules is not due to the lesser ability of the sorbate to swell the wool but is a consequence of the larger holes needed to accommodate the molecules. Similarly the initial rate of uptake of isopropyl alcohol is less than the initial rate of uptake of n-propyl alcohol because of the more bulky configuration of the molecule. The volume occupied by each of the two molecules is comparable, but at equilibrium the weight absorbed and the volume occupied is less for isopropyl alcohol than for n-propyl alcohol. It is possible that in wool it is easier to distort the polypeptide chains to create the long narrow holes to accommodate n-propyl alcohol than the wider holes for isopropyl alcohol.

Comparisons of Sorbates with Different Functional Groups

It is evident that the sorbates of the aliphatic alcohol series show less variation in their sorption behavior than the sorbates of the aliphatic acid series. The dipole moments of the alcohols vary little in an homologous series or when the configuration of the molecule changes from a straight chain to a branched chain. There is a large difference in polarity between formic acid and acetic or propionic acids. It is notable that the absorption of butyric acid at saturation vapor pressure at 35°C. is very slow. In this respect the absorption of butyric acid is similar to the absorption of n-butyl alcohol, that is, for large molecules such as butyl alcohol and butyric acid the uptake is initially very slow because of the difficulty of diffusing into the dry wool.

The uptake of the sorbates acrylonitrile and acetone may be considered in the light of the behavior of the alcohols and the acids. Acetone diffuses more slowly than acrylonitrile into the dry wool, and there is a greater amount retained on desorption because of its more bulky configuration. On the other hand, the greater ability of the carbonyl group of the acetone than the nitrile group of acrylonitrile to break hydrogen bonds allows more rapid swelling. Thus acrylonitrile is absorbed more rapidly initially but in the later stages the absorption of acetone is more rapid.

Thus by consideration of the molecular size and configuration we may predict the initial rate of uptake of an organic sorbate by dry keratin and the rate of diffusion at low relative pressures. Consideration of the ability of that molecule to rupture hydrogen bonds will give a measure of the extent of uptake and rate of approach to equilibrium.

It is probable that other polymer–penetrant systems which swell during absorption and show anomalous sorption behavior may be analyzed in this manner. In particular we have noted that the sorption behavior of collagenous materials is similar to that of the keratins.

References

1. Bradbury, J. H., and J. D. Leeder, *J. Appl. Polymer Sci.*, **7**, 533 (1963).
2. King, G., *Trans. Faraday Soc.*, **31**, 325 (1945).
3. King, G., *Trans. Faraday Soc.*, **33**, 552 (1947).
4. Speakman, J. B., *Trans. Faraday Soc.*, **26**, 61 (1930).

5. Nicholls, C. H., and J. B. Speakman, *J. Textile Inst.*, **46**, T264 (1955).

6. Watt, I. C., *Textile Res. J.*, **30**, 443 (1960).

7. Atkinson, J. C., A. Filson, and J. B. Speakman, *Nature*, **184**, 444 (1959).

8. Watt, I. C., R. H. Kennett, and J. F. P. James, *Textile Res. J.*, **29**, 975 (1959)

9. King G., *J. Colloid Sci.*, **2**, 551 (1947).

10. Leeder, J. D., and M. Lipson, *J. Appl. Polymer Sci.*, **7**, 2053 (1963).

11. Bradbury, J. H., *J. Appl. Polymer Sci.*, **7**, 55 (1963).

12. Prager, S., and F. A. Long, *J. Am. Chem. Soc.*, **73**, 4072 (1951).

13. Watt, I. C., *Textile Res. J.*, **30**, 644 (1960).

14. Watt, I. C., and J. E. Algie, *Textile Res. J.*, **31**, 793 (1961).

15. Bradbury, J. H., *Textile Res. J.*, **27**, 823 (1957).

Résumé

Le comportement lors de l'absorption et de la désorption des vapeurs organiques avec la kératine de laine est examiné. A des pressions de vapeur relativement basses la sorption suit la loi de Fick et la vitesse de diffusion est déterminée par la forme et la configuration de la molécule sorbée. Pour l'absorption à la pression de saturation de la vapeur, un deuxième mécanisme d'absorption—dépendant de la facilité avec laquelle le solvant peut rompre la structure du réseau de la kératine—est superposé au mécanisme de Fick et l'absorption présente des anomalies qui ne suivent pas la loi de Fick. Pour la désorption il y a un enlèvement initial rapide du produit sorbé, avant que la vitesse de désorption ne devienne extrêmement lente. La quantité de substance sorbée retenue dans la région de désorption lente dépend de la température, de la forme et de la configuration des molécules sorbées et a été reliée d'une façon qualitative avec les coefficients de diffusion mesurés à des pressions de vapeur relativement basses.

Zusammenfassung

Das Absorptions- und Desorptionsverhalten von organischen Dämpfen und Wollkeratin wurde untersucht. Bei niedrigem relativen Dampfdruck liegt Ficksche Sorption vor und die Diffusionsgeschwindigkeit wird durch Grösse und Konfiguration der Sorbatmoleküle bestimmt. Bei der Absorption bis zum Sättigungsdampfdruck überlagert sich dem Fickschen Mechanismus ein zweiter Absorptionsmechanismus, der von der Leichtigkeit der Spaltung des Keratinnetzwerkes durch das Sorbat abhängt; die Aufnahme weist dann nicht-Ficksche Anomalien auf. Bei der Desorption verläuft die Abgabe des Sorbate zunächst rasch und wird dann extrem langsam. Die Menge des im Bereich der langsamen Abgabe zurückgehaltenen Sorbats hängt von der Temperatur sowie von Grösse und Konfiguration der Sorbatmoleküle ab und steht in qualitativer Beziehung zu den bei niedrigem relativen Dampfdruck gemessenen Diffusionskoeffizienten.