

Sorption of Vapors in Cellulose Film

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Synopsis

The rates of sorption of water vapor and of methanol vapor in cellulose film were examined by stepwise increments of vapor pressure. In addition, the rates of sorption of the series of vapors water, methanol, ethanol, *n*-propanol, and *n*-butanol were studied at pressures just below the respective saturated vapor pressures. The results obtained from both parts of the study are explained in terms of a bimodal diffusion mechanism. This consists of the simultaneous diffusion of vapor into the microporous structure of the cellulose film and diffusion from the micropores into the polymer matrix.

INTRODUCTION

It is well established that the diffusion of water vapor and the vapors of organic solvents by cellulose and its esters is non-Fickian.¹ Thus, plots of M/M_e against $t^{1/2}$ (where M = mass sorbed at time t and M_e = mass sorbed at equilibrium) are nonlinear.

Frisch² suggested that transport in the more rigid polymers such as cellulose and its derivatives may be a concerted mechanism of simultaneous convection and diffusion. Since then, the results of diffusion studies in cellulose derivatives³ and the observed rate of alcoholysis of cellulose⁴ have been tentatively explained by postulating the presence of micropores. Recent electron microscope work has shown that regenerated cellulose film produced by the viscose process consists in the "never dried" state of fibrils about 10 nm in diameter with a network of interfibrillar pores of similar dimensions.⁵

In the present study, the interval (stepwise) sorption of water and methanol vapors in cellulose and also the sorption of water, methanol, ethanol, *n*-propanol, and *n*-butanol at high relative vapor pressures were examined. It was shown that the results obtained can be explained in terms of the microporosity of the cellulose.

EXPERIMENTAL

Materials

The cellulose used was regenerated cellulose film manufactured by the viscose process by Transparent Paper Ltd. It was taken from the casting

machine after the washing baths but before the plasticizer and anchoring baths, so that it contained neither plasticizer nor anchoring agent. Before use it was washed in hot water, then cold distilled water, and finally stored in distilled water until required. The samples used were cut while the film was wet and measured approximately 60×20 mm, although considerable shrinkage occurred during drying.

The water used was distilled, and the alcohols, which were spectroscopic grade, were stored over a molecular sieve.

Sorption Balance and Associated Apparatus

The balance used was an automatic recording balance Mark 2C manufactured by C. I. Electronics Ltd. By feeding the output through a universal matching circuit to a Smiths Servoscribe recorder, it was possible to obtain a smooth trace with a full-scale deflection of 0.5 mg; i.e., one division of the chart paper was equivalent to 5 μ g. The balance was used in a glass case which could be evacuated and then held at any desired vapor pressure at a stated temperature. It was clearly established that the vapors in no way interacted with the microbalance itself.

Experimental Procedure

The cellulose film samples were cut from the stock, washed with distilled water, wiped dry with filter paper, and then suspended from one arm of the balance. The vacuum case was sealed, the down-tube was thermostated at 20°C, and the whole system was outgassed. A pressure of 0.13 N m⁻² was normally attained within one day, but small weight losses were detectable on the fifth day of outgassing. It was therefore adopted as a routine that the system was outgassed for one week. No attempt was made to outgas at elevated temperatures because of the risk of thermal degradation.⁶ A fresh film sample was used for each experiment.

For the sorption kinetics studies at high relative pressure, the vapor source was thermostated at 19°C. The vapor was allowed to fill the previously evacuated doser system which included an expansion bulb so as to give a large volume and so minimize the change in pressure when the tap to the balance was opened. When the vapor pressure in the doser system was constant, the tap to the balance case was opened quickly so that the vapor pressure increase was as sharp as possible. This caused violent oscillations in the balance, but the recorder trace became steady within 30 sec.

For the study of the sorption kinetics of water by stepwise vapor pressure increments, the different vapor pressures were achieved by thermostating different concentrations of sulfuric acid at 19°C. In the case of methanol, the pressure increments were achieved by thermostating the methanol at different temperatures. In both cases, the procedure adopted was to isolate the balance case at the end of each step while the new vapor pressure was established in the doser system and then to reopen the balance case to the system.

RESULTS AND DISCUSSION

Sorption Kinetics at High Vapor Pressures

The data obtained from the recording balance were plots of weight gain against time. The weight gain was calculated as a fraction of the weight gain at equilibrium. The data were plotted in the form M/M_e against $t^{1/2}$, where M is the mass adsorbed at time t and M_e is the mass adsorbed at equilibrium; these data are shown in Figure 1. In the case of water vapor, the well-established sigmoid shape is seen, and this sigmoid shape is even more exaggerated with methanol vapor. The plot for ethanol shows an initial shallow "s," and the sorption appears to be tailing off when after 2 hr the gradient of the plot again increases before equilibrium is finally established. With *n*-propanol, the initial period over which the gradient is increasing lasts only 4 min and is followed by a slow approach to equilibrium, while the initial stage for *n*-butanol lasts only a little more than 1 min and thereafter the plot is virtually linear up to the final slow approach to equilibrium.

The values of M_e in these curves shown in Figure 1 are water, 202 mg/g; methanol, 108 mg/g; ethanol, 78 mg/g; *n*-propanol, 31 mg/g; *n*-butanol, 22 mg/g. In terms of the actual amount sorbed, it can then be shown that

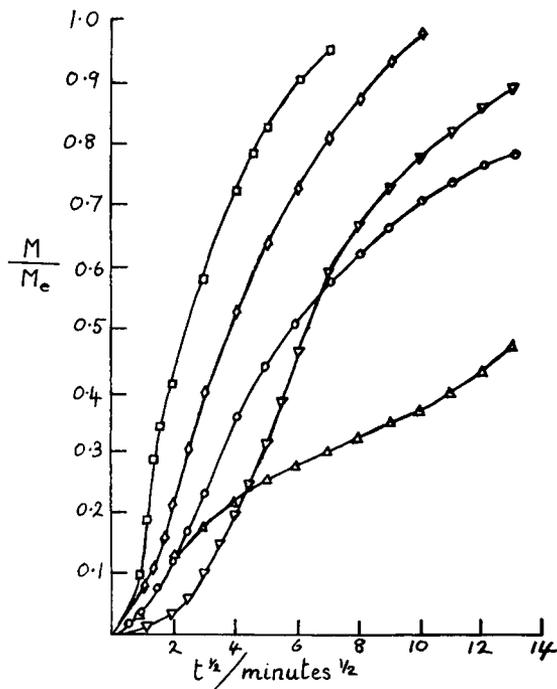


Fig. 1. Reduced sorption rates for vapors sorbed on cellulose film at 20°C: (□) *n*-butanol; (◇) *n*-propanol; (▽) methanol; (○) water; (△) ethanol. M = Mass adsorbed at time t ; M_e = mass adsorbed at equilibrium.

water is sorbed most quickly and to a far greater extent than any of the alcohols. The methanol sorption begins anomalously slowly and "accelerates" rapidly, while the curves for the three higher alcohols lie very close together, with the ethanol showing some further sigmoid character later in the sorption.

The results are that the alcohols have a lower affinity than water for the polymer and diffusion is more "anomalous" the more strongly sorbed the vapor. This behavior is consistent with a coupled diffusion-relaxation mechanism,¹ but an alternative suggestion is made here that there are two regions within the cellulose one of which is accessible to all the sorbates while the other is readily accessible to water but increasingly inaccessible to the larger molecules.

Stepwise Kinetics of Sorption

The data in these instances were plotted as before as M/M_e against $t^{1/2}$ (Figs. 2 and 3). The water vapor isotherm constructed from the equilibrium weights adsorbed after each experiment is shown in Figure 4.

The methanol/cellulose system follows the same pattern as the water/cellulose system. The first step is almost linear with a small gradient, and

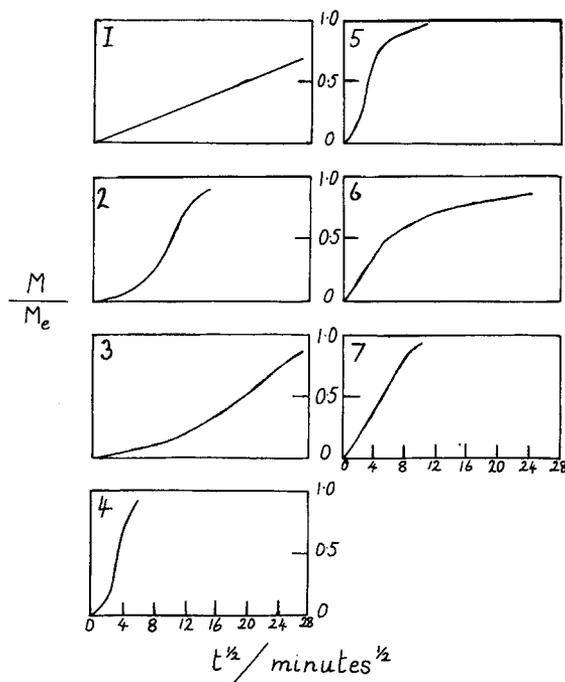


Fig. 2. Reduced sorption rates for interval sorption of water vapor onto cellulose film at 20°C. P/P_0 values: (1) 0.085; (2) 0.190; (3) 0.375; (4) 0.580; (5) 0.700; (6) 0.805; (7) 0.935.

the subsequent steps show increasingly greater gradients. The plots of M/M_e against $t^{1/2}$ for the fourth step is anomalous in that it begins in the predicted way with a greater rate of sorption than the third step, and the rate then decreases before beginning to increase again after some 4 hr. Examination of the sorption isotherm for the methanol/cellulose system (Fig. 5) constructed from the equilibrium weights sorbed after each experiment shows that this fourth step lies at the beginning of that part of the isotherm where the amount sorbed increases rapidly with relative vapor pressure. It is reasonable to assume that the later increase in sorption rate occurs at the point on the isotherm at which the amount sorbed increases greatly with a small increase in equilibrium pressure.

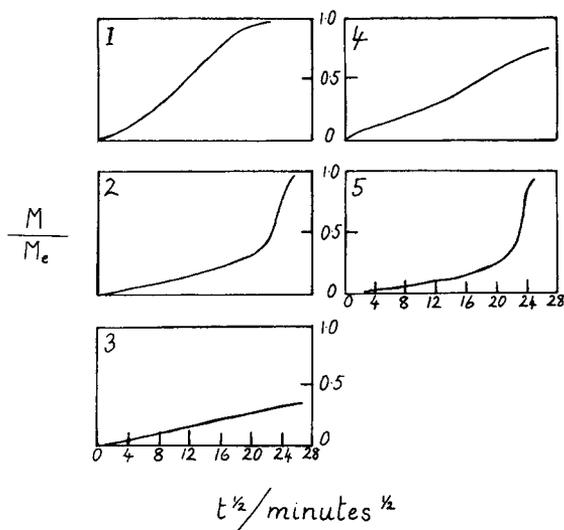


Fig. 3. Reduced sorption rates for interval sorption of methanol vapor onto cellulose film at 20°C. P/P_0 values: (1) 0.067; (2) 0.305; (3) 0.408; (4) 0.650; (5) 0.970.

The results of the sorption studies reported here lead to the proposition that the cellulose contains two regions, one of which is accessible to all sorbates, the other to only the smaller molecules. As stated in the introduction, it has been shown by electron microscopy that viscose film in the "never dried" state consists of a network of fibrils of about 10 nm in diameter and pores of similar size. On drying, it is to be expected that the system will contract but will not collapse; indeed, evidence has been presented that even after drying and carbonization the parent structure is modified but not destroyed.⁷ It is therefore reasonable to consider that the region which is accessible to all these sorbates is the interfibrillar pore structure, and only those molecules that are capable of swelling the cellulose enter the polymer matrix to an appreciable extent.

The stepwise sorption of water may now be considered in terms of this proposal. The initial step at very low vapor pressure would be the

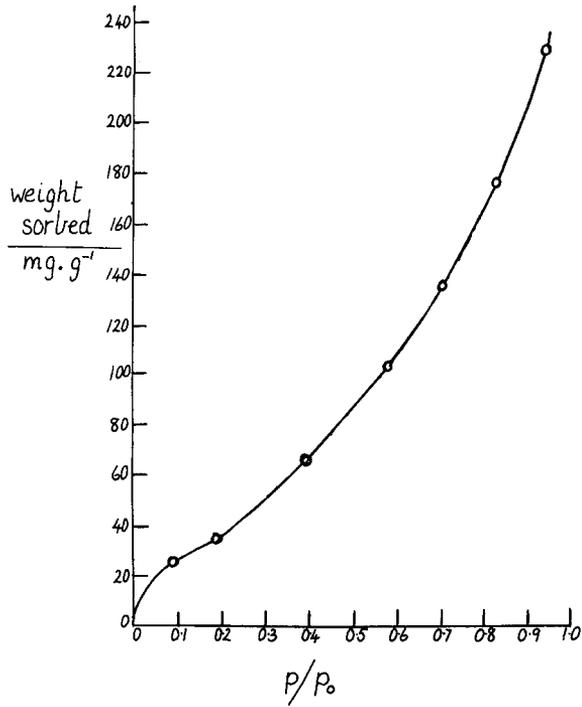


Fig. 4. Sorption isotherm for water vapor onto cellulose film at 20°C.

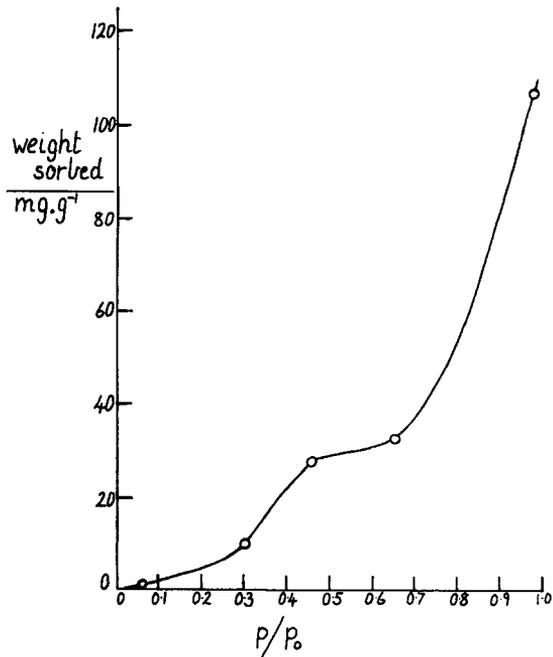


Fig. 5. Sorption isotherm for methanol vapor onto cellulose film at 20°C.

diffusion-controlled adsorption of water molecules onto the pore walls, without any appreciable adsorption into the polymer matrix. When the vapor pressure is increased for the second step, there will be further diffusion of water molecules into the pores. At some stage, the vapor pressure within the pores will be such that diffusion will occur from the pores into the polymer matrix, and since water is a strong swelling (plasticizing) agent, the secondary diffusion process will be concentration dependent.

For Fickian flow, a plot of M/M_e against $t^{1/2}$ is linear over most of its length and becomes concave to the $t^{1/2}$ axis as equilibrium is approached. Thus, a plot of M/M_e against t will be essentially parabolic.

The diffusion of water vapor into the pores of the cellulose at low pressure gives a near linear plot for M/M_e against $t^{1/2}$ and therefore a near parabola for M/M_e against t . Suppose that a similar Fickian flow into the pores

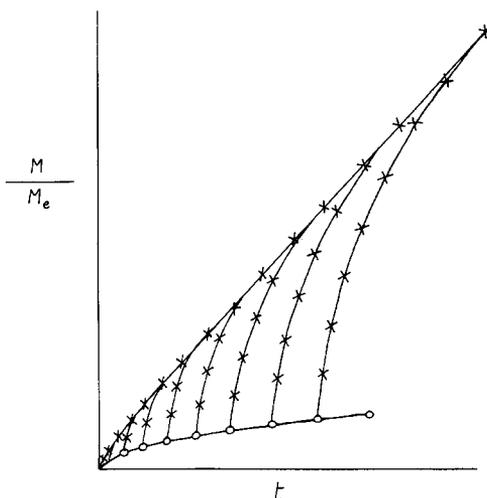


Fig. 6. Model plot for bimodal diffusion of water vapor onto cellulose film.

occurs with each pressure increment. If now there is a second process of adsorption from the pores into the polymer matrix by a concentration-dependent Fickian flow, then the net effect can be seen by imagining each point on the first parabola as being the origin of a second parabola whose amplitude will depend on the value of mass sorbed at its origin (because the second diffusion process is concentration dependent). This is shown graphically in Figure 6, from which it can be seen that the envelope of the secondary parabola is a straight line which will become concave to the t -axis as equilibrium is approached. This shape of plot for M/M_e against t will give a sigmoid M/M_e -against- $t^{1/2}$ plot.

Because the diffusion from the pores into the polymer matrix is concentration dependent, its contribution will become larger as the vapor

pressure increases, with the result that the reduced sorption curve will become more markedly sigmoid until a point is reached at which the contribution of the diffusion into the pores is negligible and the simple Fickian flow is again observed. The detailed shape of the reduced sorption plot will depend upon the concentration dependence of the adsorption process and upon changes in the dimensions of the pore system due to the swelling of the fibrils.

This bimodal diffusion mechanism can be used to explain the observed approach to simple Fickian behavior on ascending the series of vapors used in the study at high relative vapor pressure. On ascending this series, the larger molecules will have less swelling effect, therefore the secondary diffusion will become less significant and the simple diffusion into the pores will be the predominant feature. Hence the similarity in behavior of the two highest members of the series and in behavior of the early part of the ethanol sorption. The increases in sorption later in the ethanol curve is presumably a manifestation of some limited swelling.

This mechanism can also explain the results of earlier workers regarding the desorption of vapor from cellulose where there is an initial very rapid loss of sorbate followed by an extremely long approach to equilibrium (as observed qualitatively in the present study during the outgassing of the cellulose samples). Here, the initial desorption will be from the open pores of the cellulose and should therefore be very rapid; but once this easily accessible sorbate has been removed, further desorption can only occur by diffusion from the polymer matrix to the pores and thence be evaporated. The diffusion from the polymer matrix being concentration dependent, it will become progressively slower.

CONCLUSIONS

A bimodal diffusion mechanism has been proposed which can be used to explain qualitatively the results obtained by studying the sorption kinetics of a series of vapors at high relative vapor pressure and of water and methanol vapors at a series of pressures. The mechanism is based on the existence of a pore system within the cellulose. The presence of such pores had been suggested by previous studies both of diffusion of gas into ethyl cellulose³ and of alcoholysis of cellulose.⁴ The presence of a pore structure in "never dried" cellulose had been shown by Jayme and Balser's⁵ electron microscopy work.

By assuming the existence of pores in dried cellulose, it has been shown that the experimental results can be explained by a mechanism in which the vapor diffuses first into the pores and then from the pores into the polymer matrix. The principal of the mechanism is in essence that postulated on theoretical grounds by Frisch.²

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