Wood Sci. Technol. 16: 123–138 (1982)

Wood Science and Technology

A Model for Bound-Water Transport in Wood

C. Skaar

Department of Forest Products, Virginia Polytechnic Institute and State University, Blacksburg, VA, USA

M. Babiak

University College of Forestry and Wood Technology, Zwolen, Czechoslovakia

Summary. A model for the isothermal transport of bound water through the cell wall of wood is developed, based on the assumption that the driving force for moisture movement is the gradient of "spreading" pressure ϕ, as first proposed by Babbitt (1950). This pressure is a surface phenomenon, derivable from the surface sorption theory of Dent (1977), a modification of the BET sorption theory. The force resisting moisture transport is assumed to be inversely proportional to moisture content and directly proportional to the equivalent viscosity of the sorbed water, calculated to be orders of magnitude larger than that of free water. The coefficients normally used to describe isothermal moisture transport in wood are derived from the model, and their predicted behavior as functions of the relative vapor pressure h of the cell wall are described graphically. An attempt is made to calculate a quantitative magnitude for the diffusion coefficient D, based on an assumed relationship between viscosity and the activation energy for water diffusion.

Introduction

The mechanism of moisture movement through the cell wall of wood, particularly the nature of the driving force, has been the subject of some controversy recently in wood science literature. In this paper, a model for bound-water movement through the cell wall of wood is presented. It is basically a modification of Babbitt's (1950) analysis of the mechanism for the diffusion of absorbed molecules in solids, and is limited to the isothermal case.

Before discussing the model, some of the forms for expressing the driving force for moisture transport will be given, together with the relationships among them. The driving force in each case is taken to be the space gradient of the assumed potential, such as moisture content, moisture concentration, vapor pressure, etc., as well as the spreading pressure as defined by Babbitt (1950). These equations are summarized in Table 1, together with their relationship to Fick's first law (additional equations included in Table 1 are discussed later). In Fick's first law, the flux J of moisture is

0043-7719/82/0016/0123/$ 3.20

Table 1. Summary of some of the moisture transport coefficients used for wood, their assumed potentials, and their relationships to the diffusion coefficient D

Assumed potential	Symbol cgs units	Transport coefficient cgs units	Relation to diffusion coefficient D
Moisture concentration	c g/cm^3	$D = -J/(\partial c/\partial x)$ cm^2/s	$D = D$
Fractional moisture content	m g/g	$K_m = -J/(\partial m/\partial x)$ $g/cm\text{-}s$	$K_m = D(\partial c/\partial m)$
Percent moisture content	M $g/100\,g$	$K_M = -J/(\partial M/\partial x)$ $g/100\text{-}cm\text{-}s$	$K_M = D(\partial c/\partial M)$
Vapor pressure	p $dyne/cm^2$	$K_p = -J/(\partial p/\partial x)$ $g\text{-}cm/dyne\text{-}s$	$K_p = D(\partial c/\partial p)$
Relative vapor pressure	h ratio	$K_h = -J/(\partial h/\partial x)$ $g/cm\text{-}s$	$K_h = D(\partial c/\partial h)$
Osmotic pressure	Π $dyne/cm^2$	$K_\Pi = -J/(\partial \Pi/\partial x)$ $g\text{-}cm/dyne\text{-}s$	$K_\Pi = D(\partial c/\partial \Pi)$
Spreading pressure	ϕ $dyne/cm$	$K_\phi = -J/(\partial \phi/\partial x)$ $g/dyne\text{-}s$	$K_\phi = D(\partial c/\partial \phi)$

assumed to be directly proportional to the product of the gradient of moisture concentration c and the material parameter D, defined as the diffusion coefficient. For simplicity, this discussion is confined to movement in one dimension, the x-direction.

It should be noted in Table 1 that the moisture transport coefficients K can each be related to the diffusion coefficient D if the rate of change of the assumed potential with respect to moisture concentration c is known. They can also be related to each other in an analogous manner. The coefficient D which is based on the gradient of concentration c is unique in that it appears in unmodified form in the second form of Fick's law. All other forms of K are modified, in analogy with the relationship between thermal conductivity and thermal diffusivity in heat transport. It is also of interest to note that D has the same dimensions as the thermal diffusion coefficient, i.e., area per unit time.

Moisture Transport Model

The model proposed here is based on that proposed by Babbitt (1950) in that the driving force for the transport of sorbed gases through solids is taken to be the space gradient of the spreading pressure ϕ, rather than of concentration c as is assumed when Fick's law is applied.

Babbitt (1950) applied his diffusion model to wood, using the Brunauer, Emmett, Teller (or BET) isotherm, first proposed by Brunauer et al. (1938), to explain multilayered adsorption of gases on surfaces. Babbitt predicted how the coefficient K_h should vary with relative vapor pressure h based on the assumptions used in his model.

In the present paper, the Babbitt model is extended to cover a refinement of the BET sorption theory, the Dent (1977) theory, which gives a better fit to moisture sorption data for wood. Furthermore, some of Babbitt's final equations have been simplified into alternate forms which are more convenient for making calculations in certain cases. Finally, Babbitt's model is interpreted more explicitly in terms of a simplified cell wall structure for wood.

Dent Moisture Sorption Theory

Before discussing the Babbitt moisture transport model, certain aspects of the Dent (1977) sorption model will be summarized. The Dent model is similar to the BET sorption model in that water in a polymer such as the wood cell wall is presumed to be sorbed in two forms. These are "primary" water molecules, sorbed directly on "primary" sorption sites in the cell wall and "secondary" water molecules sorbed on "secondary" sites. The primary sites are taken to be sites of high binding energy such as accessible hydroxyl groups in the case of wood. The secondary sites are of lower binding energy and may be thought of as sites superposed on primary sites or other secondary sites, as is shown schematically in Fig. 1.

The model described thus far is identical with the BET model which assumes that the thermodynamic properties of the secondary water are identical with those of ordinary liquid water. The Dent model differs from the BET model in that the secondary water is assumed to be thermodynamically different from liquid water. However, in common with the BET model, the Dent model assumes that the water in the various secondary layers, that is, the second, third, fourth, etc. layers, has identical properties. The Dent model, therefore, requires three fundamental constants to describe the sorption isotherm rather than only two as for the BET model. These constants are designated as m_0, the moisture content corresponding to complete monolayer coverage, b_0 related to the binding energy of the primary water, and b, related to the binding energy of secondary layers. The constants m_0 and b_0 are identical with the corresponding BET constants in which b is taken to be unity as in the BET model.

If the three Dent constants m_0, b_0 and b are known, the following equations can be used to calculate the total moisture content m, the primary water content m_1, and the secondary water content m_2, respectively, at any relative vapor pressure h.

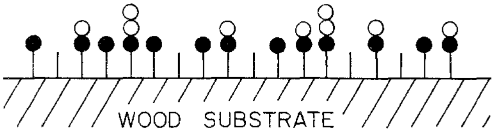

Fig. 1. Schematic diagram showing primary sorption sites (vertical lines) in the cell wall, some of which are unoccupied and others occupied by primary water molecules (dark circles) and sometimes by secondary sorbed molecules (open circles)

$$m = m_1 + m_2 = \frac{m_0\, b_0\, h}{(1 - bh)\,(1 + b_0 h - bh)} \tag{1a}$$

$$m_1 = m\,(1 - bh) = \frac{m_0\, b_0\, h}{(1 + b_0 h - bh)} \tag{1b}$$

$$m_2 = mbh = \frac{m_0\, b_0\, bh^2}{(1 - bh)\,(1 + b_0 h - bh)} \tag{1c}$$

Similar relationships can be written in terms of moisture concentration c, recalling that $c = \rho_w G m$, where ρ_w is the density of water and G is the specific gravity of the wood (or of the cell wall in the case of bound-water movement) based on dry weight and volume at moisture content m. If the swelling of the cell wall is neglected, i.e., G is assumed to be constant, as it is in this paper, c, c_0, c_1 and c_2 can be substituted for m, m_0, m_1 and m_2 in Eqs. (1, a, b, c).

The Dent model predicts a sorption isotherm of the form

$$h/m = A + Bh - Ch^2 \tag{2}$$

where the empirical constants A, B and C are related to the fundamental constants m_0, b_0 and b as follows:

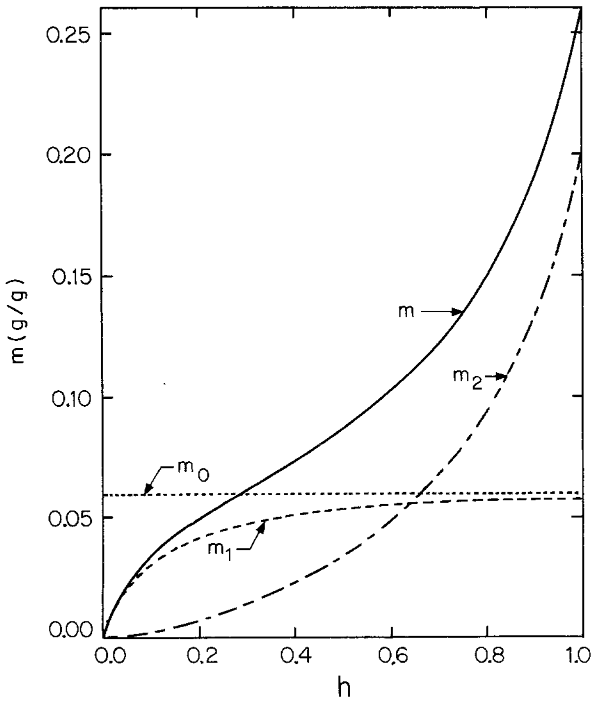

Fig. 2. Adsorption isotherm (25 °C) showing m, m_1, and m_2 as functions of h, and also the constant m_0, based on the Dent (1977) sorption model

$$A = 1/(b_0 m_0) \tag{3a}$$

$$B = A(b_0 - 2b) = (b_0 - 2b)/(b_0 m_0) \tag{3b}$$

$$C = Ab(b_0 - b) = b(b_0 - b)/(b_0 m_0) \tag{3c}$$

Figure 2 shows a typical sigmoid sorption isotherm for wood, m vs. h, together with curves of m_1 and m_2, as well as the value m_0.

In the model proposed by Babbitt, moisture migration is considered to occur on a surface rather than in bulk as is the case for diffusion in a liquid or in a gas. The sorbent, water in this case, is considered to form a film on internal surfaces of the sorbate or cell wall where it has condensed into one or more layers. The condensed water, designated here as bound water, migrates in the sorbed form as individual water molecules in the water film. This is in agreement with the viewpoint of surface sorption theories such as the BET and Dent theories, as discussed previously. Figure 3 is a schematic diagram of such a surface, showing the sorption sites distributed uniformly over the surface, with some of the sites occupied by water molecules.

Spreading Pressure

The spreading pressure ϕ is a surface analog of hydraulic pressure P or of osmotic pressure π. For the three-dimensional case, the hydraulic pressure P (or π), according to Babbitt (1951), is given by

$$\pi = P = -(\partial F/\partial v) = (kT/v) \ln h \tag{4}$$

where F is the free energy content per water molecule, v the molecular volume, k the Boltzmann constant, T the Kelvin temperature and h the relative vapor pressure. The analogous two-dimensional spreading pressure ϕ as defined by Babbitt (1950) is

$$\phi = -(\partial F/\partial a) \tag{5}$$

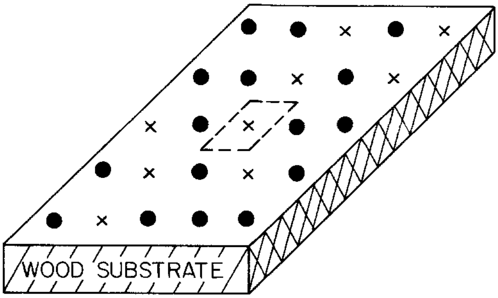

Fig. 3. Diagram showing sorption sites, both occupied (●) and unoccupied (x), on the internal wood surface. The area per sorption site a is shown as the area within the parallelogram in the center of the diagram

where ϕ has dimensions of energy per unit surface area if a is the surface area per sorption site or the area per water molecule when there is one molecule of water on each sorption site, that is, complete monolayer coverage (Fig. 3).

For a system described by the BET sorption model, Babbitt (1950) gives the spreading pressure ϕ in terms of the total number of localized sorption sites and the fraction θ of these which are occupied by at least one water molecule (monolayer coverage). This can be written, for the Dent as well as for the BET sorption model, as

$$\phi = (kT/a) \ln [1/(1 - \theta)] = (kT/a) \ln [1/(1 - (m_1/m_0))] \qquad (6)$$

since $\theta = m_1/m_0$. Equation (6) can also be written as,

$$\phi = (kT/a) \ln [m_0/(m_0 - m_1)] \qquad (7)$$

If moisture is expressed in terms of moisture concentration c (mass of water/volume of wood), Eq. (7) takes the form,

$$\phi = (kT/a) \ln [c_0/(c_0 - c_1)] \qquad (8)$$

The spreading pressure can be expressed in terms of relative vapor pressure h and the constants b_0 and b by substituting for m_1/m_0 in Eq. (6) its equivalent given by Eq. (1 b). Making this substitution and rearranging gives

$$\phi = (kT/a) \ln [(1 + b_0 h - bh)/(1 - bh)] \qquad (9)$$

This equation is identical with the spreading pressure equation as given by Dent (1977), except that it includes the term a. Thus, the spreading pressure as defined by Dent has dimensions of energy per sorption site whereas ϕ as used here has dimensions of energy per unit area of sorption surface, in agreement with Babbitt's convention.

Figure 4 shows how the spreading pressure ϕ, given by Eq. (9), varies with h for the case of $b_0 = 10.26$ and $b = 0.777$, using adsorption isotherm data for wood at 25 °C as given by Okoh and Skaar (1980). For convenience, the dimensionless ratio $\phi/(kT/a)$ is plotted rather than ϕ itself, since (kT/a) is constant. For comparison, a similar curve is shown based on the BET model, given by Eq. (9) with b taken as unity. The BET spreading pressure approaches infinity as h approaches unity but the Dent pressure approaches a finite value.

Driving Force

Babbitt (1950) assumed that the gradient $d\phi/dx$ of the spreading pressure was the driving force for the diffusion of bound water on the internal surfaces of the cell wall. He took as the fundamental dynamical equation of diffusion for unidirectional flow, the relationship

$$u = -(1/f)(\partial\phi/\partial x) \qquad (10)$$

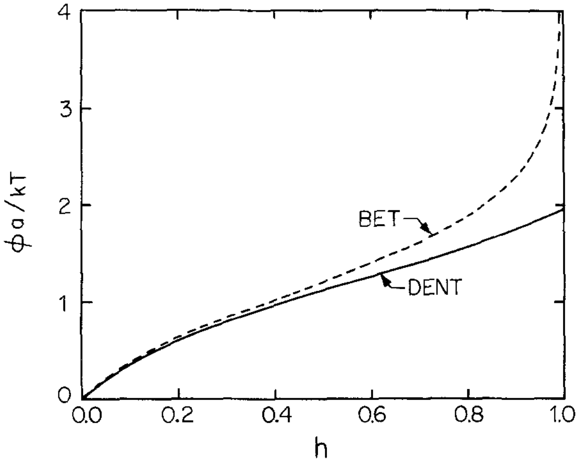

Fig. 4. Curves of the dimensionless ratio $\phi/(kT/a)$ against h, based on the BET and Dent sorption isotherms

where u is the component of molecular velocity in the x-direction and f is a coefficient of frictional resistance.

In the discussion which follows, the driving force $d\phi/dx$ and its relationship to the potential gradients normally measured in wood will be considered first, followed by discussion of the resistance force f.

The gradient $\partial\phi/\partial x$ of spreading pressure, that is, the driving force for diffusion according to Babbitt (1950), can be obtained from Eqs. (7), (8), or (9). Using Eq. (7) it becomes,

$$\frac{\partial\phi}{\partial x}=\frac{kT}{a}\cdot\frac{1}{m_0-m_1}\cdot\frac{\partial m_1}{\partial m}\cdot\frac{\partial m}{\partial x} \tag{11}$$

Equation (11) can be shown (Babbitt, 1950) to be equivalent to

$$\frac{\partial\phi}{\partial x}=\frac{kT/a}{[(m-m_1)^2+4mm_0(b/b_0)]^{1/2}}\cdot\frac{\partial m}{\partial x} \tag{12}$$

which relates $\partial\phi/\partial x$ to $\partial m/\partial x$ as used in Fick's law. Similar equations can be obtained in terms of c or of M, by substituting the appropriate terms for m and m_0 in Eq. (12). The relationship between spreading pressure gradient and relative vapor pressure gradient can be obtained by taking the space derivative of Eq. (9) and rearranging to,

$$\frac{\partial\phi}{\partial x}=\frac{kT}{a}\cdot\frac{b_0}{(1-bh)(1+b_0h-bh)}\cdot\frac{\partial h}{\partial x} \tag{13}$$

Equation (13) can be modified to relate $\partial\phi/\partial x$ to the vapor pressure gradient $\partial\rho/\partial x$ under isothermal conditions. Thus

$$\frac{\partial\phi}{\partial x}=\frac{kT}{a}\cdot\frac{b_0p_0}{(p_0-bp)(p_0+b_0p-bp)}\cdot\frac{\partial p}{\partial x} \tag{14}$$

where p_0 is the vapor pressure of water at temperature T.

Other potential gradients such as $\partial\pi/\partial x$, the gradient of osmotic or swelling pressure π can be related to $\partial\phi/\partial x$. The pressure P in Eq. (4) is equivalent to π for the wood-water system. Taking the space derivative of π (= P) in Eq. (4) and combining it with Eq. (13) yields, after rearrangement,

$$\frac{\partial \phi}{\partial x} = \frac{v}{a} \cdot \frac{b_0 h}{(1 - bh)(1 + b_0 h - bh)} \cdot \frac{\partial \pi}{\partial x} \qquad (15a)$$

It may also be written in terms of m or c. For example,

$$\frac{\partial \phi}{\partial x} = \frac{v}{a} \cdot \frac{c}{c_0} \cdot \frac{\partial \pi}{\partial x} \qquad (15b)$$

The gradient of chemical potential $\partial\mu/\partial x$ is equal to $\partial\pi/\partial x$ multiplied by the molar volume V of water.

The relationship between the gradient $\partial\phi/\partial x$ of spreading pressure and any of the gradients such as $\partial h/\partial x$, $\partial m/\partial x$ or $\partial c/\partial x$, which are commonly used to describe moisture transport coefficients for wood (Table 1), can be shown by plotting curves of $\partial\phi/\partial m$, $\partial\phi/\partial c$ or $\partial\phi/\partial h$ against h or m. Figure 5 shows such curves for $\partial\phi/\partial m$ and $\partial\phi/\partial h$ as functions of h using Eqs. (12) and (13), for both the BET and Dent sorption models. Curves of $\partial\phi/\partial c$ against h are essentially similar in form to those of $\partial\phi/\partial m$ against h.

Resistive Force

Returning to the frictional resistance f, it is evident, after writing Eq. (10) in the form

$$-fu = \partial\phi/\partial x \qquad (16)$$

that the *resistive force* is given by $-$ fu, which is equal in magnitude and opposite in sense to the driving force $\partial\phi/\partial x$, for the steady-state condition.

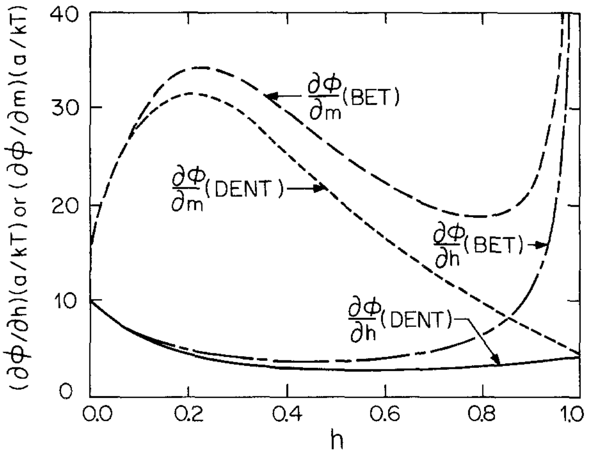

Fig. 5. Curves of ($\partial\phi/\partial h$) (a/kT) and of ($\partial\phi/\partial m$) a/kT) as functions of h, for both the BET and Dent sorption isotherm models

In order to determine the effect of moisture concentration c on the resistance to moisture movement, it should be recalled that the flux J (mass of water per unit time per unit cross-sectional area of the cell wall) is given by the product $c \cdot u$. Multiplying both sides of Eq. (10) by c and equating this to J gives

$$J = cu = -(c/f)(\partial\phi/\partial x) \tag{17}$$

The term c/f is the moisture *conductivity* based on the spreading pressure gradient $\partial\phi/\partial x$. Its reciprocal f/c, therefore, is the moisture *resistivity*. As Babbitt (1951, 1958) noted, therefore, the resistance to movement of each molecule sorbed is inversely related to the number already sorbed.

Transport Coefficients

The moisture transport coefficients, based on gradients of moisture concentration $\partial c/\partial x$ (D), moisture content $\partial m/\partial x$ (K_m), relative vapor pressure $\partial h/\partial x$ (K_h), etc., can be expressed in terms of Eq. (17) by substituting the appropriate relationships for $\partial\phi/\partial x$ given by Eqs. (11) thru (15). The equations obtained for these coefficients as well as the other coefficients defined in Table 1 are given in Table 2.

It is possible to predict how the moisture tranport coefficients based on various assumed driving forces as given in Tables 1 and 2 should vary with wood moisture

Table 2. Equations for the moisture transport coefficients obtained by use of the basic and modified Babbitt transport models

Coefficient	Basic model	Modified model
D	$\dfrac{(c_0\,kT/fa)\,(c/c_0)}{[(c-c_0)^2+4cc_0\,(b/b_0)]^{1/2}}$	$\dfrac{(c_0\,kT/f_0\,a)\,(c/c_0)^2}{[(c-c_0)^2+4cc_0\,(b/b_0)]^{1/2}}$
K_m	$\dfrac{(c_0\,kT/fa)\,(m/m_0)}{[(m-m_0)^2+4mm_0\,(b/b_0)]^{1/2}}$	$\dfrac{(c_0kT/f_0\,a)\,(m/m_0)^2}{[(m-m_0)^2+4mm_0\,(b/b_0)]^{1/2}}$
K_M	$\dfrac{(c_0\,kT/fa)\,(M/M_0)}{[(M-M_0)^2+4MM_0\,(b/b_0)]^{1/2}}$	$\dfrac{(c_0\,kT/f_0\,a)\,(M/M_0)^2}{[(M-M_0)^2+4MM_0\,(b/b_0)]^{1/2}}$
K_p	$\dfrac{(c_0\,kT/fa)\,(b_0^2\,p_0^2\,p)}{[(p_0-bp)\,(p_0+b_0\,p-bp)]^2}$	$\dfrac{(c_0\,kT/f_0\,a)\,(b_0^3\,p_0^3\,p^2)}{[(p_0-bp)\,(p_0+b_0\,p-bp)]^3}$
K_h	$\dfrac{(c_0\,kT/fa)\,(b_0^2\,h)}{[(1-bh)\,(1+b_0\,h-bh)]^2}$	$\dfrac{(c_0\,kT/f_0\,a)\,(b_0^3\,h^2)}{[(1-bh)\,(1+b_0\,h-bh)]^3}$
K_Π	$(v/a)\,(c/f)\,(c/c_0)$	$(v/a)\,(c/f_0)\,(c/c_0)^2$
K_ϕ	(c/f)	$(c/f_0)\,(c/c_0)$

content or relative vapor pressure. Babbitt (1950) for example, gives the equivalent of the ratio $K_h/(c_0\,kT/fa)$ as a function of h for the cell wall of wood, based on the BET model with $b_0 = 11.6$. Figure 6 shows similar ratios for the coefficients D and K_h, both based on the Dent model, using adsorption isotherm data for wood at 25 °C given by Okoh and Skaar (1980), who found $m_0 = 0.0594$, b_0 10.26, $b = 0.777$, $A = 1.64$, $B = 14.28$, and $C = 12.09$ (Eqs. 2 and 3). Also plotted in Fig. 6 are similar curves based on the BET model, with b taken as unity, and $b_0 = 10.26$. It is evident from the curves that the BET isotherm model predicts higher values of K_h than does the Dent model, approaching infinity as H approaches unity. The corresponding curves for D are notably similar for the two sorption isotherm models.

Modification of Transport Model

The bound-water diffusion coefficient D as measured for wood by Stamm (1959) increased with moisture content over the entire moisture range in contrast to the behavior predicted by the model, which indicates that D remains nearly constant for h greater than about 0.4 (Fig. 6). Babbitt (1951) noted that experimental data on water vapor flow through keratin (a hygroscopic solid with sorption properties similar to those of wood) showed considerably greater increases in flow rate J with increasing h above h = 0.4 to 0.5, than were predicted from his model. He hypothesized that the water molecules were even more mobile at high moisture contents than his model predicted.

A possible modification of Babbitt's model which would further increase the mobility of water molecules at higher values of h is to assume that the frictional coefficient f is not constant but decreases with increasing moisture content. Such a relationship can be obtained by noting that f is the surface analog of the volume

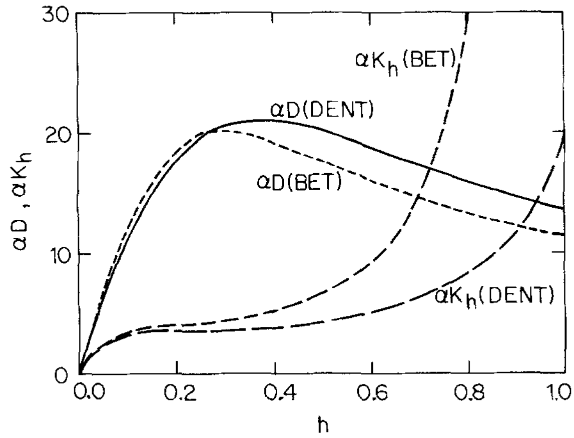

Fig. 6. Curves of αD and of αK_h ($\alpha = fa/c_0\,kT$) as functions of h, for both the BET and Dent sorption isotherm models

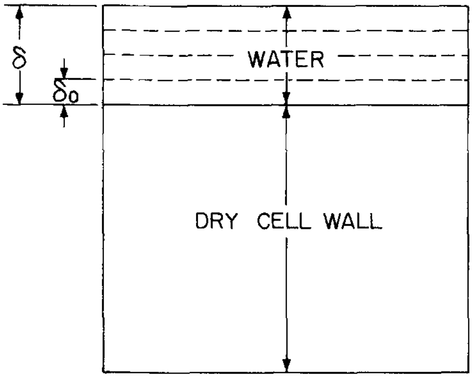

Fig. 7. Schematic diagram showing four layers of water sorbed on a portion of the internal surface of the dry cell wall. The thickness of each layer is δ_0 and the total thickness is δ, equivalent to $4\delta_0$ in this case

coefficient of friction η, to which it can be related dimensionally by setting $\eta = f\delta$ or $f = \eta/\delta$, where δ is the mean thickness of the sorbed water film. The thickness δ may be taken to be equivalent to $\delta_0\,(c/c_0)$, where δ_0 is the thickness of a single layer (Fig. 7). Thus, f varies inversely with c if η is constant, or

$$f = (\eta/\delta_0)\,(c_0/c) = f_0\,(c_0/c) \tag{18}$$

where $f_0 = \eta/\delta_0$.

If f_0 rather than f is now considered to remain constant, the transport coefficient equations given in Table 2 can be modified by substituting $f_0\,(c_0/c)$ for f in each case. The effect of this is to introduce the ratio c/c_0 as an additional multiplying factor for the transport coefficient. Table 2 lists the coefficients D, K_h, etc. as predicted for the modified model for comparison with those based on the original model. The equations for K_h and K_p were modified to eliminate variables other than h (or p) by substituting for c/c_0 ($= m/m_0$) its equivalent in terms of h as given by Eq. (1 a).

Figure 8 shows curves of the ratios $D/(c_0\,kT/f_0\,a)$ and of $K_h/(c_0\,kT/f_0\,a)$ for the modified transport model plotted against h, for the Dent sorption model only. Also shown for comparison are the curves for the same coefficients taken from Fig. 6. The corresponding curves intersect at $h = 0.278$, the point at which $c = c_0$ or $m = m_0 = 0.0594$ g/g in this case, the moisture content equivalent to complete monolayer coverage (Fig. 2).

It is apparent from Fig. 8 that D, based on the modified model, increases with h over the entire range as anticipated, because of the multiplying factor c/c_0. This is qualitatively in agreement with the experimental results obtained by Stamm (1959), although his curves are steeper at higher moisture contents than even the revised model predicts. It is also apparent that K_h (and, therefore, K_p) also increases at a greater rate with increasing h in the modified than in the unmodified transport model, particularly for large values of h.

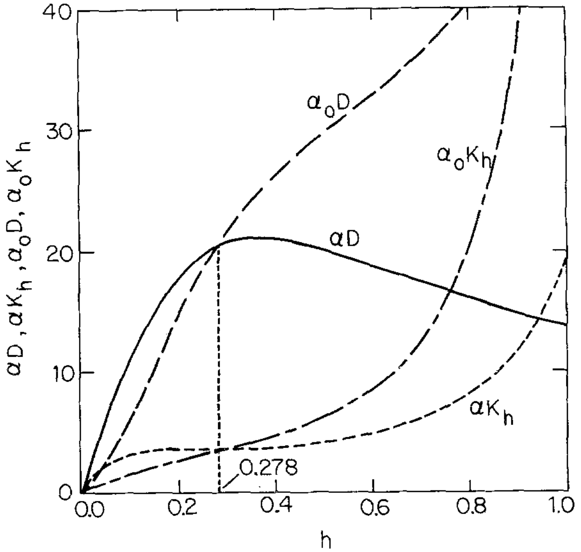

Fig. 8. Curves of $\alpha_0 D$ and of $\alpha_0 K_h$ ($\alpha_0 = f_0 a/c_0 kT$) against h for the modified transport model, for comparison with those of αD and αK_h ($\alpha = fa/c_0 kT$) for the unmodified model. All curves are based on the Dent isotherm. The corresponding curves intersect at h = 0.278, the point at which $c = c_0$ and therefore $f = f_0$

As noted earlier, swelling of the cell wall with increase in moisture has been neglected in relating m and c. The diffusion coefficient D can be modified to account for this swelling by multiplying D by $(G_0/(1 + G_0 m))$ where G_0 is the dry volume specific gravity of the cell wall taken as 1.5. This factor assumes that the partial specific volume of the sorbed water is equal to that of liquid water. Although this assumption is not strictly correct (Stamm 1964) it simplifies the model somewhat.

Evaluation of the moisture transport coefficients

The absolute magnitudes of the diffusion coefficient D and of the other transport coefficients can be evaluated if the term (kT/fa) is known. The value kT is known at any temperature, but the area a per sorption site and the frictional term f can only be estimated. The area a will be estimated first followed by consideration of f.

An approximate *lower* limit a' for the term a can be calculated as the square of δ', the mean spacing between water molecules in the liquid state. Thus, δ' is essentially equivalent to the cube root of v, the molecular volume of water as used in Eq. (4). This is about $30 \times 10^{-24}\,\mathrm{cm}^3$ for liquid water assuming cubic spacing, giving values of 3.1×10^{-8} cm for δ', and $10 \times 10^{-16}\,\mathrm{cm}^2$ for a'.

An *upper* limit a'' for a can be calculated from c_0, or from m_0, by assuming a uniform dispersal of sorption sites throughout the entire cell-wall volume. This gives

$$a'' = (\delta'')^2 = (v'')^{2/3} = [18/(c_0 N_0)]^{2/3} \tag{19}$$

where N_0 is Avogadro's number (6.02×10^{23}) and $c_0 = \rho_w G m_0$, where G is the specific gravity of the dry cell wall and ρ_w is the density of water. Taking $\rho_w G = 1.5$ g/cm^3 and $m_0 = 0.0594$ g/g, gives $\delta'' = 7.0 \times 10^{-8}$ cm, $a'' = 48.3 \times 10^{-16}$ cm^2, and $v'' = 335 \times 10^{-24}$ cm^3 per sorption site for the dry cell wall.

The preceding calculation of a″ gives too high an estimate for a because the crystalline regions of the cell wall are inaccessible to water which is confined to the amorphous regions and the surfaces of the crystalline regions. Stamm (1977) for example, has calculated probable crystallite diameters ranging *upwards* from 15.8×10^{-8} cm for wood cellulose of 65 % crystallinity. He also estimated that only 20 to 30 percent of the hydroxyl groups on the surface of these crystallites and within the amorphous regions are available for sorbing water. The sorption sites, therefore, are outside of the crystalline regions. If it is assumed that they are excluded from 65 percent of the wood volume the effective value of v″ decrease to 35 percent of 335×10^{-24} or to 117×10^{-24} cm^3 per site. The corresponding effective value of a, therefore, is 24×10^{-16} cm^2 per site.

Although wood contains other constituents besides cellulose, the figure of 24×10^{-16} cm^3/site will be taken as an estimate of a. Likewise, the effective mean distance δ between sorption sites in the non-crystalline portions of the wood is approximately the square root of a, or 5×10^{-8} cm. Since the crystallites are elongated in the direction of the microfibrils, the simple model will consist of elongated prisms oriented lengthwise of the cell axis (the dominant orientation) with the sorption sites confined to the surfaces (Fig. 9). This is similar in concept to the model first proposed by Stamm (1946) in his pioneering effort to calculate the diffusion coefficients for wood based on its structure as understood at that time. This simple model also partially explains the higher longitudinal diffusion rate in the cell wall compared with the transverse rate since in the latter case the moisture must migrate around the non-accessible regions of the cell wall.

The last and most difficult term to evaluate in the transport model is the resistance term f, or f_0 in the modified transport model. If it is assumed that $f = f_0 (c_0/c)$ and

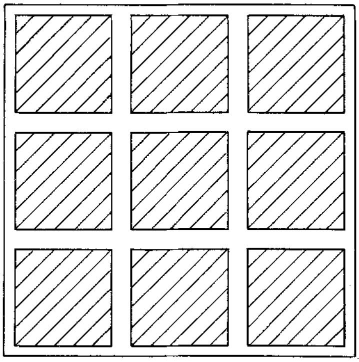

Fig. 9. Schematic diagram of a portion of the cross-section of the cell wall showing inaccessible crystallites (shaded areas) which are oriented lengthwise of the cell axis. In this simple model, water sorption and transport is limited to the spaces between the crystallites

that $f_0 = \eta/\delta_0$ (equation 18), the problem reduces essentially to evaluating the viscosity term η, since δ_0 can be approximated by $\delta' = 3.1 \times 10^{-8}$ cm, already given as the mean spacing between liquid water molecules.

It is proposed, in the discussion which follows, to obtain an estimate of η by virtue of its inverse relationship to the diffusion coefficient D, particularly with respect to the effect of temperature.

In Stamm's (1946) attempt to calculate the diffusion coefficient D for bound water movement in the cell wall of wood, he used the viscosity of liquid water η_w and the Einstein diffusion equation,

$$D_w = kT/(6\pi\, r\, \eta_w) \qquad (20)$$

where r is the particle radius, approximately equal to half of δ', to calculate D_w, the self-diffusion coefficient for water in the cell wall of wood. Although Stamm (1959) later rejected this model as inadequate, the Einstein equation is useful for the present discussion since it shows that D is inversely related to η, that is, the product $D \cdot \eta$ is nearly constant with temperature except for the small direct effect of T in Eq. (20).

Jost (1960) uses the relationship of constant $D \cdot \eta$ for liquids to point out that the activation energy E, obtained by application of the Arrhenius equation to diffusion in liquids (or solids) based on the "hole" theory, is essentially the same as the activation energy obtained by application of the same equation to the variation of the viscosity η of the same liquids. This is basically because the energy required to form "holes" in a liquid is the most important factor affecting the viscosity, just as it is for diffusion.

Jost (1960) shows that the relationship of D to T is given essentially by

$$D = D_0 \exp(-E/RT) \qquad (21)$$

where D_0 is a constant. If D and η are interchanged in Eq. (20) and the equivalent for D given by Eq. (21) is substituted for D, the result obtained can be rearranged to

$$\eta = (D_0\, kT/6\pi\, r) \exp(+E/RT) \qquad (22)$$

A comparison of Eqs. (21) and (22) shows that, except for T in the kT term, which is essentially negligible compared with the exponential term, the effect of temperature is the same on D and $1/\eta$.

If T in k/T is neglected, it can be shown from Eqs. (21) and (22) that

$$\eta/\eta_w = D_w/D = \exp[(E - E_w)/RT] \qquad (23)$$

where η, D and E apply to the bound water, and η_w, D_w and E_w to the free liquid water.

Equation (23) can now be applied to estimate a value of η to be used in Eq. (18). For example, if η_w, E and E_w are known, η can be evaluated. The viscosity η_w of water is 0.0089 at 25 °C, and E_w, obtained from the rate of change of η_w with T based on the Arrhenius equation is about 4000 calories per mole. The activation energy E for bound-water movement has been measured experimentally with varying results (Bramhall, 1979). Choong (1963) gives a value of 8500 calories per mole, which will be used here. It will be assumed to be constant with moisture content, although one would expect it to decrease with increasing moisture content (Skaar and Siau 1981).

Using these values in Eq. (23) gives $\eta = 1990\,\eta_w = 1990\,(0.0089) = 17.7$ dynes-s per cm^2, almost 2000 times the value for free water at 25 °C. The corresponding value of f_0 is $17.7/(3.1 \times 10^{-8})$, or 5.7×10^8 dynes-s per cm^3. The term $(c_0\,kT/af_0)$, with a taken as 24×10^{-16} cm^2 per site, and $c_0 = 1.5\,m_0$, becomes 2.68×10^{-9} g/cm^3 at 25 °C.

The predicted value for the bound-water diffusion coefficient D can now be obtained by multiplying the values of $D/(c_0\,kT/af_0)$ shown in Fig. 8 by 2.68×10^{-9}. Figure 10 shows a plot of D against h obtained in this way. Also shown is an experimentally measured curve given by Stamm (1959), for comparison. Clearly, the values predicted from the revised model are lower than those measured by Stamm, averaging about 30 percent of the measured values. Furthermore, the measured values increase more rapidly with h than do those predicted by the model at the higer relative vapor pressure.

Using the present model, it is obvious that the value of η is extremely sensitive to the value assumed for the activation energy E. For example, if a value of 12,000 calories per mole as given by Stamm (1959) for Sitka spruce bound-water movement is substituted in place of 8500 as used here, the calculated values of D are more than two orders of magnitude lower than those given above. Furthermore, if E decreases with increasing m, as Skaar and Siau (1981) propose, the calculated value of D increases even more rapidly with h than the curve shown in Fig. 9 indicates.

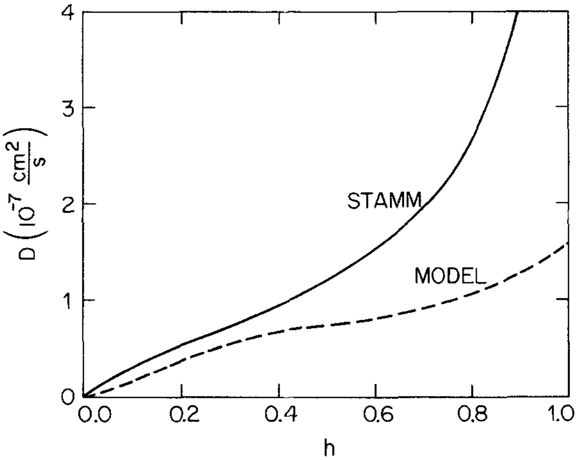

Fig. 10. Curves of D against h as measured by Stamm (1959) and as predicted by the modified transport model

Conclusions

The Babbitt (1950) moisture transport model, which proposes that the driving force for bound-water moisture transport is a two-dimensional spreading pressure ϕ, can be related to any of the empirical driving forces normally assumed for isothermal moisture transport in wood. Application of the Babbitt transport model in terms of the Dent (1977) moisture sorption model yields moisture transport coefficients based on gradients of c or m which are not very different from those based on the BET sorption model which Babbitt used. However, the coefficients based on gradients of h or p increase much less rapidly with increasing h for the Dent than for the BET (1938) sorption model, in the latter case approaching infinity as h approaches unity.

Calculation of the magnitudes of the moisture transport coefficients, based on the transport model used, requires knowledge of the magnitudes of a, the effective area per sorption site, and also the equivalent viscosity of the bound water. The value of a can be approximated, but quantitative information is not available for calculating the viscosity η of the bound water. This is believed to be orders of magnitude greater than that of ordinary liquid water, based on the close relationship between the activation energy for diffusion and that for viscosity. Both energies may be related to the energy required for "hole" formation (Jost 1960) in the water.

References

Babbitt, J. D. 1950: On the differential equations of diffusion. Can. J. Res., Sect. A. 28: 449–474

Babbitt, J. D. 1951: On the diffusion of adsorbed gases through solids. Can. J. Phys. 29: 437–446

Babbitt, J. D. 1958: Diffusion of adsorbed molecules. Nature 182: 201–202

Bramhall G. 1979: Sorption diffusion in wood. Wood Sci. 12 (1): 3–13

Brunauer, S.; Emmett, P. H.; Teller, E. 1938: Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 60: 309–319

Choong, E. T. 1963: Movement of moisture through a softwood in the hygroscopic range. For. Prod. J. 13 (11): 489–498

Dent, R. W. 1977: A multilayer theory for gas sorption. Part I: Sorption of a single gas. Text. Res. J. 47: 145–152

Jost, W. 1960: Diffusion in solids, liquids, gases. Third printing, with addendum. Academic Press: New York

Okoh, K. I. A.; Skaar, C. 1980: Moisture sorption isotherms of the wood and inner bark of 10 southern U.S. hardwoods. Wood and Fiber 12: 98–111

Skaar, C.; Siau, J. F. 1981: Thermal diffusion of bound water in wood. Wood Sci. Technol. 15: 105–112

Stamm, A. J. 1946: Passage of liquids, vapors and dissolved materials through softwoods. U.S. Dept. Agr. Tech. Bull. 929: 1–80

Stamm, A. J. 1959: Bound-water diffusion into wood in the fiber direction. For. Prod. J. 9 (1): 27–32

Stamm, A. J. 1977: Monomolecular adsorption and crystallite diameters of cellulose from structural and adsorption considerations. Wood Sci. Technol. 11: 39–49

(Received August 21, 1981)

Ch. Skaar
Department of Forest Products
Virginia Polytechnic Institute and State University
Blacksburg, VA 24061, USA

M. Babiak,
University College
of Forestry and Technology
Zwolen, Sturova 4, Czechoslovakia