SHORT COMMUNICATION

A NOTE ON THE DIFFUSION OF WATER ACROSS OIL AND WAX LAYERS AND INSECT CUTICLES

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The terms diffusion and permeability are frequently confused and misused. For example, Barrer (1941) in the preface of his book defines permeability constant in contradictory ways in successive sentences and both are incorrect. In the case of diffusion of gases and water, confusing systems of units have been employed. Taylor *et al.* (1936) define a coefficient as g/hr/cm/mmHg and Barrer (1941) uses cc(vapour at N.T.P.)/sec/cm^2/cmHg/mm thick. The use of more than one solidus leads to ambiguity and may, for example, disguise that the thickness term is in the numerator and Machin (1980) does, indeed, manage to invert this term. Other errors can also easily occur. Thus Beament (1958) writes mmHg when cmHg is intended and this is repeated by Machin (1980). Also Machin & Lampert (1987) use both the coefficients $mg\,h^{-1}\,cm^{-2}\,torr^{-1}$ and $cm\,s^{-1}$ without relating them.

It seems, therefore, that it would be useful to derive, rigorously, simple relationships between the parameters involved in the diffusion of water across oil and wax layers and to relate these to the diffusion of water across insect cuticles.

The diffusion of water across a wax layer can be described in terms of the equation:

$$J = -mc\frac{d\mu}{dx},\tag{1}$$

where J is net flux/area, m is mobility, c is concentration and $d\mu/dx$, the gradient of chemical potential, is the driving force. This equation is a general form of the Nernst–Planck equation (Schultz, 1980).

The chemical potential of water (μ) can be expanded in terms of water vapour pressure (p) (Denbigh, 1961):

$$J = -RTm\frac{c}{p}\frac{dp}{dx}.\tag{2}$$

The diffusion coefficient (D) is defined as RTm, where R is the gas constant and T

is the absolute temperature. For a dilute solution, such as water in wax, the ratio c/p is constant and is termed a solubility coefficient (α). Then:

$$J = -D\alpha\frac{dp}{dx} . \tag{3}$$

Integrating across the wax layer:

$$J = \frac{D\alpha}{\delta}\Delta p , \tag{4}$$

where δ is the thickness of the layer. If water is in equilibrium across the interfaces on either side of the wax layer, Δp is the difference in water vapour pressure between the media on either side of the wax layer.

A dimensionless partition coefficient (K_p) can be used in place of the solubility coefficient (α). A partition coefficient is defined as the ratio of the equilibrium concentrations in two phases, in this case water in wax/water in an aqueous phase. Then:

$$K_p = \alpha p^* V_w , \tag{5}$$

where p^* is the vapour pressure of pure water and V_w is the molar volume of liquid water. This partition coefficient is the concentration of water in wax (v/v) in equilibrium with pure water. Substituting in equation 4:

$$J = \left[\frac{DK_p}{\delta}\right]\frac{1}{V_w}\frac{\Delta p}{p^*} , \tag{6}$$

where $\Delta p/p^*$ is equivalent to ΔRH, the difference in relative humidity between the media on either side of the wax layer. The bracketed term in equation 6 defines the permeability coefficient (P_d) of the wax layer to water:

$$P_d = \frac{DK_p}{\delta} . \tag{7}$$

The diffusion coefficient (D) and the partition coefficient (K_p) are properties of the material comprising the layer, whereas the permeability coefficient (P_d) is also dependent on the thickness of the layer.

In the present situation, it is more convenient to define water flux/area in mass terms (J') rather than mole terms. Then:

$$J' = \left[\frac{DK_p}{\delta}\right]\rho\frac{\Delta p}{p^*} , \tag{8}$$

where ρ is the density of water and $K_p\rho$ is the solubility of water in wax (w/v).

Now, in the situation where there is essentially pure water on one side of the wax layer and dry air on the other, $\Delta p/p^* = 1$ and equation 8 is much simplified and is identical to the equation used by Schatzberg (1965). If J' is expressed as $kg\,s^{-1}\,m^{-2}$, δ as m and ρ as $kg\,m^{-3}$, then D is $m^2\,s^{-1}$ and P_d is $m\,s^{-1}$. These are the units in which these coefficients should always be expressed.

These coefficients could also be investigated using isotope-labelled water, most

conveniently radioactive THO. Exchange of isotope-labelled water in terrestrial arthropods was first studied by Govaerts & Leclercq (1946). Treating isotope-labelled water as a solute dissolved in water, a diffusion equation (Fick equation) is readily derived from equation 1:

$$J^* = P_d \Delta c^* , \qquad (9)$$

where J^* is the flux/area of the isotope (counts $min^{-1} s^{-1} m^{-2}$) and c^* is the concentration of isotope (counts $min^{-1} m^{-3}$) in the solutions in contact with the wax layer. Wharton & Devine (1968) expressed the flux of water between a mite and the surrounding air in terms of rate constants. The permeability coefficient is related to the efflux rate constant (k_e):

$$P_d = k_e \frac{V}{A} , \qquad (10)$$

where V/A is the ratio (volume of water in animal)/(surface area across which diffusion is occurring). Although the diffusion coefficients of various isotopic forms of water differ (Kohn, 1965), House (1974) concludes that this is unlikely to be a serious source of error in determinations of P_d for biological membranes. The presence of unstirred layers in the media can give rise to problems, particularly in the case of diffusion of isotope-labelled water (House, 1974). However, in the situation where water permeability is very low, this effect will be negligible. An advantage of using isotope-labelled water is that, as unidirectional flux is measured, it is possible to determine permeability even in saturated air, where there would be no net loss of water.

Although a permeability coefficient can be readily determined, a diffusion coefficient requires further information. If the solubility of water is unknown or ignored, the products $D\alpha$ or DK_p are found. In Table 1, a series of quantities and units that have been employed are defined and conversion factors to convert them to preferred quantities and units are given.

Using the data of Taylor *et al.* (1936) and making the appropriate conversion, the value of DK_p for hydrocarbon wax is $0.32 \times 10^{-15} m^2 s^{-1}$ at $21 °C$, a very low absolute value that must partially reflect a low solubility of water in wax (solubility not given). Values for the liquid hydrocarbon hexadecane are given by Schatzberg (1965), who also measured the solubility of water in liquid hydrocarbons (Schatzberg, 1963). His value for the diffusion coefficient is $4.16 \times 10^{-9} m^2 s^{-1}$ at $25 °C$ and for the solubility corresponds to a partition coefficient of 41.7×10^{-6} (v/v). This diffusion coefficient is rather greater than that for water in water (Kohn, 1965). The product DK_p is $173 \times 10^{-15} m^2 s^{-1}$. This is considerably greater than the value for hydrocarbon wax. However, the molecular interactions that result in a solid state would undoubtedly reduce both the diffusion coefficient and solubility of water.

The data on hydrocarbons can be compared to data on insect cuticles. Only the epicuticular layers seem to be significant in waterproofing. In the cockroach, Beament (1958) has interpreted the waterproofing layers as a thick unorganized

Table 1. *Conversion of quantities and units for diffusion and permeability*

Source and name given to quantity	Quantity and units	Conversion factor and units	Numerical value of conversion factor	Preferred quantity and units
Taylor *et al.* (1936) 'Diffusion constant'	$D\alpha M$ g h^{-1} cm^{-1} (mmHg)$^{-1}$	p^*/ρ g^{-1} h s^{-1} cm m^2 (mmHg)	519×10^{-9} (21°C)	DK_p m^2 s^{-1}
Barrer (1941) 'Permeability constant'	$D\alpha V_g$ cm^3 (vapour at NTP) s^{-1} cm^{-2} (cmHg)$^{-1}$ mm	$p^*M/\rho V_g$ m^2 cm^{-1} mm^{-1} (cmHg)	14.1×10^{-9} (20°C) 19.2×10^{-9} (25°C)	DK_p m^2 s^{-1}
Machin & Lampert (1987) 'Permeability'	$P_d\rho/p^*$ mg h^{-1} cm^{-2} Torr^{-1}	p^*/ρ mg^{-1} h s^{-1} cm^2 m Torr	48.8×10^{-9} (20°C) 66.2×10^{-9} (25°C)	P_d m s^{-1}

Quantities: D, diffusion coefficient; P_d, permeability coefficient; α, solubility coefficient; K_p, partition coefficient; M, molar mass of water; p^*, vapour pressure of water; ρ, density of water; V_g, molar volume of water vapour at NTP.

The numerical value of the conversion factor is the number by which values expressed in the units given in the quantity and units column must be multiplied to convert them into a value in the units given in the preferred quantity and units column.

fluid grease layer ($\delta = 0.25\,\mu m$) and a much thinner solid packed layer ($\delta = 100\,\text{Å} = 10\,\text{nm}$). The overall permeability calculated from the data of Beament (1958) using equation 8 is $1.3 \times 10^{-9}\,\text{m s}^{-1}$. Taking the thickness as $0.25\,\mu m$, this corresponds to a value of DK_p of $0.33 \times 10^{-15}\,\text{m}^2\,\text{s}^{-1}$, the same as for solid hydrocarbon wax. It seems unlikely that a liquid grease could have a value as low as this. A much higher value, similar to a liquid hydrocarbon, would be expected. Beament (1958) also measured the rate of water loss through a thin solid packed layer derived from the grease and the value of DK_p that can be estimated from this is $0.070 \times 10^{-15}\,\text{m}^2\,\text{s}^{-1}$, a value considerably less than that of solid hydrocarbon wax. However, even with such a layer in series with the grease layer, an unreasonably low value of DK_p in the grease layer has to be postulated. The problem is, in fact, greater than this as recent estimates of water permeability in the cockroach are much less. The permeability calculated from the data of Noble-Nesbitt & Al-Shukur (1987) is as low as $0.39 \times 10^{-9}\,\text{m s}^{-1}$ and from the data of Machin & Lampert (1987) is only $0.10 \times 10^{-9}\,\text{m s}^{-1}$. Permeabilities as low as these cannot be explained in terms of our current knowledge of the system.

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