

Transmission, sorption and diffusivity: methods for determining the transport of water vapour through films

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Introduction

The transport of water molecules through solids is commonplace and of significance to diverse industries. Broadly speaking the interest lies in preventing ingress of water vapour and the associated product protection. Equally there are applications dependent on the transport of water vapour such as where a controlled release of water vapour is required. In all such cases knowledge of the physical properties governing the rate of transport in different climatic conditions is essential.

Molecular transport through solids is termed permeation or transmission and can either be due to absorption where molecules diffuse in the solid or due to adsorption where molecules diffuse through the pore structure of the solid. The permeation or transmission rate, F , will be a function of three parameters:-

- i) The solid dimensions (i.e. the ratio of area, A , to thickness, t , for a film)
- ii) Temperature, T : Molecular diffusion in solids is an activated process which requires energy to overcome a potential barrier and increasing temperature will therefore assist diffusion.
- iii) Concentration gradient, ΔC : Net transport requires a difference in the concentration of molecules across the solid so that there will be a corresponding net rate of transfer from the region of high concentration (analogous to the flow of heat from a region of high temperature in the presence of a thermal gradient).

A concentration gradient will always exist if the solid is not in equilibrium and this can in practice be achieved in two controlled ways, which correspond to the experimental methods described in this article.

Direct transmission rate determination

This method uses the film to seal an impermeable chamber and is directly analogous to packaging applications where

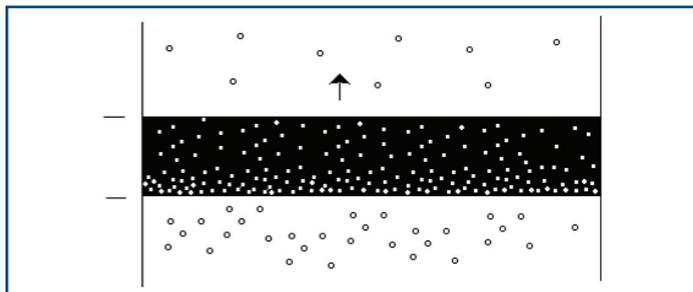


Figure 1: Schematic showing the permeation of water vapour through a film



there will be a rate of transfer if the humidity is not the same inside and outside the package.

At constant temperature, $\%RH_1$ and $\%RH_2$, a steady state will be reached with a net rate of transfer, called the transmission rate. For the majority of experiments in this configuration the measurement is performed by sealing a container containing a desiccant ($\%RH_2 \sim 0$) and then placing the container in a humidity controlled enclosure. A high humidity (e.g. $\%RH_1 = 80\%RH$) would be used and the rate of transfer can then be determined by periodic weighing of the container which is commonly expressed in terms of a moisture vapour transmission rate (MVTR) calculated from:

$$MVTR = \frac{\text{weight change } (\mu\text{g}) \times \text{thickness (cm)}}{\text{Area (cm}^2\text{)} \times \text{time (hours)}} \quad (1)$$

The MVTR is not a fundamental property and will vary according to the operating conditions previously discussed.

The IGAsorp moisture sorption analyser can measure MVTR *in situ* by continuous weighing of a special container illustrated above, Fig. 2. The climate controls of the instrument are used to set the temperature and the external humidity ($\%RH_2$) of a special film holder. The holder houses a circular section of the film under test (area $\sim 120\text{mm}^2$) compressed between two aluminium flanges. The base flange is a 'well' for a saturated salt solution which sets the humidity, $\%RH_1$. The upper flange is initially sealed with a thin aluminium foil in order that the seal integrity can be assessed independently in the different



Figure 2: Permeation Cell with calibration salt solutions

gradient is therefore from the centre plane to the surface over the thickness $l/2$.

- ii) The concentration gradient is not constant but varies from a maximum when humidity is changed to zero at equilibrium.

The simplest treatment of transport is based on Fick's Law (i.e., by direct analogy with heat conduction) where, by definition, in steady state, the rate of transfer, F , is given as:

$$F = -D\partial C/\partial x \quad (2)$$

Which defines the fundamental rate constant, D , (the macroscopic or chemical diffusion coefficient) for a

operating conditions required. The actual experimental data is then recorded after the foil is punctured.

Continuous *in situ* weighing provides a direct recording of the approach to steady state followed by the linear trend due to water vapour transmission without operator intervention. The linearity of the trend both confirms the measurement is in steady state and also reflects the quality of climate control offered by the IGAsorp. MVTR can be determined from weight changes as small as $10\mu\text{g}$ and moreover the measurement can be readily repeated at different operating conditions. An example of data from such a measurement is displayed over in Fig. 3.

Simultaneous sorption-diffusivity determination

By changing the climate around the film, the entire sample is exposed to water vapour at the same humidity and transport properties are calculated from the change in uptake with time following a change in humidity. This experiment does not yield a steady state rate and transport differs in two basic ways as illustrated in Fig. 4:

- i) All surfaces are exposed and the concentration

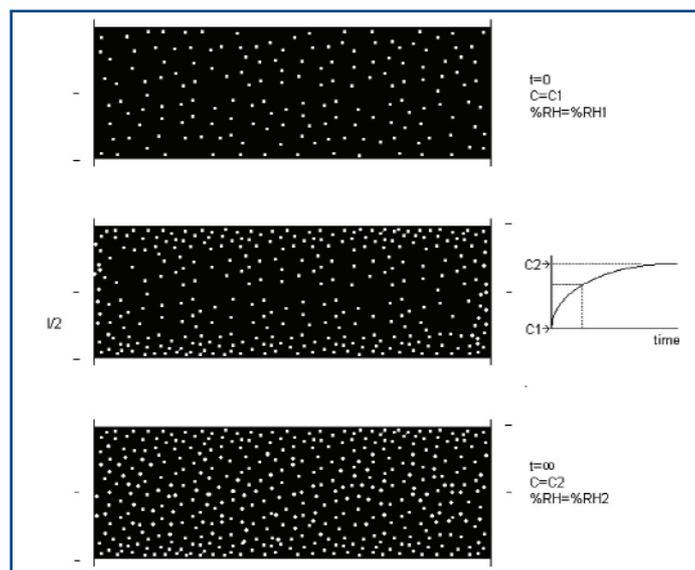


Figure 4: Distribution of water molecules during a sorption study (i) at equilibrium $t = 0$, (ii) during the uptake phase resulting from a step in RH $0 < t < \infty$ and (iii) at the new equilibrium concentration $t = \infty$.

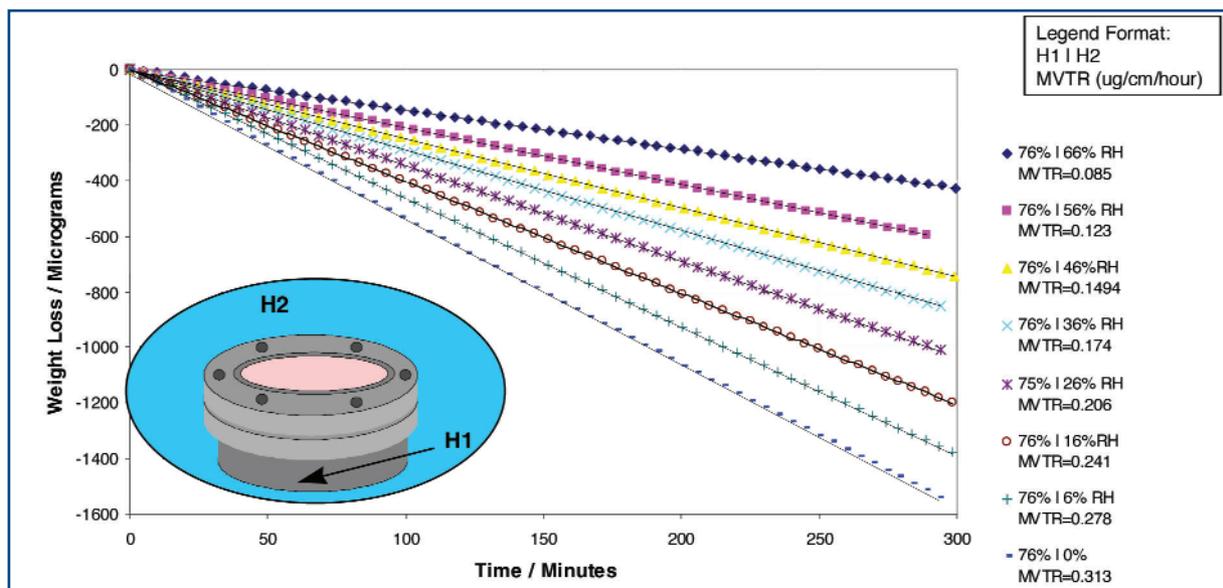


Figure 3: Results of a MVTR study at 35°C of a film using the permeation container.

concentration gradient $\partial C/\partial x$. This definition has a more fundamental form since the behaviour is expressed solely in terms of two physical properties, diffusivity and concentration. Measurement of the transmission or permeation rate alone therefore does not discriminate between these two contributions.

Direct determination of isothermal uptake can simultaneously determine both quantities as illustrated below. The concentration is measured from the equilibrium uptake and the sorption-time curve is a function of the diffusivity. The mathematical models of this behaviour depend on the geometry and transport process(es) involved. The simplest case is for Fickian diffusion in a thin film where diffusivity is independent of concentration. In this case the uptake as a function of time, $m(t)$, is given by:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp[-D(2n+1)^2\pi^2/l^2 t] \quad (3)$$

where M_∞ is the asymptotic uptake, D is the chemical diffusion coefficient and l is the thickness of the specimen.

Experimentally determined sorption-time curves do not always exhibit Fickian characteristics and this can be assessed by plotting fractional uptake versus $t^{1/2}$ as illustrated in Fig. 5. The linearity of the initial uptake is a guide to the classification.

The IGAsorp moisture sorption analyser used for the preceding method also provides the means to directly determine equilibrium concentration and sorption-time curves. In these experiments the film of known dimensions is directly suspended from the IGAsorp balance and one or more isotherms are measured at a series of fixed humidity set-points.

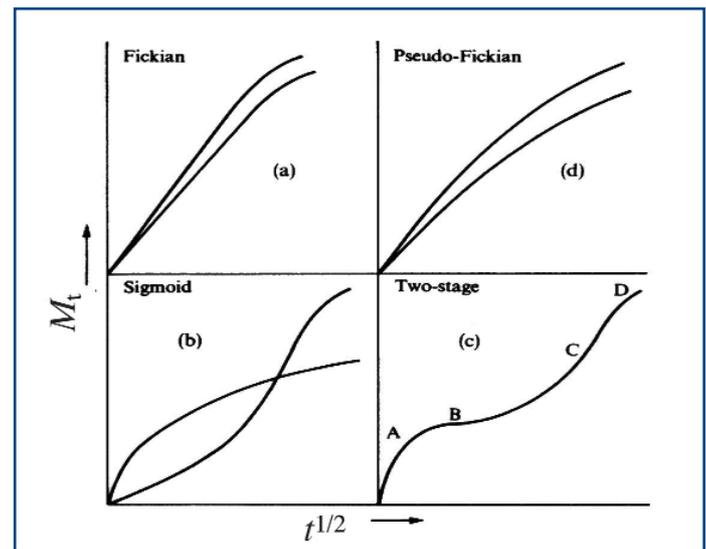


Figure 5: The classification of sorption time curves

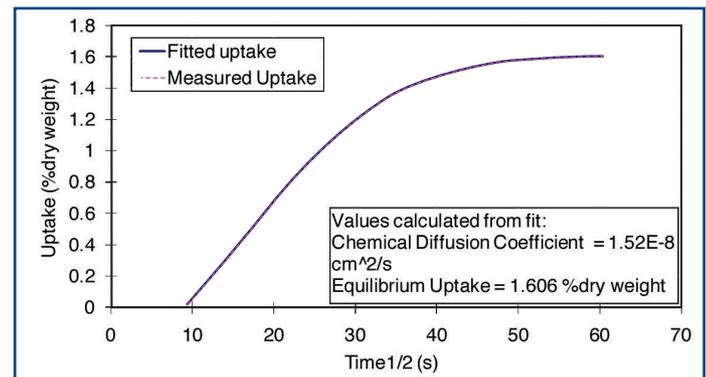


Figure 6: Sorption time curve for a polymer film measured at 25°C and fitted for a step in RH between 0 and 85%RH.

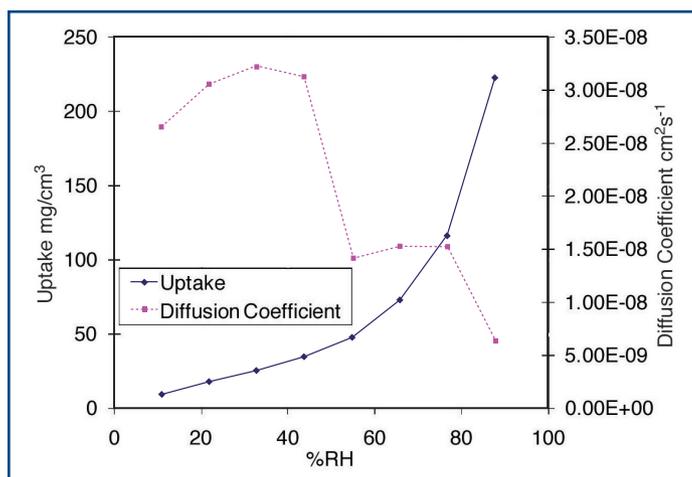
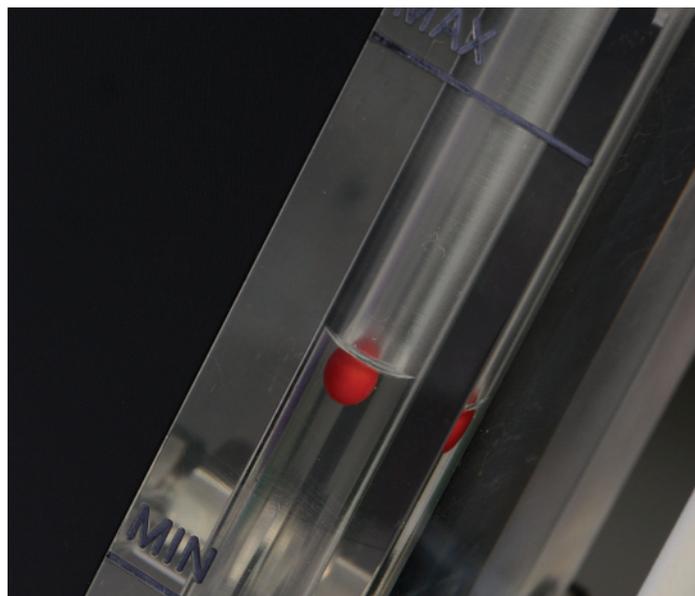


Figure 7: Sorption isotherm and diffusion coefficients as a function of relative humidity for a polymer film.



coefficient will be at best an average value over the measured range. The IGA-sorp allows the concentration-dependence to be studied. In addition, systems with non-Fickian behaviour cannot be simply modelled and in this instance and the diffusion coefficient is replaced by an equilibration time calculated by the IGA-sorp. However, in all cases the trends of behaviour are important information when comparing materials given that extremes of variation of the diffusivity as a function of concentration can give rise to anomalous transmission rates.

Summary

The *in situ* measurement and characterisation of water vapour transport has been reviewed in terms of two experimental methods offered by the same IGA-sorp instrument. Both methods provide the means to assess physical properties as a function of climatic conditions.

Transmission rate

Advantages: Suitable for heterogeneous materials. Direct measurement without dependence on theoretical model

Disadvantages: Seal integrity must be separately assessed. Suitable for thin films only, to avoid transport at the edges

Sorption | Sorption-Time

Advantages: Uptake and diffusivity behaviour can be separately assessed. No experimental errors due to seal integrity. Suitable for thick films/slabs (three-dimensional modelling)

Disadvantages: Suitable only for homogeneous materials. Rarely predicts absolute MVTR (most materials are not 'ideal')



This method is identical to that used for characterisation of water-solid interactions with the IGA-sorp and differs only in that uptake is conventionally expressed in terms of mass or water per unit volume of solid (e.g. mg/cm³) and that additional kinetic analysis can be used after the measurement. An example is shown in Fig. 6 where uptake-time is plotted versus time^{1/2} and directly compared to the Fickian model (Eqn. 3) by curve fitting to determine the diffusion coefficient.

This analysis is repeated for the various sorption-time curves and the final results are then plotted as an overlay of two trends, the equilibrium concentration and the calculated diffusion coefficient as a function of relative humidity (Fig. 7).

The experimental determination of diffusivity by this method will rarely be used to predict MVTR since real-world materials are not ideal Fickian systems. Concentration-dependence of diffusivity is common which means that a single calculated

