

New Methods for Measuring Water Desorption and Vapour Permeation Rates in Membranes

L. I. Ciortea, D. O'Driscoll, E. P. Berg, P. Xiao, F. C. Pascut and R. E. Imhof

School of Engineering, South Bank University, 103 Borough Road, London SE1 0AA, UK

Abstract

We report new methods for measuring water desorption and vapour permeation rates in membranes. They make use of a new instrument, the AquaFlux, for measuring water vapour flux density from arbitrary surfaces. In the present study, the AquaFlux measurement head was combined with purpose-designed test cells for characterising membranes. An important feature of the instrument for such measurements is the precise control of the microclimate to which the samples are exposed, irrespective of ambient conditions. Results from cotton and polyester textiles are used to illustrate the methods.

Introduction

The AquaFlux is a newly developed instrument for the non-invasive measurement of water vapour flux density from arbitrary surfaces [1,2]. It uses a cylindrical measurement chamber of 8mm diameter and 12mm length, one end of which is in contact with the surface of interest. Water vapour from this surface diffuses towards the opposite end of the measurement chamber, where it is removed by freezing onto an electronically cooled condensing surface. To a first approximation, a steady vapour flux gives rise to a linear distribution of vapour density along the length of the measurement cylinder. According to Fick's first law of diffusion, the flux density can be determined from the gradient of vapour density. In the AquaFlux, this gradient is measured by means of humidity and temperature sensors.

The aim of this work was to assess the potential of the AquaFlux for characterising membranes. The instrument was developed in the form of a hand-held probe, equipped with a measurement head that can be placed onto an arbitrary surface, human skin in particular. However, with some additional apparatus, it has proved possible to characterise water desorption and water vapour permeation dynamics in membranes. Water desorption rates can be studied by enclosing small samples, hydrated under standard conditions, in the base of the AquaFlux measurement head, and recording time-dependent flux density curves as the water evaporates into the controlled microclimate of the

AquaFlux measurement head. Water vapour permeation rates can be studied in a similar way, by clamping the membrane of interest between the top opening of a reservoir containing a hydrating solution and the measurement orifice of the AquaFlux measurement head.

Theory

The AquaFlux measurement chamber has the form of a cylinder, whose interior space is assumed small enough for convection and other forms of mass transport to be damped out by boundary losses, leaving diffusion as the only transport mechanism. Its geometry, illustrated schematically in Figure 1, is open at one end and closed at the opposite end. The open end acts as a measurement orifice, which can be placed in contact with a test surface in order to measure the water vapour flux emanating from it. The closed end is a metal surface, acting as a condenser whose temperature is maintained below the freezing point of water in order to remove water vapour from the air in its immediate vicinity. The geometry is described by a cylindrical co-ordinate system with the z -axis coincident with the axis of the measurement chamber. The measurement orifice and test surface are at the origin ($z=0$), and the condensing surface is at $z = L_C$. A combined sensor for relative humidity (RH) and temperature, referred to as an RHT sensor, is located at $z = L_S$, typically half way between the test and condensing surfaces.

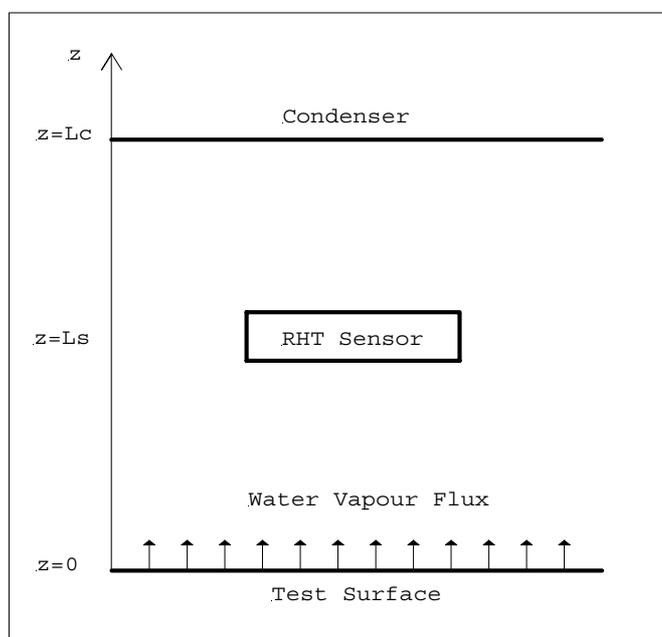


Figure 1: Schematic cross-section through the AquaFlux measurement chamber.

During a measurement, water vapour from the test surface enters the air in the measurement chamber and diffuses towards the condenser, where it is deposited as ice. In the absence of natural convection and other forms of mass flow, molecular diffusion remains as the only transport mechanism, described by the one-dimensional form of Fick's first law

$$J = -D_{VA} \frac{\partial \rho_V}{\partial z} \quad (1)$$

In Eq.(1), J ($\text{kgm}^{-2}\text{s}^{-1}$) is the flux density, D_{VA} (m^2s^{-1}) is the mass diffusion coefficient for water vapour in air and ρ_V (kg/m^3) is the water vapour density. If the test surface emits a constant flux density, then a steady-state water vapour distribution is eventually established within the measurement chamber, where all of the water vapour entering the measurement orifice at $z = 0$ is removed by the condenser at $z = L_C$. This steady state solution of Eq.(1) leads to a linear distribution of water vapour density with position, given by

$$\rho_V(z) = \rho_{VC} + \frac{J \cdot (L_C - z)}{D_{VA}} \quad (2)$$

where ρ_{VC} is the water vapour density at the condenser.

The temperature distribution within the measurement chamber can be approximately modelled using the one-dimensional form of Fourier's law of thermal conduction

$$Q = -k_A \cdot \frac{\partial \theta}{\partial z} \quad (3)$$

where Q is the heat flux density and k_A is the thermal conductivity of air. This model assumes that heat exchange with the walls of the measurement chamber can be neglected compared with heat exchange between the test surface and the condenser. The temperatures of the test surface and condenser are assumed to be unaffected by this heat flux. Since Q is constant once thermal equilibrium has been reached, Eq.(3) can be solved subject to the boundary conditions ($\theta(z=0) = \theta_0$) at the test surface and $\theta(z=L_C) = \theta_C$ at the condenser. The linear temperature distribution along the axis of the measurement chamber is then give by

$$\theta(z) = \theta_0 + [\theta_c - \theta_0] \cdot \frac{z}{L_c} \quad (4)$$

Eqs.(2) and (4) define the microclimate within the measurement chamber, which depends on external conditions through J and θ_0 only. The vapour density distribution of Eq.(2) can usefully be converted to a directly measurable relative humidity distribution using

$$\chi(z) = \frac{\rho_{VE}(\theta_c) + \frac{J \cdot (L_c - z)}{D_{VA}}}{\rho_{VE}(\theta_0)} \quad (5)$$

where $\chi(z)$ is the fractional relative humidity and ρ_{VE} is the equilibrium (or saturation) vapour density, which can be computed from a parameterisation of the saturation vapour pressure curve (eg [3]) and the ideal gas law.

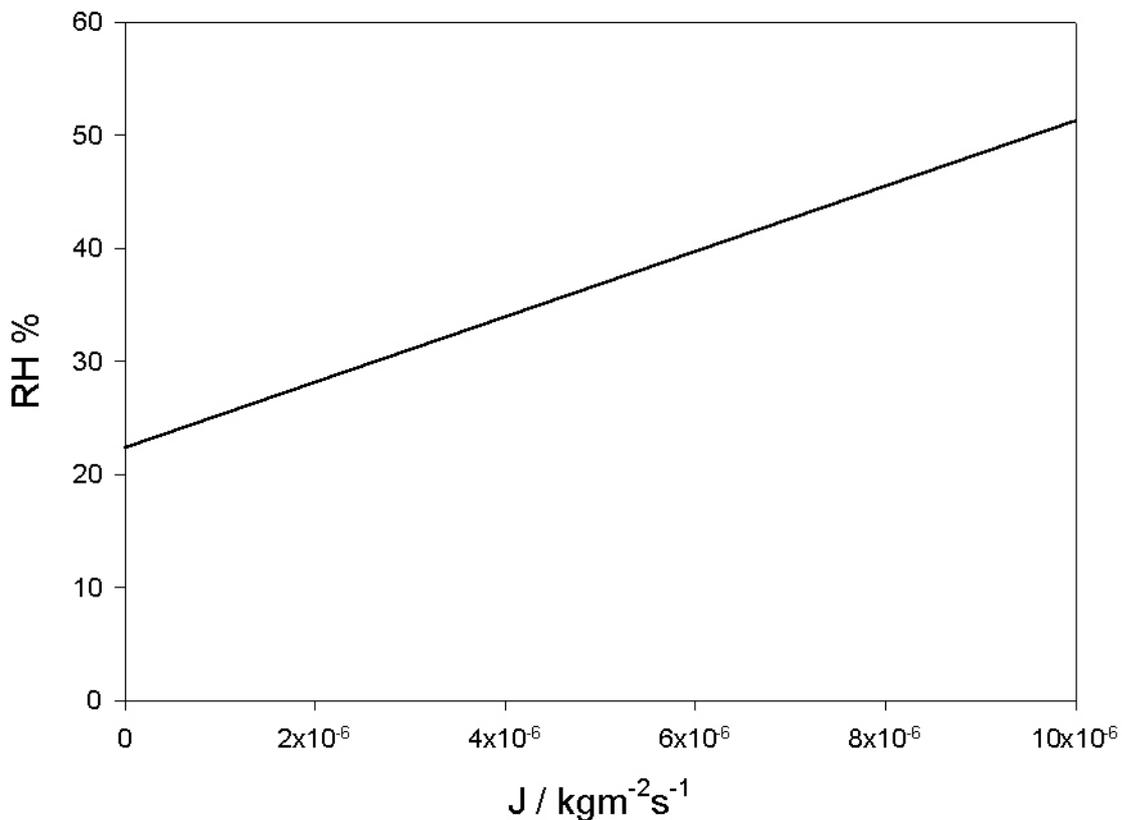


Figure 2: Microclimate RH immediately above a test surface at a sample temperature of 21^oC.

Figure 2 shows the percentage RH immediately above the test surface, ie $100 \cdot \chi(z=0)$, for typical conditions, $D_{VA} = 2.42 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$, $L_C = 12 \text{ mm}$, $\theta_C = -3^\circ \text{ C}$, and a test surface at room temperature, $\theta_0 = 21^\circ \text{ C}$. This curve defines the boundary conditions for evaporation from the test surface. Note that the theory predicts a linear rise, with a consequent possibility of RH values exceeding 100% at high flux density values. This is clearly not attainable physically, and the approach to saturation is more likely to be asymptotic in nature, with the instrument responding non-linearly at high flux density.

Results and Discussion

Experiments to study water desorption from a membrane surface were conducted using the apparatus shown in Figure 3. The test membrane was placed into the chamber cap and pre-treated at room temperature by wetting it with $2 \mu\text{l}$ of distilled water, dispensed by means of a micro-syringe, before mounting the cap onto the sensing end of the measurement chamber.

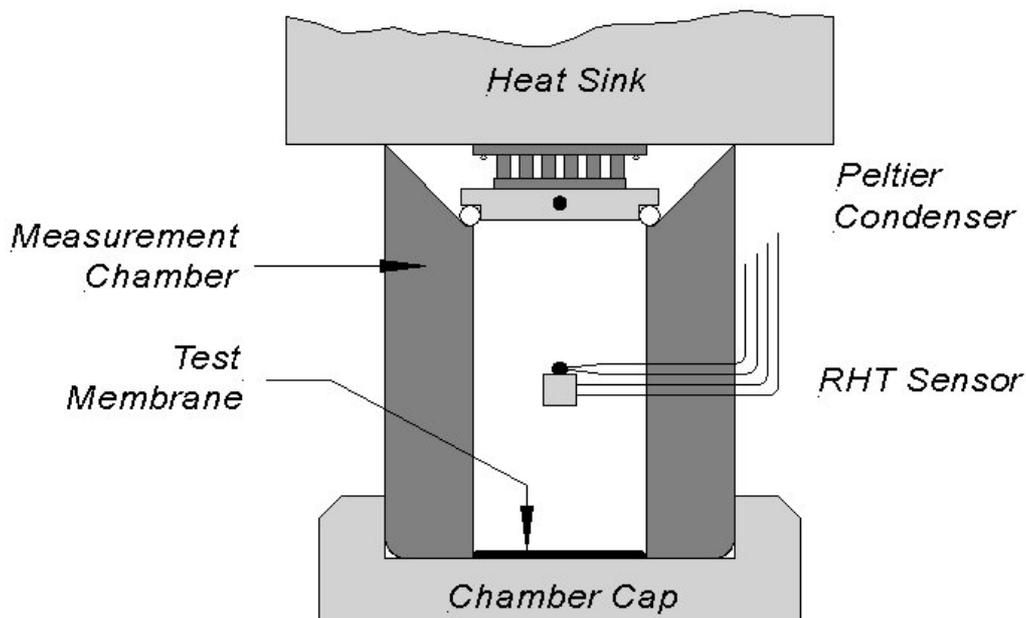


Figure 3: Apparatus for studying water desorption from a membrane.

Water vapour flux densities were measured at $\sim 1\text{s}$ intervals, until all the free water from the test membrane had been deposited as ice onto the condenser. Typical flux density curves for cotton and polyester textiles are shown in Figure 4.

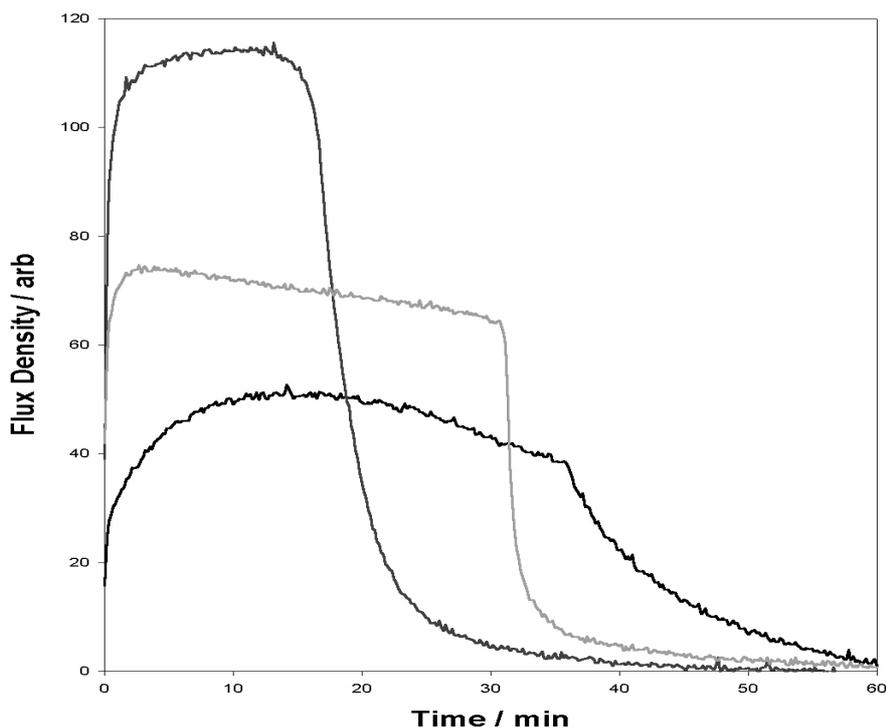


Figure 4: Water vapour flux density curves for, from top to bottom, polyester textile, water alone, and cotton textile.

These curves can be characterised by three properties, namely (i) the peak flux density, (ii) the rate of rise and decay of flux density, and (iii) the enclosed area. The membranes can be characterised by three properties, namely (a) the surface area, (b) the permeability and (c) the water affinity. The relationships between these six quantities are complex, but some general statements can be made in the above case. The polyester and water samples have similar rise and decay times, indicating that polyester has a low affinity for water. The peak flux density is larger for polyester than for water, indicating that polyester has a larger effective surface area than water alone. The negative slope on the peak flux plateau of the water curve indicates that the effective surface area of the droplet is decreasing progressively with time. The cotton flux density curve differs markedly from the other two, with much longer rise and decay times, indicating that cotton has a larger affinity for water.

The parameters of such experiments can be varied to study different aspects of the desorption process. Pre-conditioning can be performed in atmospheres of known RH, in order to measure water uptake under equilibrium conditions. The temperature can be varied by as much as $\sim 20^{\circ}\text{C}$ above and below room temperature in order to measure sorption isotherms.

Experiments to study water transpiration through membranes were conducted using the apparatus shown in Figure 5. The test membrane was clamped onto the measurement face of the instrument by means of a reservoir containing a hydrating solution.

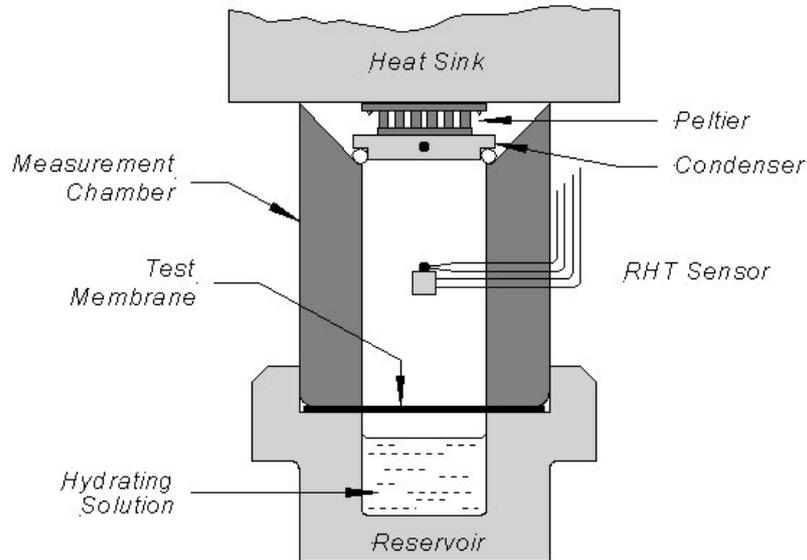


Figure 5: Apparatus for studying water vapour transpiration through a membrane.

Water vapour flux densities were measured at ~1s intervals, until a steady flux density had been reached. Typical flux density curves for cotton and polyester textiles are shown in Figure 6.

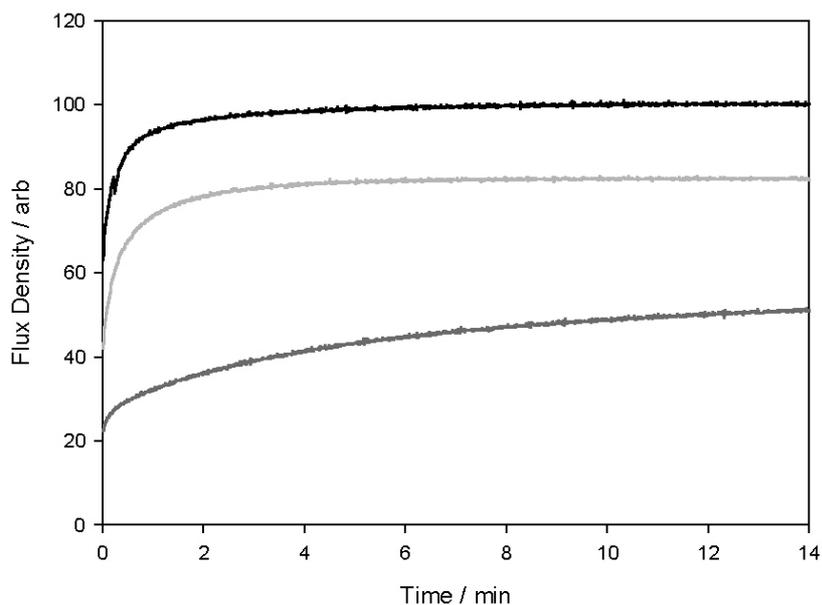


Figure 6: Water vapour transpiration curves for, from top to bottom, no membrane, polyester textile, and cotton textile. The hydrating solution used NaCl to produce a relative humidity below the membranes of 75%.

These curves can be characterised by two properties, namely (i) the rate of rise of flux density and (ii) the steady peak flux density. The membranes can be characterised by two properties, namely (a) the permeability and (b) the water affinity. Clearly, the steady peak flux density gives a direct measure of permeability, whereas the rate of rise of flux density gives a measure of water affinity. The polyester and water samples have similar rise times, indicating that polyester has a low affinity for water, whereas the much longer rise time of the cotton flux density curve indicates a larger affinity for water. Such experiments can be performed with different hydrating solutions in order to study the dependence of transpiration on humidity.

Conclusions

The experiments illustrate the ability of the AquaFlux to characterise water desorption and transpiration properties of membranes. Work is now in progress to develop a theoretical framework within which such measurements can be evaluated quantitatively.

Acknowledgement

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References

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