

Determination of Diffusion Rates in Swelling Systems

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Synopsis

A new method of measuring diffusion coefficients of ethyl alcohol in keratin is described. Ethyl alcohol, which is retained in keratin on desorption by evacuation, is released by swelling the keratin with water vapor. The essential measurement is the loss of weight of the keratin as the ethyl alcohol diffuses out after the absorption of water. Values of the diffusion coefficients at 35°C. are given for a range of volume swelling of keratin where it is not possible to obtain the data by absorption or permeation measurements. The change of diffusion coefficient with swelling is in agreement with values obtained by absorption at lower and higher levels of swelling. The method should have general applicability to many polymer sorption systems where swelling occurs.

The ability of a penetrant to diffuse into a material is the important first step in swelling. Frequently the kinetic behavior of absorption by swelling systems does not follow Fick's law of diffusion. However, part of the absorption may occur by a diffusion mechanism. In this case it is desirable to know the rate of diffusion at a constant degree of swelling.

Diffusion coefficients may be determined at constant swelling by the method of successive differential absorptions by which the sorbate concentration is changed in small steps after equilibrium has been established at each concentration. To a first approximation the concentration is constant throughout the step, and consequently the coefficient of diffusion is constant. This method is time-consuming, and it is known in some cases that the state of the system is also time-dependent,¹ with consequent changes in the subsequent sorption behavior.

For glassy polymers and keratin the uptake curves obtained by this method may occur in two stages,^{1,2} the first stage being characteristic of Fickian diffusion with a concentration-dependent diffusion coefficient and the second stage of absorption resulting from the slow rearrangement of interchain bonds following the entry of penetrant in the first stage of absorption. The measurement of diffusion coefficients is only possible for systems in which the first stage of absorption is completed rapidly and the system reaches a quasi-equilibrium. For slower absorption the second-stage absorption may commence before the first-stage uptake is complete, so that the mechanism of absorption is no longer diffusion alone and the observed kinetics will not be fitted by Fick's equation for diffusion.

A second method, termed the steady-state permeation method, allows the determination of diffusion coefficients from the rate of transfer of sorbate through a sorbent membrane.

The interpretation of permeation data obtained from glassy polymers or partially crystalline materials is difficult. Deviations between sorption- and permeation-derived diffusion coefficients have been reported even for amorphous polymers.³ It is possible that the polymer contains holes of considerable size so that channelling may occur.

Permeation experiments require that the concentration of penetrant at the ingoing and outgoing surfaces be different, and it is usual to have the ingoing pressure much greater than the outgoing pressure in order to obtain an appreciable flow. Thus although in the steady-state condition the degree of swelling is unchanging, it is not constant throughout the membrane and the distribution of the swelling is not necessarily linear from surface to surface.

This paper describes a new method of determining diffusion coefficients, and the method may have general applicability for determining diffusion rates of large molecules in polymeric systems. The essential measurement is the rate of release of larger sorbate molecules from a system swollen with a sorbate of much smaller molecules. Diffusion coefficients at various degrees of swelling have been obtained in this manner for the keratin-ethyl alcohol system. Because the keratin was in the form of fine fibers the permeation method was impracticable, and the method of successive differential absorptions did not separate the diffusion and relaxation mechanisms over a considerable range of swelling.

METHOD

Because of the small diffusion coefficients normally encountered at low levels of swelling, large sorbate molecules are frequently retained or removed at a very slow rate from polymers or fibrous proteins on desorption by evacuation.⁴ Swelling the polymeric material increases the rate of diffusion, and if the concentration of the large sorbate molecules outside the sorbent is zero, desorption takes place. This is the basis by which polymers are purified by leaching out the solvent or monomer molecules with water before drying. If the action is carried out in the vapor phase the desorption of the sorbate can be followed from the loss of weight of the sorbent.

The rates of diffusion of ethyl alcohol in keratin at various levels of swelling were determined with the use of water vapor as swelling agent. The keratin saturated with alcohol was desorbed on a sorption balance until the rate of desorption dropped to a very low value. At this stage a measured amount of ethyl alcohol remained in the keratin and presumably was uniformly distributed throughout the sample. Water vapor was then admitted to the system and rapidly absorbed to establish a higher degree of swelling of the keratin. The rate of diffusion of ethyl alcohol was increased at the higher level of swelling of the keratin. The concentration of ethyl alcohol outside the keratin was zero, the alcohol desorbed and the sample decreased in weight. Because of the disparity in molecular size the absorption of water was virtually complete before much alcohol could diffuse out, except at high levels of swelling. The manner in

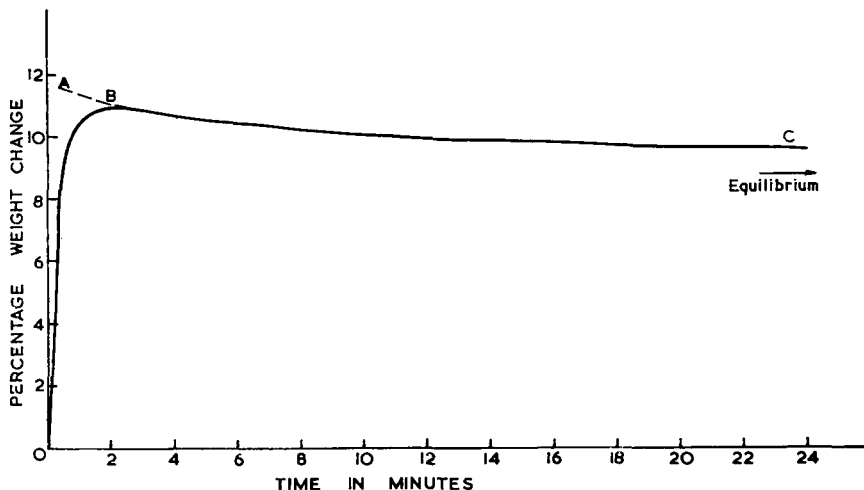


Fig. 1. Change of weight of keratin containing 5.2% ethyl alcohol following exposure to water vapor at relative pressure 58% and 35°C. Diameter of fibers 2.0×10^{-3} cm.

which the weight of the sample changed following admission of water vapor to the sorption vessel is shown in Figure 1.

The initial uptake of water vapor is represented by the curve from the origin to point B and the loss of weight owing to the desorption of ethyl alcohol is represented by BC on the curve, and continues until equilibrium is established. The dotted curve AB is an extrapolation of BC back to the time at which half the water uptake had taken place. This point A is assumed to be the zero point of the desorption although during the whole of the uptake of water, alcohol would diffuse out at a variable rate. The curve ABC is then the desorption curve for ethyl alcohol. However, some

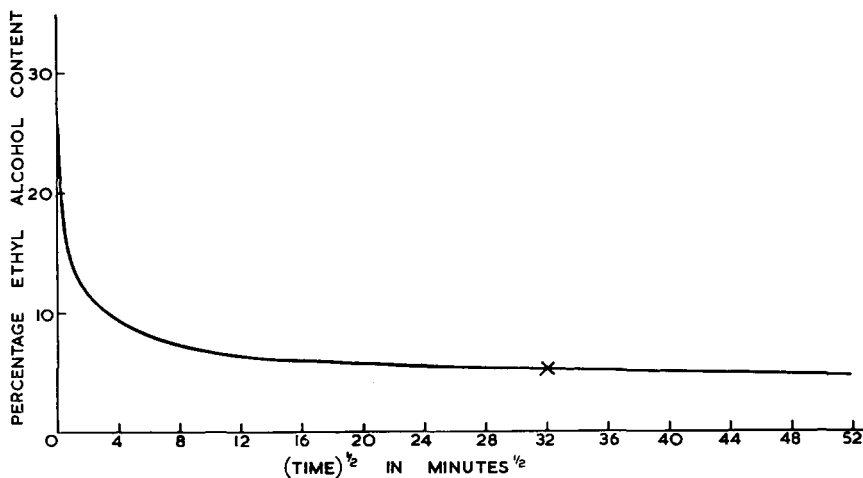


Fig. 2. The desorption of ethyl alcohol from saturated keratin at 35°C. Diameter of fibers 2.0×10^{-3} cm.

water is taken up to replace the alcohol and the observed weight loss does not account for all the desorbed alcohol. If the extra water taken up is proportional to the alcohol lost, the diffusion coefficients calculated from the desorption curve would be unchanged.

The desorption curves were replotted as a function of the square root of time, and for Fickian diffusion from a cylinder the curves are initially linear.⁵ Diffusion coefficients were calculated from the initial slope of the desorption curve and the amount desorbed at equilibrium. After desorption equilibrium had been established, the chamber was again evacuated to check that all the ethyl alcohol had been removed from the keratin.

The degree of swelling of the keratin at point A was calculated from the measured weight of each sorbate in the keratin and published data of the swelling of keratin in ethyl alcohol and water.^{6,7} Full details of the apparatus and experimental procedure have been reported elsewhere.⁸

RESULTS

Retention of Ethyl Alcohol in Keratin

The difficulty in removing organic vapors from polymeric materials by evacuation is exemplified by the desorption of ethyl alcohol from saturated keratin and shown in Figure 2. The desorption was carried out at 35°C., and the keratin was in the form of wool fibers of 2.0×10^{-3} cm. diameter.

It is apparent that the rate of removal of ethyl alcohol which is initially quite rapid becomes decreasingly slow after $(\text{time})^{1/2} = 16 \text{ min.}^{1/2}$, so that the concentration of ethyl alcohol in the keratin changes only slightly with time. The shape of the desorption curve is similar at other temperatures but the amount of ethyl alcohol retained in the wool at the point of slow desorption progressively decreased as the temperature of desorption was increased. For the purposes of determining diffusion coefficients the desorption was interrupted at $(\text{time})^{1/2} = 32 \text{ min.}^{1/2}$, at which time the change in ethyl alcohol concentration was of the order of 0.03%/hr. and the ethyl alcohol content 5.2% on the weight of dry keratin.

Determination of Diffusion Coefficients

At the point $(\text{time})^{1/2} = 32 \text{ min.}^{1/2}$ the desorbing keratin was exposed to water vapor at various relative pressures and the change of weight of the sample followed as a function of time elapsed after the entry of water vapor to the sorption vessel. Curves similar to that illustrated in Figure 1 were obtained. The portion ABC of Figure 1 was replotted as a function of $(\text{time})^{1/2}$ and, where appropriate, diffusion coefficients calculated. The degree of swelling of the keratin before admission of the water vapor was taken from published data of the volume swelling of keratin by ethyl alcohol. This degree of swelling was then transferred to a curve of keratin swelling versus water content and the additional swelling at point A of Figure 1 estimated from the weight of water absorbed and the swelling curve. This procedure was necessary as the volume swelling versus water

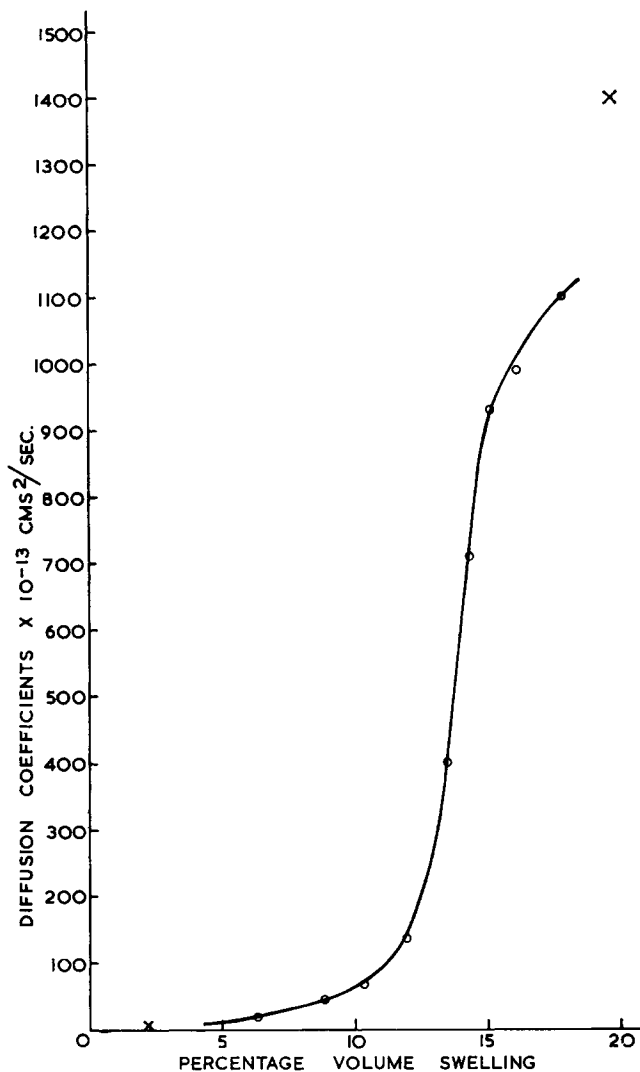


Fig. 3. Diffusion coefficients of ethyl alcohol in keratin at 35°C. as a function of volume swelling: (O) values obtained by desorption from water swollen keratin; (X) values obtained by absorption into keratin equilibrated with ethyl alcohol.

content curve is not linear for keratin. A plot of calculated diffusion coefficients as a function of the percentage volume swelling is shown in Figure 3.

At levels of swelling higher than those shown much of the ethyl alcohol desorbed from the keratin while water absorption was occurring and in fact when exposed to saturation vapour pressure of water all the alcohol was desorbed before equilibrium uptake was established. At low levels of swelling the release of alcohol was too slow to obtain meaningful desorption curves.

It is not possible to check the values of diffusion coefficients obtained here directly with values obtained by another method at the same levels of swelling. The crosses in Figure 3 represent diffusion coefficients obtained by small absorption steps of ethyl alcohol at a lower and a higher level of swelling. At the low level of swelling absorption occurs by diffusion only and at the high level of swelling the Fickian uptake occurs sufficiently rapidly to be separated from a subsequent relaxation mechanism of absorption.

DISCUSSION

For diffusion by a Fickian mechanism the rate of desorption is usually less than the rate of absorption if the diffusion coefficient is concentration dependent. When the limits of concentration change are brought closer together this disparity is lessened as the diffusion coefficient becomes virtually constant over a small concentration range, and the rate of desorption and absorption should be equivalent. It has been shown in the cellulose acetate-acetone⁹ and keratin-water¹ systems that for small concentration changes from a particular level of swelling, the rates of absorption and desorption are the same if the conditions are such that the mechanism of sorption can be characterized as Fickian.

It is probable therefore that the diffusion coefficients calculated from the rate of desorption of alcohol from keratin are close to the values which would be obtained on absorption at the same degree of swelling. This should apply to the values reported in this paper because of the small range of concentration change of the sorption step. The values obtained by absorption at a lower level and a higher level of swelling are in good agreement with the curve of Figure 3.

For desorption no steep concentration fronts are moving through the sorbent,¹⁰ and the level of swelling may be considered essentially uniform throughout the sorbent although decreasing as desorption proceeds. Thus the degree of swelling at point A of Figure 1 is the swelling at which initial desorption takes place.

The greatest value of this method of determination of diffusion coefficients is probably as a measure of the variation of diffusion coefficients with swelling. There are, of course, several assumptions made in the calculation of the diffusion coefficients which could introduce some error. For instance, the observed desorption curve does not represent all of the alcohol leaving the keratin, and extra water must be absorbed simultaneously. It is assumed here that the replacement of alcohol by water occurs proportionally.

It is also assumed in calculation of the swelling that there is no interaction between the sorbates and that the water entering the keratin increases the swelling to the same extent as if water was the sorbate already present. Such interaction is unlikely to be of great importance in the case of water and alcohol. However, these assumptions which may introduce errors

into the quantitative calculation of diffusion coefficients would have little effect on the shape of the curve of diffusion coefficient versus swelling.

The limitations to the range of swellings at which diffusion coefficients can be conveniently investigated are at low levels of swelling where the rate of diffusion is extremely slow and at high levels of swelling where the rate of diffusion is so fast that much of the alcohol is lost before equilibrium uptake is established. However, the range of swelling at which diffusion coefficients may be measured may be extended in either direction by the choice of temperature.

The significant feature of the variation of diffusion coefficients of ethyl alcohol with the degree of swelling of keratin is the rapid increase after a volume swelling of about 10%. The rate of increase appears to lessen at higher volume swellings. It is notable that the dependence of the diffusion coefficients on the swelling of the keratin is greater for ethyl alcohol than has been reported for water¹ and that the rapid change of the diffusion coefficient of ethyl alcohol occurs at a higher degree of swelling of the keratin. It has been shown that when sorption is diffusion-controlled that the rate of diffusion is related to the size and conformation of the diffusing species.^{4,11} Thus, the values of diffusion coefficients for ethyl alcohol are lower than the values for water. It appears that the movement of the sorbate molecules is greatly facilitated at a certain degree of swelling and this level of swelling increases for the larger molecules. Below this degree of swelling the movement of the sorbate through the keratin is difficult, and in the case of the alcohol much of the sorbate is retained on desorption.

The figure of 10% as the volume swelling at which diffusion coefficients rapidly increase can be compared with the observation of King¹² that the rate of absorption of ethyl alcohol to saturation, as a function of initial ethyl alcohol content, shows a rapid increase after an initial ethyl alcohol content of 8% by weight. It must be remembered, however, that the absorption observed by King was in part controlled by the changing conformation of the keratin owing to swelling. On the other hand, diffusion of ethyl alcohol into the keratin is a necessary prerequisite to swelling, and King's observation probably indicates a markedly increased rate of diffusion above 8% ethyl alcohol content. These results taken together show that the rate of diffusion is dependent on the degree of swelling, although the swelling may be caused by another sorbate. It is more realistic to express diffusion coefficients as a function of swelling rather than initial concentration of sorbate.

This method may be applied with advantage in the keratin system to sorbates of larger molecular size and different configurations. The sorbent may be swollen with water or heated to facilitate the entry of the large sorbate molecules. In the subsequent desorption the water is removed and the sorbate consisting of large molecules retained.⁴ Thus, even for sorbates of large molecular size, the overall time of the experiment is not unduly long. A similar advantage would be obtained in other sorption

systems in which the slow rate of absorption would require long periods of time to establish equilibrium at a particular level of swelling. This would allow a wider choice of molecular size and configuration of sorbates used in studying polymer structure.

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Résumé

On décrit une nouvelle méthode de mesure des coefficients de diffusion de l'alcool éthylique dans la kératine. L'alcool éthylique est retenu dans la kératine lors de la désorption sous vide, est libéré par gonflement de la kératine avec de la vapeur d'eau. La mesure essentielle est la perte de poids de la kératine lorsque l'alcool éthylique s'échappe après l'absorption d'eau. On donne les valeurs des coefficients de diffusion à 35°C pour un domaine de gonflement de volume de la kératine où il n'est pas possible d'obtenir de résultats par mesure d'absorption ou de pénétration. Le changement du coefficient de diffusion avec le gonflement est en accord avec les valeurs obtenus par absorption à plus faible et plus haut degrés de gonflement. La méthode aurait une application générale pour beaucoup de systèmes de sorption sur polymère ou le gonflement a lieu.

Zusammenfassung

Eine neue Methode zur Messung des Diffusionskoeffizienten von Äthylalkohol in Keratin wird beschrieben. Äthylalkohol, der im Keratin bei der Desorption durch Evakuierung zurückgehalten wird, wird durch Quellung des Keratins in Wasser in Freiheit gesetzt. Im wesentlichen wird der Gewichtsverlust des Keratins beim Herausdiffundieren des Äthylalkohols nach der Wasserabsorption gemessen. Werte des Diffusionskoeffizienten bei 35°C werden für einen Quellungsbereich von Keratin angegeben, wo es nicht möglich ist die entsprechenden Daten durch Absorptions- oder Permeationsmessungen zu gewinnen. Die Abhängigkeit des Diffusionskoeffizienten von der Quellung stimmt mit den aus der Absorption bei niedrigeren und höheren Quellungsgraden erhaltenen Werten überein. Die Methode sollte sich allgemein auf viele Polymersorptionsysteme anwenden lassen, bei welchen Quellung eintritt.

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