

Sorption Effects in the Measurement of the Time Lag for Water Vapor

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The time-lag method^{1,2} has proved to be particularly useful for the determination of the diffusion constant D of a gas or vapor in a polymer membrane. Frisch³ extended the analysis to systems with concentration-dependent D and obtained a general expression for the concentration dependence of the time lag L . Usually, a constant pressure of gas is maintained at the ingoing face of an initially outgassed membrane and the increase of the pressure at the outgoing face recorded as a function of time. Extrapolation of the linear or steady-state portion of this plot back to the time axis gives the time lag as intercept. When water is the diffusate, the sorption of vapor on the glass walls of the measuring section can affect the build-up of the pressure. Consequently there have been relatively few attempts to measure time lags for water vapor in polymers. An exception is the work of Stannett et al.,⁴⁻⁷ who attempted to allow for the effects of sorption by subjecting the measuring section to an equilibrium pressure of ~ 0.02 mm-Hg prior to commencing a run. With this modified procedure, L and hence the diffusion coefficient for several water-polymer systems were found to be constant, whereas steady-state and sorption-desorption kinetic analyses indicated that $D(c)$ decreased with increasing concentration C of vapor. When $D(c)$ decreases with C the variation of L with C is relatively small and the more difficult to measure accurately.⁸ However, for at least some of the water-polymer systems examined the variation of L with C predicted by using steady-state data and the Frisch equation was considered to be significant even allowing for the experimental scatter of points expected of a constant L system. It is of interest, therefore, to examine the effect on L of sorption of water on the walls of the apparatus, particularly in relation to the pretreatment technique of Stannett et al.

The data of Frank⁹ and Barrett and Gauger¹⁰ for the sorption of water by washed Pyrex glass at 25°C in the relative humidity range $(1-30) \times 10^{-3}$ are well represented by

$$Q(\text{cc STP/cm}^2) = 1.73 \times 10^{-4} p_e^{0.422} \quad (1)$$

where Q is the amount sorbed at an equilibrium pressure p_e (in mm Hg). In a typical permeation run the final pressure in the measuring section may be several times the "pretreatment" pressure of 0.02 mm Hg. Clearly,

appreciable sorption of water by the glass walls will occur as permeation proceeds. Further, sorption equilibrium was virtually attained in ~ 15 min,⁹ a time which is short compared with that taken to complete a permeation experiment.⁴ To examine in more detail the effect of sorption on the glass we consider for simplicity a constant D system for which permeation measurements are made at a series of constant ingoing pressures and we distinguish between two experimental procedures. In the first (method a), the volume V of the measuring section of the apparatus is kept constant so that the higher the ingoing pressure the higher is the outgoing pressure; in the second (method b), the volume V is so adjusted as to confine the outgoing pressure to approximately a fixed range, independent of the ingoing pressure.

The following calculations were based on data for the water-ethylcellulose system at 25°C.^{4,6} The diffusion coefficient in this system decreased with concentration, but for the purpose of the calculation it was treated as constant and equal to 2.7×10^{-7} cm²/sec¹. The ingoing concentration C was in the range 0-80 cc STP/cc of polymer, and the membrane thickness l and cross-sectional area G were taken as 0.108 cm and 0.3 cm², respectively. When there is no sorption of water vapor by the walls of the measuring section then the increase in the outgoing pressure p_1 with time is given by

$$p_1 = \frac{DG(298.2)(760)}{V(273.2)} \left[\frac{Ct}{l} - \frac{Cl}{6D} \left(1 + \sum_{n=1}^{\infty} \frac{12(-1)^n}{\pi^2 n^2} \right) \exp\{-n^2 \pi^2 Dt/l^2\} \right] \quad (2)$$

which gives a time lag $L = 120$ min.

The effect of sorption on the glass is to reduce the pressure p_1 at time t to some value p_2 . In the absence of accurate sorption kinetic data for the water-glass system in the region of low pressures the amount of water sorbed by the walls at time t is taken as the amount in equilibrium with a pressure p_e' . Here p_e' is equated with the value of p_1 at a time $(t - 600)$ sec. (It is to be emphasized that this procedure is an approximation and, if anything, will tend to overestimate the sorption slightly.) From eq. (1) the amount sorbed at time t is $1.73 \times 10^{-4} (p_e')^{0.422} A$, where A is the surface area of the glass walls. This amount of sorption corresponds to a reduction in the pressure p_1 by an amount p' given by

$$p' = 1.73 \times 10^{-4} (p_e')^{0.422} A [(760)(298.2)/273.2V] \quad (3)$$

As $p_2 = p_1 - p'$, the change in p_2 with time follows from eqs. (2) and (3). In the pretreatment method of Stannett et al., the initial pressure in the measuring section is not zero but 0.02 mm Hg, so that the vapor-phase pressure p_3 is now given by

$$p_3 = p_2 + p' + 0.02 - p'' \quad (4)$$

as illustrated in Figure 1 by a typical example from the calculations. Permeation curves of p_1 , p_2 , and p_3 versus t were constructed for several

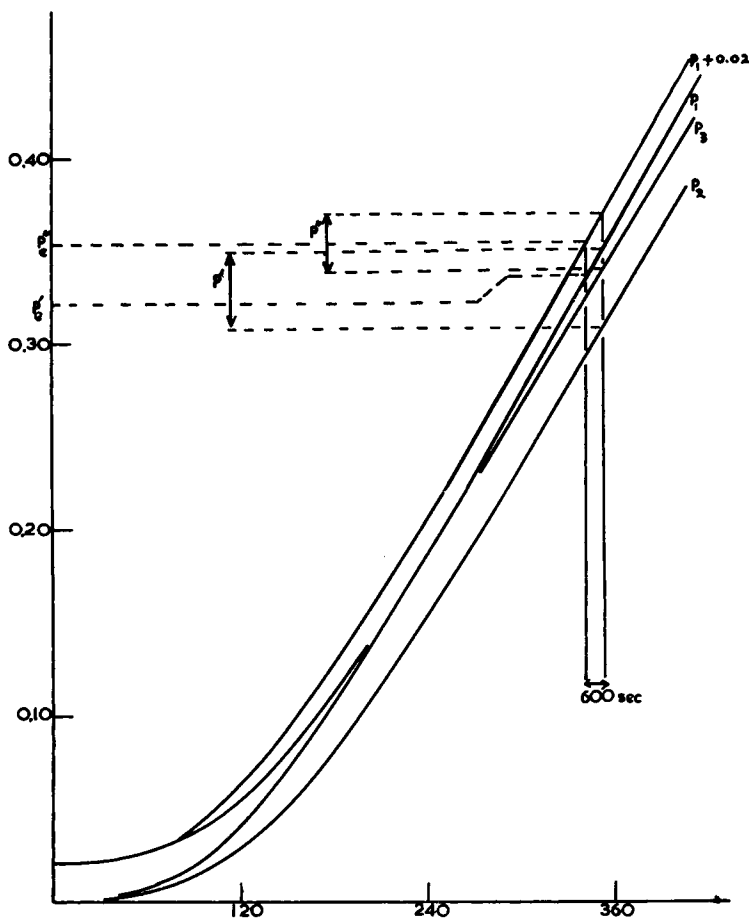


Fig. 1. Permeation curves; p_1 -zero sorption on the glass and zero initial pressure [eq. (2)]; p_2 -sorption on the glass and zero initial pressure [eqs. (2) and (3)]; p_3 -sorption on the glass and 0.02 mm Hg initial pressure [eqs. (2) and (4)]. For all curves $V = 1000 \text{ cm}^3$ and $C = 40 \text{ cc STP/cc}$ of polymer.

ingoing pressures, assuming the volume of the measuring section was spherical, i.e., $A = 4.84V^{2/3}$. For method a, V was constant and equal to 1000 cm^3 ; for method b, V was varied with the ingoing concentration according to $V = 25C$. The effect of sorption on the variation of L with C is shown in Figure 2, and the effect on the steady state flux is shown in Figure 3.

Clearly the sorption of water by the glass walls of the apparatus can have a marked effect on the time lag both in methods a and b. Pretreatment of the glass surface reduces this effect considerably but does not eliminate it completely. As indicated previously, the calculations are only approximate, and in addition factors such as the nature, treatment, temperature, and geometry of the glass surface will also affect the final result. For example, in method b if the volume of the measuring system is increased

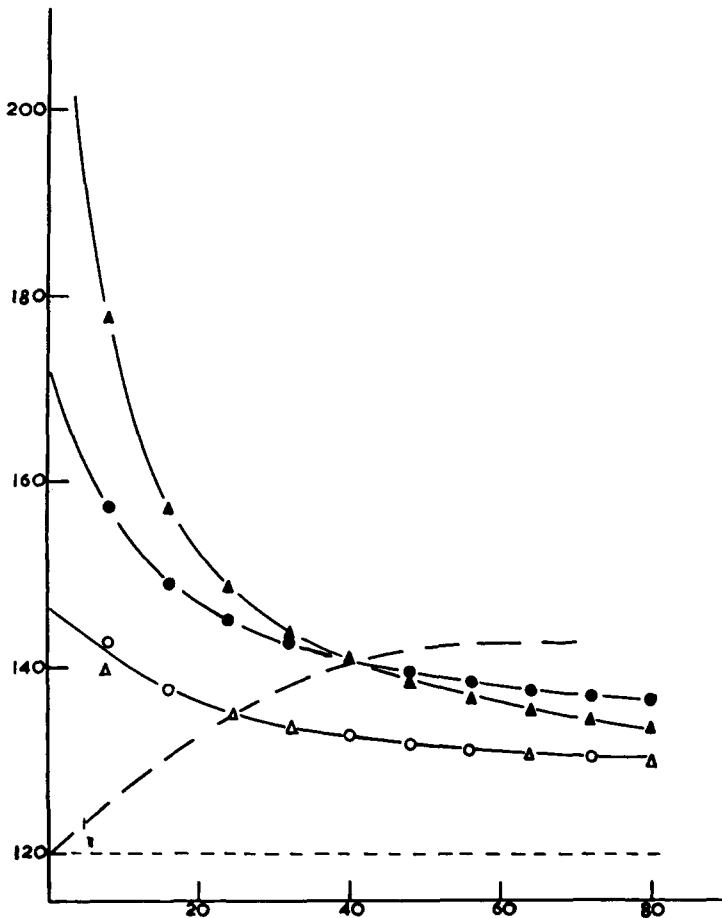


Fig. 2. Variation of the time lag with concentration: (▲) method a with no pretreatment of glass; (●) method b with no pretreatment of glass; (Δ) method a, with pretreatment of glass; (○) method b, with pretreatment of glass; (---) no sorption on the glass (D constant); (-·-) calculated from steady-state data^{4,6} with the use of the Frisch equation.

without changing the ratio A/V in eq. (3), then the time lag will be independent of concentration and in error by a constant amount. In general, however, sorption by the glass in the region of low pressures will tend to cause L to decrease with increasing C . For water-polymer systems $D(c)$ may be either an increasing or decreasing function of C . If the former, then L decreases with increasing C so that the sorption effect will reinforce and exaggerate the true $L-C$ dependence. When $D(c)$ decreases with increasing C , L will increase with C , as shown by the example (Fig. 2) calculated for the water-ethylcellulose system by using the Frisch equation and the steady-state D versus C relation. In this case, sorption effects will counteract and reduce the concentration dependence of the time lag and

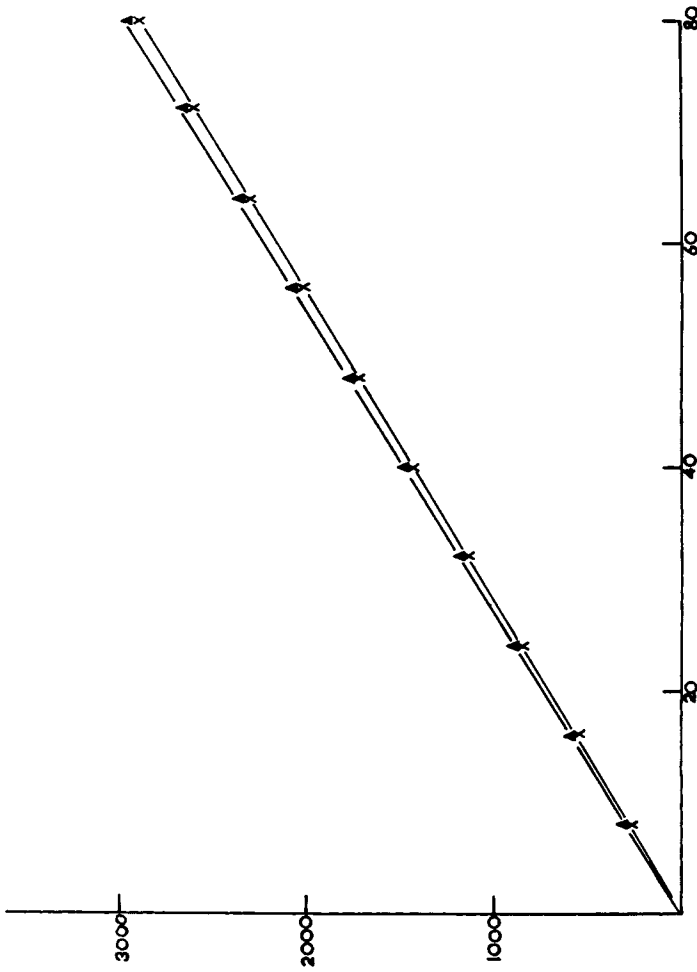


Fig. 3. Variation of the steady-state permeation rate with concentration: (▲) zero sorption on the glass; (×) methods a and b, sorption on the glass.

could presumably in certain circumstances lead to an apparent constant D . It is not suggested that the differences between steady-state and time-lag measurements observed by Stannett et al. can be explained in terms of sorption effects. In fact, certain features of their data would seem to rule out such an explanation. Nevertheless, these calculations, although approximate, would appear to indicate that the pretreatment technique may not be entirely successful in allowing for sorption effects and that water vapor time lags must be interpreted with some caution. Perhaps a better solution to this problem lies in the use of an all-metal measuring section incorporating a sensitive diaphragm-type of pressure transducer in which sorption of water by the walls would be very much reduced.

This work is part of an investigation of water and similar vapors in polymer films. The paper is British Crown Copyright, published with permission of the Controller, Her Britannic Majesty's Stationery Office.

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