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MATERIALS AND INTERFACES

Parallel Diffusion of Moisture in Paper. Part 1: Steady-State Conditions

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A theoretical model describing the steady-state transport of moisture in the thickness direction of a stack of paperboard sheets placed in a diffusion cup that accounts for the parallel diffusion of water vapor in the pore space and of bound water in the fiber phase is presented. The predictions of the model compare favorably with experimental measurements of the moisture transmission rate through a bleached kraft paperboard stack, average moisture content of the stack, relative humidity profile in the stack, and average moisture content of the individual sheets of the stack under steady-state conditions.

Introduction

Moisture has a profound effect on the mechanical and electrical properties of paper, which loses its strength when subjected to a changing relative humidity (RH) of the surrounding environment. The phenomenon of accelerated creep of paper under cyclic RH results from the interaction of tensile loading and moisture gradients.[1] To understand transient moisture gradients in paper, it is necessary to analyze both the moisture sorption equilibria (with the associated hysteretic effect) and the moisture-transport characteristics of the paper under consideration. The present work addresses the second aspect, specifically, the steady-state transport of moisture in the thickness direction of paper.

Moisture can migrate in paper by a number of transport mechanisms: vapor-phase diffusion in the interfiber pore space, Knudsen diffusion in pores of diameters less than 100 Å, surface diffusion over fiber surfaces, bulk-solid diffusion within fibers, and capillary transport.[2,3] The first two mechanisms occur in the gas phase, whereas the rest occur in the condensed state of the liquid (adsorbed, absorbed, and liquid water, respectively). Liang et al.[2] found gas-phase transport to be the dominant mode of moisture movement, whereas condensed-phase or bound-water movement could occur when the moisture content (MC) was high. Nilsson et al.[3] concluded from their experimental work that moisture transport in paper occurred via gas-phase diffusion at RH levels below 58% rather than via the transport of absorbed water molecules. However, according to an earlier study of Ahlen,[4] the transport of water in the condensed or bound state could be significant even at RH levels as low as 30−40%. Hashemi et al.[5] observed the in-plane diffusivity of moisture in paper to be a strong function of its MC. Hellén et al.[6] analyzed gas diffusion through uncoated paper and board sheets using one-dimensional diffusion theory and random-walk simulations in three-dimensional fiber networks; however, their theory does not include bound-water transport. Yoon and co-workers[7−9] recognized the combined nature of the diffusion of moisture in paper but did not present a comprehensive analysis of the transport process.

Lescanne et al.[10] developed an unsteady-state moisture-transport model for paper that considered water-vapor diffusion in the z or thickness direction of the paper and intrafiber diffusion of moisture assuming the fibers to be cylindrical. However, they neglected bound-water diffusion in the z direction and external resistance to mass transfer. In their model of transient moisture transport in paper under cyclic RH, Ramarao et al.[11] accounted for vapor-phase diffusion and external mass-transport resistance but neglected bound-water transport in the z direction. Foss et al.[12] and Ramarao and Chatterjee[13] developed similar analyses for transient moisture transport in paper under ramp RH changes. Ramarao and Chatterjee,[13] neglecting bound-water transport, represented water-vapor diffusion in the z direction via Fick's law and intrafiber diffusion of moisture with a linear driving force approximation, a concept that has been used for describing intrapellet or intraparticle diffusion in adsorption processes.[14] Assuming the surface of the fibers to be in equilibrium with the local RH, they obtained an analytical solution for the case of a linear sorption isotherm. Bandyopadhyay et al.[15] extended Ramarao and Chatterjee's model to the case of a nonlinear isotherm. Estimating all other parameters in their transport model by independent means, they found that a single value of the intrafiber mass-transfer coefficient was able to fit the experimental dynamic average MC of a bleached kraft paperboard (BKP) sheet subjected to a variety of RH ramps. Hägglund et al.[16] obtained the parameter values of Ramarao and Chatterjee's model (effective water-vapor diffusion coefficient, external mass-transfer coef-

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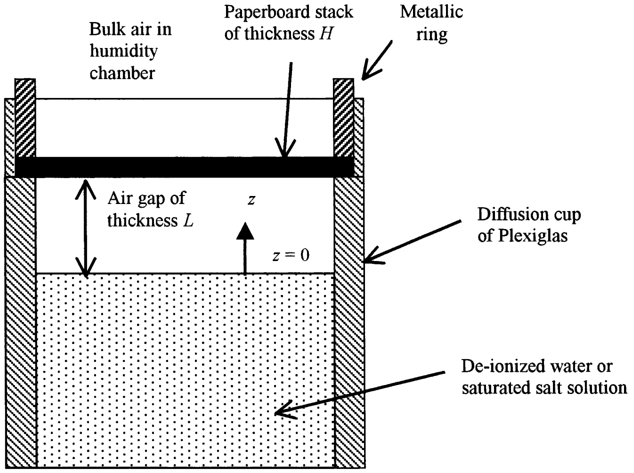

Figure 1. Schematic diagram of diffusion-cup apparatus used by Radhakrishnan et al.[19] and in the present work.

ficient, and intrafiber mass-transfer coefficient) simultaneously by fitting the model to the experimental dynamic MC of paper sheets of four different basis weights (52, 102, 209, and 431 g/m^2) that were subjected to RH ramps of 0−90% RH. Although the agreement between prediction and experiment was reasonably good, they concluded that the diffusion of moisture on fiber surfaces and within the fiber phase in the thickness direction of paper (i.e., bound-water diffusion) was probably responsible for discrepancies between theory and experiment. Assuming diffusion to occur only in the fiber phase and the diffusion coefficient to be constant, Roisum[17] presented an unsteady-state model for describing transient moisture profiles in paper webs and rolls. Recently, Amiri et al.[18] extended this work to consider both axial and radial diffusion of moisture in paper rolls under unsteady-state conditions assuming the axial and radial moisture diffusion coefficients to be independent of the local MC.

Thus, a majority of the available moisture-transport models for paper are for the unsteady-state situation and consider neither bound-water diffusion in the thickness direction of paper nor the profound influence of the local MC on the bound-water diffusion coefficient (see below). In our opinion, a comprehensive theoretical and experimental understanding of steady-state moisture transport is crucial before one can properly address the unsteady-state situation. A beginning was made by Radhakrishnan et al.,[19] who conducted a preliminary investigation of the steady-state transport of moisture in a stack of BKP sheets of mean basis weight 230 g/m^2 at approximately 23 °C in the diffusion-cup apparatus shown in Figure 1. The steady-state effective moisture diffusivity in the paperboard (D_{eff}), based on a vapor-phase concentration driving force, was observed to be approximately constant up to an average stack RH of 60%, indicating the dominance of vapor-phase diffusion at moderate RH levels. Beyond this RH value, D_{eff} increased sharply with the average RH of the stack, showing that the bound-water or condensed-phase transport of moisture became increasingly important. To correlate the experimental results, they developed a theoretical expression for D_{eff} that accounted for both water-vapor and bound-water diffusion in the thickness direction of the paperboard. To our knowledge, this was the first systematic application of the parallel diffusion concept, previously used in the adsorption field,[20−24] to describe moisture movement in paper. Chatterjee and Gupta[25] developed a mathematical model to describe the transport of moisture in the thickness direction of a stack of paper sheets contained in a diffusion cup under steady-state conditions (the precursor of the transport model presented in this paper). This model considered external mass-transport resistances, moisture diffusion in the pore and fiber phases in the thickness direction (described by D_p and D_q, respectively), and intrafiber diffusion of bound water (represented by the intrafiber mass-transfer coefficient k_{fib}). Using a set of provisional moisture-diffusion and sorption parameters for the BKP employed in the steady-state experiments of Radhakrishnan et al.,[19] they presented sample calculations of the RH, MC, and fractional water-vapor flux profiles in the stack. Bandyopadhyay et al.[26] extended the model to the unsteady-state situation in which the external RH (outside the cup) was varied in a step fashion. They used the preliminary BKP sorption/diffusion parameters of Chatterjee and Gupta in their numerical solution, emphasized the role of the intrafiber mass-transfer coefficient (which they called k_i) in the transport process, and provided no experimental validation of their model.

The origin of the intrafiber mass-transfer coefficient lies in past mathematical descriptions of moisture transport in paper that visualized the transport process as consisting of water-vapor diffusion in the z direction (represented by D_p) and intrafiber moisture transport (represented by k_{fib}) but that did not consider bound-water diffusion in the z direction.[10,12,13,15,16] The use of k_{fib} introduces a third parameter into the theoretical framework besides D_p and D_q. Einstein[27] recommended two desirable features in a scientific theory: it should have the fewest possible logically independent elements (basic concepts and axioms), and it should enable the closest and most complete coordination of the totality of sense experiences. It is our opinion that only two parameters (D_p and D_q) are sufficient in the theoretical framework to describe both steady- and unsteady-state moisture transport in paper. That is, in our present work, we conceptualize the paper sheet as consisting of a dual network of pores (pore space or phase) and fibers (fiber phase). We also assume that the transfer or exchange of moisture between the pore and fiber phases is much faster than moisture diffusion in the z direction (i.e., equilibrium prevails between the pore and fiber phases); thus, the concept of an intrafiber mass-transfer coefficient (k_{fib}), used by previous researchers, is not necessary. The validity of the above conceptual picture is based on the following evidence: (a) agreement of the predictions of the steady-state transport model presented here with steady-state experimental measurements (of moisture transmission rates, RH and moisture profiles, and average MC values) carried out with stacks of BKP sheets in a diffusion-cup apparatus and (b) use of the values of D_p and D_q derived from the steady-state investigation to predict the empirically observed transient weight change and RH profile of stacks of BKP sheets subjected to RH ramps, without using any additional fitting parameter in the unsteady-state model; this aspect is presented in the second part of our work.[28] The correlation of our current theoretical framework with this experimental data set obtained under both steady-state and transient conditions, which is more extensive than the data sets used by earlier investigators,[2−13,15−19] seems to validate Einstein's criterion of the "naturalness" or "logical simplicity" of the fundamental concepts of a scientific theory.

In the present study, the following tasks are accomplished: (1) A comprehensive mathematical framework for describing the steady-state transport of moisture in the thickness direction (z) of a paperboard stack contained inside a diffusion cup, which is suspended from a balance and placed inside a controlled-humidity chamber, is presented. The transport model accounts for mass-transfer resistances outside the stack, water-vapor diffusion in the pore space, and bound-water diffusion in the fiber phase. It assumes local equilibrium between the pore and fiber phases and insignificant dimensional changes of the paperboard under RH changes from their average values at 50% RH. (2) By comparing the theoretical expression for D_{eff} with its experimental value over a wide range of experimental conditions, the water-vapor and bound-water diffusion coefficients of a BKP sample (used in our previous work) are estimated. (3) The transport model is then tested against additional experimental data for its ability to predict the RH and moisture profiles in the stack, the average MC of the stack, and the moisture transmission rates through the stack. Good agreement between model and experiment is found, which validates the model.

Moisture Diffusivity

Figure 1 shows a diffusion cup containing a stack of M paperboard sheets that is suspended inside a controlled-humidity chamber. We denote the water-vapor concentration in the air layer adjacent to the water or saturated-salt solution surface inside the cup by c_0 and the concentration of water vapor in the bulk air of the humidity chamber (inside which the diffusion cup containing the paper stack is suspended) by c_{b}. The overall driving force for the transfer of water vapor through the paper stack is then $c_0 - c_{\mathrm{b}}$. The three main resistances to mass transfer in this experimental setup are offered by the (assumed) stagnant layer of air between the water or saturated-salt solution surface and the bottom surface of the stack, the stack of paperboard sheets, and the air boundary layer at the top surface of the stack. The question of the contact resistance between any two adjacent sheets of the stack is discussed later. L and H (assumed to be constants) represent the height of the stagnant air layer (under the stack) and the thickness of the stack of paperboard sheets, respectively; D_{w} and D_{eff} are the diffusion coefficient of water vapor in the air and the effective diffusivity of moisture in the paperboard, respectively, at the experimental temperature and pressure; k_{f} is the mass-transfer coefficient above the paper stack (measured experimentally in this work); and c_{i} and c_{e} are the water-vapor concentrations at the inner and outer surfaces of the stack, respectively. Under steady-state conditions, the total flux of moisture through any cross section of the stack, j_{tot}, can be expressed, to a very good approximation, by

$$j_{\mathrm{tot}} = \frac{D_{\mathrm{w}}}{L}(c_0 - c_{\mathrm{i}}) = k_{\mathrm{f}}(c_{\mathrm{e}} - c_{\mathrm{b}}) \equiv \frac{D_{\mathrm{eff}}}{H}(c_{\mathrm{i}} - c_{\mathrm{e}}) \qquad (1)$$

At specified values of c_0 (determined by the vapor pressure of the solution in the diffusion cup) and c_{b} (determined by the RH level of the humidity chamber), j_{tot} can be measured experimentally by monitoring the rate of weight loss (or gain) of the diffusion cup. Thus, the three unknowns c_{i}, c_{e}, and D_{eff} can be calculated from eq 1, as all other quantities are known. For example, D_{eff} can be obtained from

$$j_{\mathrm{tot}} = \frac{(c_0 - c_{\mathrm{b}})}{\left(\frac{L}{D_{\mathrm{w}}} + \frac{H}{D_{\mathrm{eff}}} + \frac{1}{k_{\mathrm{f}}}\right)} \qquad (2)$$

Let us postulate that the transport of moisture in the paperboard occurs via the parallel diffusion of water vapor and bound water in the pore and fiber phases, respectively. The mass conservation equations, assuming Fick's law, are then given by

$$\frac{\mathrm{d}}{\mathrm{d}z}\left(D_{\mathrm{p}}\frac{\mathrm{d}c}{\mathrm{d}z}\right) - \rho_{\mathrm{p}}S(c,q) = 0 \qquad (3)$$

$$\frac{\mathrm{d}}{\mathrm{d}z}\left(D_{\mathrm{q}}\frac{\mathrm{d}q}{\mathrm{d}z}\right) + S(c,q) = 0 \qquad (4)$$

where D_{p} and D_{q} are the effective diffusivities of water vapor and bound water, respectively, in the stack; c is the water-vapor concentration at any location z in the stack where the bound-water concentration is q; and ρ_{p} is the oven-dry density of the paperboard. The function $S(c,q)$ denotes the rate of transfer or exchange of moisture between the pore and fiber phases at any z. Multiplying eq 4 by ρ_{p} and adding the result to eq 3 gives

$$\frac{\mathrm{d}j_{\mathrm{tot}}}{\mathrm{d}z} = 0 \qquad (5)$$

where

$$j_{\mathrm{tot}} = j_{\mathrm{wv}} + j_{\mathrm{bw}} \qquad (6)$$

Here, j_{wv} and j_{bw} are the local fluxes of water vapor and bound water, respectively, in the stack; i.e.

$$j_{\mathrm{wv}} = -D_{\mathrm{p}}\frac{\mathrm{d}c}{\mathrm{d}z} \qquad (7)$$

$$j_{\mathrm{bw}} = -\rho_{\mathrm{p}}D_{\mathrm{q}}\frac{\mathrm{d}q}{\mathrm{d}z} \qquad (8)$$

D_{p} is relatively independent of c,[3,4,19] but D_{q} is a strong function of q.[4,19,29,30]

In our experimental work, we used four, six, and eight individual sheets of a machine-made BKP (mean basis weight = 230 g/m^2) in the stack, which was loaded down with a metallic ring by means of springs. This raises the question of how to represent the contact region between any two adjacent sheets of the stack in a theoretical treatment. We can make the following two extreme assumptions: (a) perfect contact, in which there is complete or perfect contact between any two adjacent paper sheets (i.e., zero contact resistance between adjacent sheets), so that the paper stack becomes one continuous whole, or (b) no contact, in which there is an air gap that completely separates any two adjacent paper sheets of the stack.

The actual situation lies somewhere between these two extremes. Even in the second case, we assume that there is no resistance to mass transfer offered by the air gap between any two adjacent sheets in the stack, as the maximum experimentally measured value of D_{eff} was at least 1 order of magnitude smaller than D_{w}. We tested this hypothesis by measuring the steady-state moisture flux by introducing a hollow ring of paperboard between two adjacent sheets of the stack and found that this flux differed insignificantly from the flux in the case of the stack with no ring in it.

Assuming that q and c are in equilibrium at the interior (i) and exterior (e) surfaces of the stack, i.e.

$$q_{\mathrm{i}} = f(c_{\mathrm{i}}) \quad \text{and} \quad q_{\mathrm{e}} = f(c_{\mathrm{e}}) \tag{9}$$

with $f(c)$ being the sorption isotherm, integration of eq 6 over the thickness of the stack, followed by use of eqs 1 and 6−9, yields

$$D_{\mathrm{eff}} = D_{\mathrm{p}} + \frac{\rho_{\mathrm{p}}}{(c_{\mathrm{i}} - c_{\mathrm{e}})} \int_{q_{\mathrm{e}}=f(c_{\mathrm{e}})}^{q_{\mathrm{i}}=f(c_{\mathrm{i}})} D_{\mathrm{q}}(q)\,\mathrm{d}q \tag{10}$$

Equation 10 shows that D_{eff} depends on the individual RH levels prevailing on the two surfaces of the stack, i.e., eq 10 is the equation of a surface. We also note that all water-vapor concentrations such as c_0, c_{i}, c, c_{e}, and c_{b} can be related to the corresponding RH values via the ideal-gas law; e.g., see eq 38. A special case of eq 10 can be derived by assuming a particular functional form for $D_{\mathrm{q}}(q)$. In the case of paper with moisture contents up to approximately 25%, $D_{\mathrm{q}}(q)$ can be adequately represented as[19,29,30]

$$D_{\mathrm{q}}(q) = D_1 \mathrm{e}^{mq} \tag{11}$$

where D_1 and m are constants for the particular paper under consideration. A theoretical justification for eq 11 is given in the Appendix. For this case, eq 10 reduces to

$$D_{\mathrm{eff}} = D_{\mathrm{p}} + \frac{D_1\rho_{\mathrm{p}}}{m} \frac{[\mathrm{e}^{mf(c_{\mathrm{i}})} - \mathrm{e}^{mf(c_{\mathrm{e}})}]}{(c_{\mathrm{i}} - c_{\mathrm{e}})}, \quad c_{\mathrm{i}} \neq c_{\mathrm{e}} \tag{12}$$

For $c_{\mathrm{i}} = c_{\mathrm{e}}$, it can easily be shown that

$$D_{\mathrm{eff}} = D_{\mathrm{p}} + D_1\rho_{\mathrm{p}}\mathrm{e}^{mf(x)} \frac{\mathrm{d}f(x)}{\mathrm{d}x}, \quad x = c_{\mathrm{i}} = c_{\mathrm{e}} \tag{12a}$$

By systematically varying the nature of the solution in the diffusion cup (i.e., c_0) and the RH of the humidity chamber (i.e., c_{b}), the D_{eff} surface can be mapped experimentally as a function of c_{i} and c_{e} by using eq 1. The parameters D_{p}, D_1, and m can then be obtained by numerically fitting the surface given by eq 12 to these experimental D_{eff} data.

Estimation of Diffusion Parameters (D_{p}, D_1, and m)

When c_{i} and c_{e} are close to one another, we showed in our previous work[19] that eq 12 reduces to

$$D_{\mathrm{eff}} = D_{\mathrm{p}} + D_1\rho_{\mathrm{p}}\mathrm{e}^{mq_{\mathrm{avg}}}\left[\frac{f(c_{\mathrm{i}}) - f(c_{\mathrm{e}})}{c_{\mathrm{i}} - c_{\mathrm{e}}}\right] \tag{13}$$

where q_{avg} is the average bound-water concentration of the paperboard stack. Over a moderate RH range, the sorption isotherm $f(c)$ can be approximated to be linear; i.e.

$$f(c) = k_{\mathrm{iso}}(c - c_{\mathrm{ref}}) + q_{\mathrm{ref}} \tag{14}$$

where q_{ref} is the equilibrium bound-water concentration of the paper at a water-vapor concentration of c_{ref} and k_{iso} is the slope of the isotherm. Let us assume that q_{avg} and c_{avg} (average water-vapor concentration in stack) are also approximately related by eq 14, i.e.

$$q_{\mathrm{avg}} \approx f(c_{\mathrm{avg}}) = k_{\mathrm{iso}}(c_{\mathrm{avg}} - c_{\mathrm{ref}}) + q_{\mathrm{ref}} \tag{15}$$

The relationship between c_{avg} and $\mathrm{RH}_{\mathrm{avg}}$ [average RH of the stack = $(\mathrm{RH}_{\mathrm{i}} + \mathrm{RH}_{\mathrm{e}})/2$)] is expressed by

$$c_{\mathrm{avg}} = \frac{\mathrm{RH}_{\mathrm{avg}}P_{\mathrm{sat}}}{100RT} \tag{16}$$

where P_{sat} is the vapor pressure of water at the temperature of the experiment T and R is the universal gas constant. Substituting eqs 14−16 into eq 13 yields

$$D_{\mathrm{eff}} = D_{\mathrm{p}}(1 + a\mathrm{e}^{b\mathrm{RH}_{\mathrm{avg}}}) \tag{17}$$

where a and b are constants given by

$$a = \frac{D_1\rho_{\mathrm{p}}k_{\mathrm{iso}}}{D_{\mathrm{p}}}\mathrm{e}^{m(-k_{\mathrm{iso}}c_{\mathrm{ref}}+q_{\mathrm{ref}})} \tag{18}$$

$$b = \frac{mk_{\mathrm{iso}}P_{\mathrm{sat}}}{100RT} \tag{19}$$

According to eq 17, which is a degenerate form of eq 12, as $\mathrm{RH}_{\mathrm{avg}} \to 0$, $D_{\mathrm{eff}} \to D_{\mathrm{p}}(1 + a)$. However, as $\mathrm{RH}_{\mathrm{avg}} \to 0$, the bound-water concentration in the paper should also approach zero, which implies that $a \ll 1$. Ahlen[4] measured D_{p} in paper independently by the counterdiffusion of nitrogen and argon (nonadsorbing gases) and made the important observation that it coincided with the value obtained by extrapolating the experimental D_{eff} vs $\mathrm{RH}_{\mathrm{avg}}$ data to zero $\mathrm{RH}_{\mathrm{avg}}$. Equation 17 is an analogue of expressions that have been presented in the literature to describe the parallel transport of adsorbate in adsorbent via solid-phase and macropore diffusion.[20−24]

The procedure for estimating unique values of the diffusion parameters (D_{p}, D_1, and m) is as follows: (1) Fit the approximate eq 17 to experimental D_{eff} values as a function of $\mathrm{RH}_{\mathrm{avg}}$ and obtain D_{p}, a, and b from the regression; then calculate initial estimates of D_1 and m from eqs 18 and 19. (2) Using these initial estimates of the parameters, fit eq 12 to the experimental D_{eff} values as a function of c_{i} and c_{e} by nonlinear regression. This will yield a more accurate value of D_{p}, which should be accepted, and also new values of D_1 and m, which should be discarded, because they might not be unique. (3) Guess different values of m and plot $\ln(D_{\mathrm{eff}} - D_{\mathrm{p}})$ versus $\ln[(\mathrm{e}^{mf(c_{\mathrm{i}})} - \mathrm{e}^{mf(c_{\mathrm{e}})})/(c_{\mathrm{i}}-c_{\mathrm{e}})]$. The value of m that gives a magnitude of 1 for the average slope of the plot is the correct value of m. Then, $D_1 = \mathrm{e}^{I}m/\rho_{\mathrm{p}}$, where I is the value of the intercept of the above plot.

It is possible to bypass the second step in the above procedure because the values of D_{p} obtained in steps 1 and 2 will generally be very close to one another, as was the case for our data.

Moisture Distribution

To obtain the c and q profiles in the stack, it is necessary to solve eqs 3 and 4 subject to appropriate boundary conditions. This will entail assuming a specific form for $S(c,q)$. As mentioned before, previous researchers have used a linear driving force assumption to represent $S(c,q)$.[13,15,16,25,26] However, as discussed earlier, in the following development, we assume that water vapor and bound water are in equilibrium at every point in the paperboard stack, i.e.

$$q = f(c) \tag{20}$$

This assumption and the assumption made earlier about negligible contact resistance between any two adjacent sheets in the stack reduce the two extreme cases of perfect contact and no contact between adjacent sheets to a single idealized case, which greatly simplifies the mathematical analysis.

We introduce the following quantities

$$C = \frac{c}{c_0},\quad C_b = \frac{c_b}{c_0},\quad Z = \frac{z - L}{H},\quad q_0 = f(c_0)$$

$$Q = \frac{q}{q_0} = \frac{f(c)}{f(c_0)} = \frac{f(c_0 C)}{f(c_0)} = F(C)$$

$$\alpha = \frac{\rho_p D_1 q_0}{D_p c_0},\quad \beta = m q_0,\quad \gamma = \frac{D_w H}{D_p L},\quad Bi = \frac{k_f H}{D_p}$$

The mass conservation equation describing the transport of moisture in the stack is given by eq 5, which, upon integration and use of eqs 6–8, gives

$$\frac{dC}{dZ} + \alpha e^{\beta Q}\frac{dQ}{dZ} = K_1 \tag{21}$$

where K_1 is a constant whose negative is the dimensionless total flux of moisture through the paper stack. The Q profile in the stack is related to the C profile by

$$Q = F(C) \tag{22}$$

Integrating eq 21 and using eq 22 gives

$$C + \frac{\alpha}{\beta}e^{\beta F(C)} = K_1 Z + K_2 \tag{23}$$

where K_2 is another constant. Equation 23 is a nonlinear algebraic equation that can be solved for C in $0 < Z < 1$ provided that K_1 and K_2, which are related to the dimensionless boundary water-vapor concentrations ($C_{Z=0}$ and $C_{Z=1}$), are known.

At the lower and upper surfaces of the stack, we invoke the assumption of equilibrium between water vapor and bound water and the conservation of the total flux of moisture to obtain

$$\gamma(1 - C) = -\left[\frac{dC}{dZ} + \alpha e^{\beta F(C)}\frac{dF(C)}{dZ}\right] \quad \text{at } Z = 0 \tag{24}$$

$$Bi(C - C_b) = -\left[\frac{dC}{dZ} + \alpha e^{\beta F(C)}\frac{dF(C)}{dZ}\right] \quad \text{at } Z = 1 \tag{25}$$

From eqs 21, 24, and 25, we obtain

$$-K_1 = \gamma(1 - C_{Z=0}) = Bi(C_{Z=1} - C_b) \tag{26}$$

Evaluating eq 23 at $Z = 0$ and $Z = 1$ gives

$$K_2 = C_{Z=0} + \frac{\alpha}{\beta}e^{\beta F(C_{Z=0})} \tag{27}$$

$$K_1 + K_2 = C_{Z=1} + \frac{\alpha}{\beta}e^{\beta F(C_{Z=1})} \tag{28}$$

Subtracting eq 27 from eq 28 and utilizing eq 26, we obtain, after some algebra

$$\gamma(1 - C_{Z=0})\left(1 + \frac{1}{Bi}\right) + C_b - C_{Z=0} + \frac{\alpha}{\beta}\left[e^{\beta F[\gamma/Bi(1 - C_{Z=0}) + C_b]} - e^{\beta F(C_{Z=0})}\right] = 0 \tag{29}$$

Equation 29 is a nonlinear equation whose solution (e.g., by Newton's method) will yield $C_{Z=0}$. $C_{Z=1}$ can then be calculated from eq 26, and K_2 and K_1 can be obtained from eqs 27 and 28. Further, it can easily be shown from eqs 6–8, 21, and 22 that

$$\frac{j_{wv}}{j_{tot}} = \frac{1}{1 + \alpha e^{\beta F(C)}\dfrac{dF}{dC}} \tag{30}$$

Average Moisture Content

The average MC of the paperboard stack, q_{avg}, can be calculated from

$$q_{avg} = \frac{1}{H}\int_L^{L+H}\left[\frac{\epsilon_p c(z)}{\rho_p} + q(z)\right] dz \approx \frac{1}{H}\int_L^{L+H} q(z)\, dz \tag{31}$$

where ϵ_p is the porosity of the paperboard. The first term of the integrand in eq 31 is negligible compared to the second term. In dimensionless form, eq 31 becomes

$$Q_{avg} = \frac{q_{avg}}{q_0} \approx \int_0^1 Q\, dZ \tag{32}$$

Sorption Isotherm

In this work, we have used the GAB model[31,32] to represent the sorption isotherm $f(c)$. This is given by

$$f(c) = \frac{q_m C_{GAB}\dfrac{K_{GAB}RT}{P_{sat}}c}{18.016\left(1 - \dfrac{K_{GAB}RT}{P_{sat}}c\right)\left(1 + (C_{GAB} - 1)\dfrac{K_{GAB}RT}{P_{sat}}c\right)} \tag{33}$$

where q_m (equilibrium MC corresponding to monolayer coverage), C_{GAB}, and K_{GAB} are parameters of the isotherm.

Solution of Transport Model

The paperboard stack in the diffusion cup can be conceptually divided into N uniformly spaced grid points $j = 1-N$ in the thickness direction with the points $j = 1$ and $j = N$ representing the lower and upper stack surfaces, respectively. A value of N ranging from 17 to 21 was found to be adequate for the calculations in this work. The dimensionless spacing ΔZ between the points is given by

$$\Delta Z = \frac{1}{N - 1} \tag{34}$$

Also

$$Z_1 = 0, \quad Z_N = 1, \quad \text{and} \quad Z_j = Z_{j-1} + \Delta Z \quad \text{for } j = 2-N-1 \tag{35}$$

The boundary concentrations C_1 (i.e., $C_{Z=0}$) and C_N (i.e., $C_{Z=1}$) and the constants K_1 and K_2 were calculated as described earlier. A profile of C varying linearly with Z between the (known) values of C_1 and C_N was specified as an initial guess. Equation 23 was solved at each point Z_j in the stack by Newton's method to determine each value of C_j. The Q profile was then calculated from eq 22. The fractional water-vapor flux, j_{wv}/j_{tot}, was obtained from eq 30, and the RH and bound-water (BW) profiles in the stack were determined from

$$\mathrm{RH} = (\mathrm{RH}_0)C \tag{36}$$

$$\mathrm{BW} = (18.016 \times 100 \times q_0)Q \tag{37}$$

Here, RH_0 is the relative humidity of air at the surface of the solution in the diffusion cup, which is related to c_0 by the equation

$$c_0 = \frac{\mathrm{RH}_0 P_{\mathrm{sat}}}{100RT} \tag{38}$$

The average MC of the stack, $\mathrm{MC}_{\mathrm{avg}}$, was obtained from

$$\mathrm{MC}_{\mathrm{avg}} = (18.016 \times 100 \times q_0)Q_{\mathrm{avg}} \tag{39}$$

where Q_{avg} was calculated via eq 32 (i.e., by numerical integration of the Q profile).

Experimental Procedures

In all of the experiments reported here, we used a machine-made BKP that was free of fillers and additives and consisted of approximately 80% southern pine and 20% hardwood pulp fibers beaten to 530 mL of CSF (Canadian standard freeness). The BKP had a mean basis weight of 230 g/m^2 and was preconditioned at approximately 50% RH and 23 °C in a controlled-humidity room. Generally, eight circular sheets of the paperboard were used in the stack (i.e., $M = 8$), but in some of the experiments, six and four sheets were also used (changing the stack basis weight). A description of the controlled-humidity chamber in which the diffusion-cup experiments were conducted were provided earlier;[33] three chambers were used in this study. For a description of the experimental procedures for the measurement of D_{eff} and k_f (0.12−1.55 cm/s in this work), we refer the reader to our prior publication.[19] In addition to distilled water, saturated solutions of lithium chloride, potassium acetate, sodium dichromate, and sodium chloride were used in the diffusion cup to provide different levels of RH_0.

In the present work, in addition to obtaining a more extensive experimental database of D_{eff} values than was used by us previously,[19] we have also measured the RH profiles in the paperboard stack, the average MC of the stack, and the MCs of the individual sheets of the stack after the stack had reached steady state. The RH profile in the stack was measured by miniature RH sensors (model HC-600 from Ohmic Instruments Co., Easton, MD; dimensions: 12 mm × 15 mm × 4.5 mm) placed at the interfaces between the sheets. Each sensor (accuracy of ±2% RH) had a ceramic substrate and a thin polymer film, the variation of whose dielectric constant is directly proportional to changes in the amount of water vapor at the sensor element over a range of 0−100% RH. The ceramic substrate was connected via leads to a power supply (4.76 V) and voltmeter for the measurement of the output voltage, which was then converted to the corresponding RH by a calibration curve supplied by the manufacturer. The average MC of the stack was determined by subtracting the weights (at steady state) of the diffusion-cup assembly with and without the paperboard stack in it, subtracting from this the total oven-dry weight of the sheets in the stack, and dividing the result by the stack oven-dry weight. The MC of each individual sheet of the stack after the stack had reached steady state was measured by quickly transferring the sheet into a preweighed plastic bag, sealing the bag, weighing the bag with the sheet in it, taking the difference of the two weights, subtracting from this the oven-dry weight of the sheet, and dividing this value by the sheet oven-dry weight. The oven-dry weight of a paper sample was measured by drying the sample according to a prescribed procedure in a Mark II moisture analyzer (Denver Instrument Co., Arvada, CO) at 105 °C until a constant weight was attained.

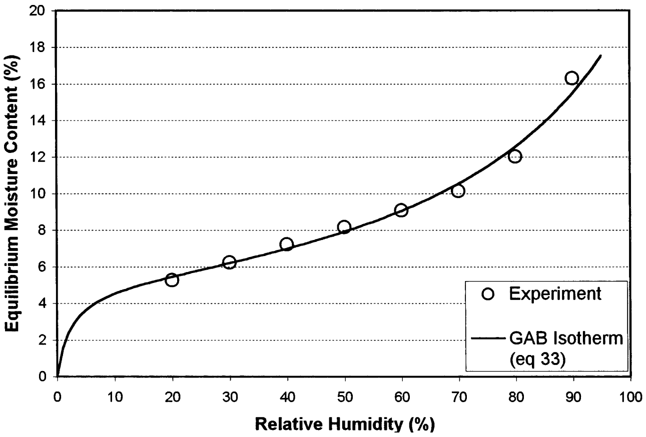

Figure 2. Sorption isotherm of BKP at 23.9 °C and atmospheric pressure (average of three replicates). Equilibrium MC is expressed as grams of moisture per 100 g of oven-dry paper; parameters of the isotherm are reported in Table 1.

Generally, most of the experimental data of the steady-state moisture-transport rate, RH and moisture profiles in the stack, and average MC of the stack reported in this work represent averages of two replicates from experiments conducted under atmospheric pressure in the average temperature range of 23.4−24.9 °C.

Results and Discussion

Figure 2 shows the boundary adsorption isotherm of the BKP at 23.9 °C. This isotherm was obtained by suspending a 10 cm × 10 cm sheet of the paperboard in the humidity chamber and allowing the sheet to reach equilibrium at RH levels of 20−90%, using a sample hold time of 6 h at each RH value. The GAB isotherm (eq 33) fits the data quite well, and its parameters are reported in Table 1 which also lists some of the other experimental conditions. In all calculations regarding moisture transport in this work, we have used this boundary adsorption isotherm, which implies that we neglect sorption hysteresis—a topic that was examined in our earlier papers.[33,34] The errors in the experimental

Table 1. Experimental Conditions and Properties of Bleached Kraft Paperboard Used in the Present Work

parameter	value
temperature	23.4−24.9 °C
pressure	atmospheric
mass-transfer area of paperboard stack[a]	37.37 cm^2
height of air layer below paperboard stack (L)	2.5 and 3 cm
number of paperboard sheets in stack (M)	4, 6, and 8
type of solution in diffusion cup	deionized water and saturated solutions of sodium chloride, lithium chloride, potassium dichromate, and potassium acetate
RH of bulk air in humidity chamber (RH$_b$)	10−90%
mean basis weight of paperboard	230 g/m^2
paperboard sheet thickness (at ~50% RH)[b]	0.035 cm
oven-dry density of paperboard (ρ_p)	0.663 g/cm^3
moisture diffusion constants of paperboard	
D_p	5.238 × 10^{-3} cm^2/s
D_1	3.821 × 10^{-8} cm^2/s
m	398 g/mol
GAB isotherm constants of paperboard (boundary adsorption isotherm)	
q_m	0.051 g/g
K_{GAB}	0.749
C_{GAB}	56.417

[a] Incorrectly reported as 35.26 cm^2 by Radhakrishnan et al.[19] [b] Used as a representative value in all calculations.

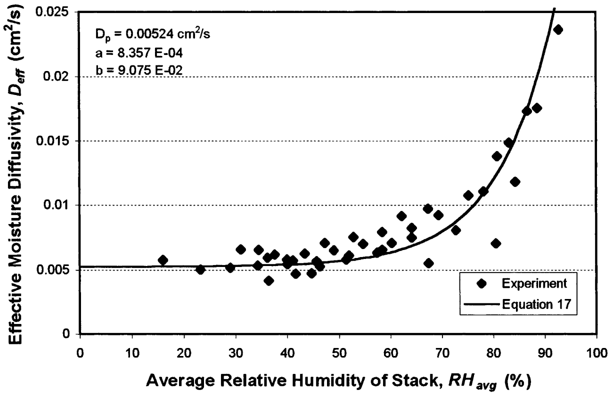

Figure 3. Effective moisture diffusivity of BKP at 23.9 °C and atmospheric pressure. Generally, $M = 8$, $L = 2.5$ cm, and $k_f = 0.12-1.55$ cm/s. Some of the experimental D_{eff} values are from Radhakrishnan et al.,[19] who used $L = 1.5$ cm. Their numbers were corrected by using the proper value of the mass-transfer area of the diffusion cup (Table 1), as mentioned in the text.

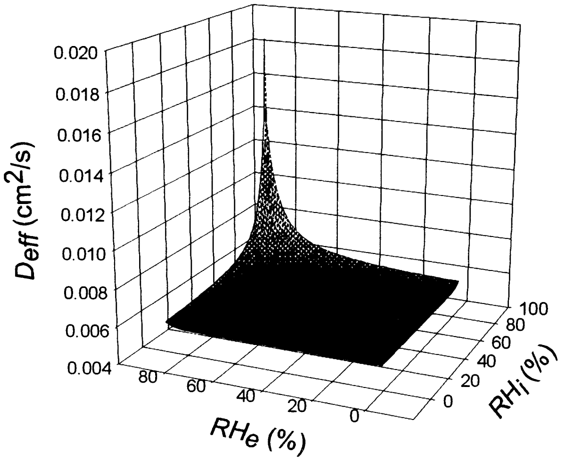

Figure 4. Effective moisture diffusivity surface of BKP at 23.9 °C and atmospheric pressure (from eqs 12 and 12a). Diffusion parameters are listed in Table 1.

measurements reported here do not warrant this extra refinement.

Model Calibration. The effective moisture diffusion coefficient of the BKP (D_{eff}), obtained experimentally with eight sheets in the stack, is shown as a function of the arithmetic average RH of the stack in Figure 3. Deionized water and saturated salt solutions were used in the diffusion cup in these experiments. In our earlier work,[19] we had used an incorrect value of the mass-transfer area of the diffusion cup (see Table 1); some of these earlier data were corrected using the proper value of the mass-transfer area and are included in Figure 3, which has a total of 45 data points. The figure exhibits the approximate correlation for D_{eff} given by eq 17, which was based on 39 data points; the values of D_p (which is basically the horizontal asymptote of the curve at RH$_{avg}$ = 0), a, and b (which are not important for our purposes) are also shown in the figure. The scatter in Figure 3 is partly due to experimental error and partly due to the fact that eq 17 is a simplistic approximation of eq 12.[19] We also fitted the more accurate eq 12 directly to the experimental D_{eff} data and obtained a virtually identical value of D_p. With D_p known, unique values of the parameters of the bound-water diffusion coefficient, D_1 and m, were obtained from the experimental D_{eff} data and eq 12 by the procedure described earlier in the theoretical section; all estimated diffusion parameters of the BKP are listed in Table 1. Note that D_p, the effective or apparent diffusivity of water vapor in the BKP, is about 48 times smaller than the water vapor diffusion coefficient in air ($D_w = 0.25$ cm^2/s at approximately 23 °C and atmospheric pressure). This implies a high tortuosity of the diffusion path in the thickness direction of the paper, an observation also made by Hashemi et al.[5] Our value of D_p (0.0052 cm^2/s) is comparable to an effective diffusivity value of 0.007 cm^2/s estimated from Figure 5 of Nilsson et al.[3] for paper having approximately the same density as the BKP used in this work. The increase of D_{eff} with RH, as exhibited in Figure 3 for the BKP, has also been observed by Gupta[35] in the case of handsheets made from Aspen and Southern Pine pulp (at two different kappa numbers) and a commercially available copy paper.

The D_{eff} surface of the BKP as a function of the RH values prevailing on its two surfaces (eqs 12 and 12a) is plotted in Figure 4. At low levels of RH, where the D_{eff} surface is approximately flat, water-vapor diffusion is the dominant mode of moisture movement. As the RH increases, bound-water diffusion becomes more important, and D_{eff} increases sharply. The theoretical and experimental moisture transmission rates through the stack of eight paperboard sheets are compared in Figure 5. The experimental data (which were used to estimate the diffusion parameters) in this figure are equivalent

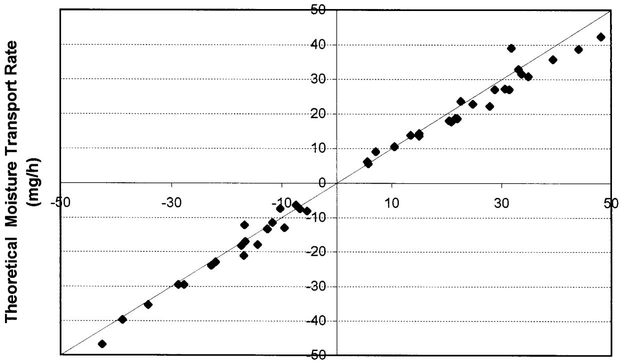

Figure 5. Steady-state moisture-transport rate through BKP stack at 23.9 °C and atmospheric pressure. The experimental data in this figure are equivalent to those in Figure 3.

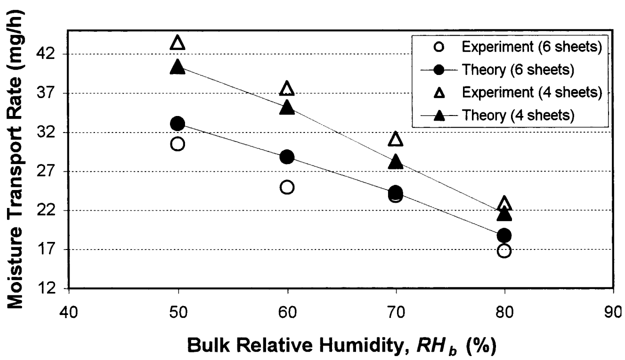

Figure 6. Steady-state moisture-transport rate through BKP stack with water in the diffusion cup ($L = 3$ cm). For $M = 4$, $k_f = 0.11-0.14$ cm/s, average temperature = 24.6 °C; for $M = 6$, $k_f = 0.12-0.15$ cm/s, average temperature = 24.1 °C.

to those shown in Figure 3. The root-mean-square deviation between theory and experiment is 15.7%. The negative moisture-transport rates in Figure 5 correspond to those situations in which the direction of transport was from the bulk air in the humidity chamber into the diffusion cup.

Model Validation. Figures 6–9 test the ability of the transport model to predict moisture transmission rates through stacks containing different numbers of BKP sheets, RH and sheet-average MC profiles in the stack, and average MCs of the whole stack under a variety of experimental conditions. Deionized water was used in the diffusion cup in all of these experiments, which implies that the RH adjacent to the liquid surface in the diffusion cup was 100%.

According to Figure 6, the moisture-transport rate in stacks of four and six sheets decreases as the bulk RH of the humidity chamber increases. On average, theory underpredicts experiment by 7% for the four-sheet stack while overpredicting it by 9% for the six-sheet stack. Figure 7 displays experimentally measured RH profiles (obtained with the miniature probes mentioned earlier) in the stack, which compare quite well with their theoretical counterparts. The experimental RH driving force across the four-sheet stack was 26.6%, while that across the eight-sheet stack was 34.7% at the same values of RH_b (50%), L (2.5 cm), and k_f (0.13 cm/s). The experimental and theoretical average MCs of the individual sheets in the eight-sheet stack (i.e., sheet-average moisture profile) compare fairly well, as shown in Figure 8. The theoretical average MC of a sheet was calculated by integrating the predicted q profile across it. The average MC of the whole stack is plotted as a function of RH_b in Figure 9. Theory and experiment again agree fairly well, with theory overpredicting experiment by 0.45% MC on average.

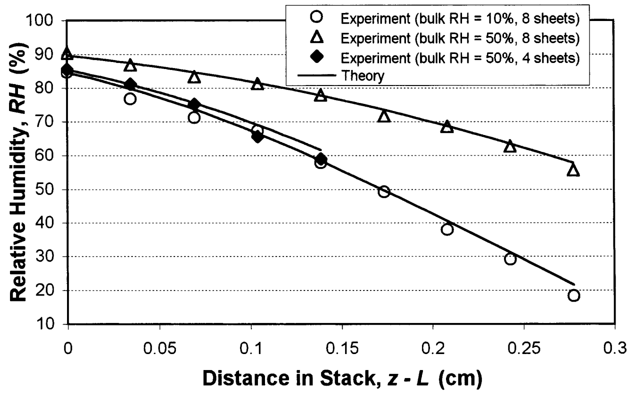

Figure 7. Steady-state relative humidity profile in BKP stack with water in the diffusion cup ($L = 2.5$ cm). For $M = 8$ and $RH_b = 10\%$, $k_f = 0.13$ cm/s, $T = 24.1$ °C; for $M = 8$ and $RH_b = 50\%$, $k_f = 0.13$ cm/s, $T = 23.6$ °C; for $M = 4$ and $RH_b = 50\%$, $k_f = 0.13$ cm/s, $T = 23.8$ °C.

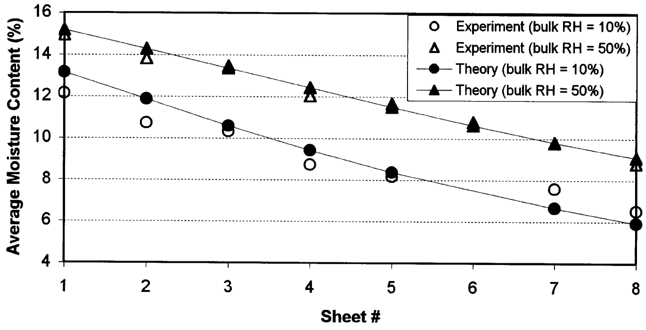

Figure 8. Steady-state average MC of individual sheets of BKP stack with water in the diffusion cup ($L = 2.5$ cm) and $M = 8$. At $RH_b = 10\%$, $k_f = 0.13$ cm/s, $T = 23.4$ °C; at $RH_b = 50\%$, $k_f = 0.13$ cm/s, $T = 23.8$ °C.

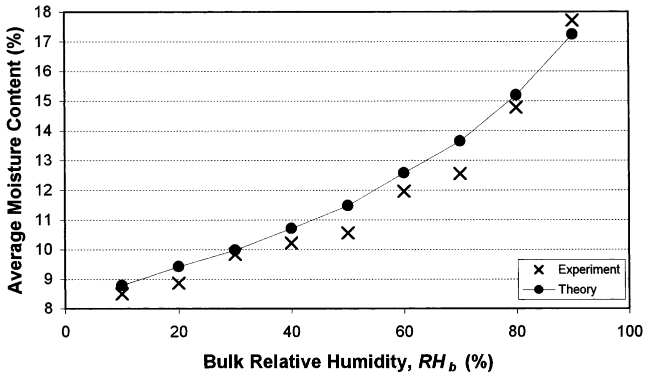

Figure 9. Steady-state average MC of BKP stack with water in the diffusion cup ($L = 3$ cm) and $M = 8$. Average temperature = 24.7 °C, $k_f = 0.13-0.21$ cm/s.

The calculated fractional moisture flux due to water vapor, j_{wv}/j_{tot} (eq 30), is shown as a function of the dimensionless distance into the stack (Z) in Figure 10. Note that these are simulations of actual experimental runs in which deionized water was used in the diffusion cup. At $RH_b = 10\%$, the fractional water-vapor flux increases from 0.49 at the lower surface of the stack to 0.95 at its upper surface; i.e., moisture transport occurs predominantly via water-vapor diffusion in the stack. For $RH_b = 50\%$, the range of variation of j_{wv}/j_{tot} is 0.35–

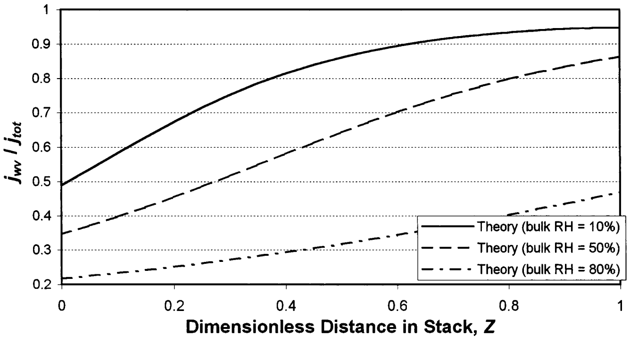

Figure 10. Calculated steady-state fractional water-vapor flux in BKP stack at 24.7 °C with water in the diffusion cup ($L = 3$ cm) and $M = 8$ (eq 30). At $\mathrm{RH_b} = 10\%$, $k_f = 0.15$ cm/s, $T = 24.6$ °C; at $\mathrm{RH_b} = 50\%$, $k_f = 0.20$ cm/s, $T = 24.5$ °C; at $\mathrm{RH_b} = 80\%$, $k_f = 0.16$ cm/s, $T = 24.9$ °C.

0.86, whereas for $\mathrm{RH_b} = 80\%$, the range is 0.22−0.47. In the first two cases, $j_{wv}/j_{tot} = 0.5$ at $Z \approx 0$ and 0.28, respectively, and it is only after these locations that water-vapor diffusion dominates over bound-water diffusion in the stack. However, in the third case ($\mathrm{RH_b} = 80\%$), bound-water diffusion is the dominant mode of moisture movement in the entire stack.

Previously, we outlined how to estimate the diffusion parameters (D_p, D_1, and m) from experimental measurements of the total moisture flux (or D_{eff}). However, such measurements can be quite time-consuming and labor-intensive, especially if a large number of RH levels are used across the stack, as was done in this work. An alternative method, capable of saving much experimental time and effort, is outlined below. For small values of $\mathrm{RH_b}$, we would expect water-vapor diffusion to dominate over bound-water diffusion at the upper edge of the stack, i.e., at $z = L + H$ (see Figure 10 for the case of $\mathrm{RH_b} = 10\%$). Under these conditions, a single measurement of the total moisture flux through the stack, along with the corresponding RH (or c) profile within it, might be capable of yielding the diffusion parameters. For low levels of $\mathrm{RH_b}$, eqs 6 and 7 give

$$D_p \approx \frac{j_{tot}}{-\left(\dfrac{dc}{dz}\right)_{z=L+H}} \qquad \text{when } j_{wv} \gg j_{bw} \tag{40}$$

Because $C(Z)$ and D_p are now known, γ [$= D_wH/(D_pL)$] can be calculated, and thus, K_1 can be obtained from eq 26. Equations 21 and 22 then give

$$\ln\left(\frac{\dfrac{K_1}{dC/dZ} - 1}{dF/dC}\right) = \ln \alpha + \beta F[C(Z)] \tag{41}$$

The left-hand side of eq 41 can be plotted against $F(C)$ to yield m and D_1 from the slope and intercept of the plot, respectively. An analytical expression for the slope of the sorption isotherm, necessary in eq 41, can be derived from eq 33. The chief requirement in the above procedure is an accurate value of the slope of the RH profile in the stack.

Conclusions

In this work, we have presented a mathematical model that describes the transport of moisture in a stack of paper sheets under steady-state conditions. The model takes into consideration external mass-transport resistances and the two-phase or parallel diffusion of moisture in the pore and fiber phases of the paper. The effective water-vapor and bound-water diffusion coefficients of a machine-made BKP of mean basis weight 230 g/m^2 were estimated by matching the theoretical expression of the effective moisture diffusivity to the experimental value measured with a stack of eight sheets of the paperboard in a diffusion cup under a wide variety of RH driving potentials across the stack. The predictions of the model were then compared against additional experimental measurements of the moisture transmission rate through the paperboard stack, average MC of the stack, relative humidity profile in the stack, and average moisture contents of the individual sheets in the stack under a variety of experimental conditions. Good agreement between the model and these experimental data validates the model.

The steady-state moisture transmission measurements presented in this work were labor-intensive and time-consuming; however, an alternative method discussed earlier offers the possibility of significantly reducing the experimental effort. Steady-state analysis does not involve the complications of transport under dynamic conditions and enables one to determine unique values of the effective water-vapor and bound-water diffusion coefficients of moisture in paper in a relatively straightforward fashion. It might be possible to complement the steady-state approach by directly measuring the temporal moisture distribution profiles by more capital-intensive techniques, such as NMR spectroscopy/MRI[36−38] and infrared thermography,[39] and thereby obtain a better understanding of the diffusion of moisture in paper. In this connection, we mention that Topgaard and Söderman[30] have measured the fiber-wall water diffusion coefficient in filter paper using ^{1}H NMR spectroscopy. They found that the diffusion coefficient also depended exponentially on the MC (see Figure 15 of their work); in the MC range of 10−20%, the diffusion coefficient has values that are of the same order of magnitude as the fiber-phase diffusion coefficient D_q of our BKP. The exponential factor in eq 11, expressed on an MC basis (by dividing m by 1801.6), has values of 0.1 (approximately) and 0.22 for the filter paper and BKP, respectively.

Acknowledgment

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Nomenclature

a = given by eq 18
b = given by eq 19
Bi = Biot number, k_fH/D_p
BW = bound-water concentration at any specific location in a paperboard stack (%)
c = water-vapor concentration at any location z in a paperboard stack (mol/cm^3)
c_{avg} = average water-vapor concentration in a paperboard stack (mol/cm^3)
c_b = water-vapor concentration in the bulk air of the humidity chamber (mol/cm^3)
c_e, c_i, = water-vapor concentrations at the exterior (upper) and interior (lower) surfaces, respectively, of the paperboard stack (mol/cm^3)

c_{ref} = reference water-vapor concentration (mol/cm^3)
c_0 = water-vapor concentration above the surface of the solution in the diffusion cup (mol/cm^3)
C = dimensionless water-vapor concentration in a paperboard stack, c/c_0
C_{GAB} = parameter of the GAB isotherm (eq 33)
C_{b} = dimensionless water vapor concentration in the bulk air of the humidity chamber, c_{b}/c_0
$C_{Z=0}$ (C_1), $C_{Z=1}$ (C_N) = dimensionless water vapor concentrations at the lower and upper surfaces, respectively, of a paperboard stack
D_{bw} = intrinsic diffusion coefficient of bound water in the paperboard (cm^2/s)
D_{eff} = effective diffusion coefficient of moisture in the paperboard (cm^2/s)
D_{p} = diffusion coefficient of water vapor in the paperboard (cm^2/s)
D_{q} = diffusion coefficient of bound water in the paperboard (cm^2/s)
D_{w} = diffusion coefficient of water vapor in the air (cm^2/s)
D_1 = constant in eq 11 (cm^2/s)
$f(c)$ = bound-water concentration in equilibrium with the water-vapor concentration c or sorption isotherm (mol/g of dry fiber)
$F(C)$ = dimensionless equilibrium bound-water concentration, $f(c)/f(c_0)$
H = thickness of a paperboard stack (cm)
I = intercept of the plot of $\ln(D_{\mathrm{eff}} - D_{\mathrm{p}})$ versus $\ln[(\mathrm{e}^{mf(c_{\mathrm{i}})} - \mathrm{e}^{mf(c_{\mathrm{e}})})/(c_{\mathrm{i}} - c_{\mathrm{e}})]$
j = index denoting grid points in a paperboard stack
j_{bw} = bound-water flux in a paperboard stack [mol/(cm^2 s)]
j_{tot} = total moisture flux in a paperboard stack given by eq 6 [mol/(cm^2 s)]
j_{wv} = water-vapor flux in a paperboard stack [mol/(cm^2 s)]
k_{iso} = slope of the linearized isotherm in eq 14 (cm^3/g)
k_{f} = mass-transfer coefficient above a paperboard stack (cm/s)
k_{fib} = intrafiber mass-transfer coefficient (s^{-1})
K_{GAB} = parameter of the GAB isotherm (eq 33)
K_1, K_2 = constants given by eqs 26 and 27, respectively
L = thickness of the air layer under a paperboard stack (cm)
m = constant in eqs 11 and A3 (g/mol)
M = number of sheets in a paperboard stack
$\mathrm{MC}_{\mathrm{avg}}$ = average MC of a paperboard stack (%)
n = number of channels conducting bound water in the paperboard
n_{init} = initial or reference value of n
N = total number of grid points in a paperboard stack
P_{sat} = vapor pressure of water at temperature T (MPa)
q = bound-water concentration at any location z in a paperboard stack (mol/g of dry fiber)
q_{avg} = average MC of a paperboard stack (mol/g of dry fiber)
q_{e}, q_{i}, = bound-water concentrations at the exterior (upper) and interior (lower) surfaces, respectively, of a paperboard stack (mol/g of dry fiber)
q_{init} = initial or reference value of q (mol/g of dry fiber)
q_{m} = equilibrium MC corresponding to monolayer coverage in eq 33 (g/g of dry fiber)
$q_0 = f(c_0)$ = equilibrium MC corresponding to a water-vapor concentration of c_0 (mol/g of dry fiber)
q_{ref} = equilibrium MC corresponding to a water-vapor concentration of c_{ref} (mol/g of dry fiber)
Q = dimensionless bound-water concentration in a paperboard stack, q/q_0
Q_{avg} = dimensionless average MC of a paperboard stack, q_{avg}/q_0
R = universal gas constant [8.3144 cm^3 MPa/(mol K)]
RH = relative humidity at any specific location z in a paperboard stack (%)
$\mathrm{RH}_{\mathrm{avg}}$ = average relative humidity of a paperboard stack (%)
RH_{e} = relative humidity at the upper surface of a paperboard stack (%)
RH_{i} = relative humidity at the lower surface of a paperboard stack (%)
RH_0 = relative humidity at the surface of the solution in the diffusion cup (%)
$S(c,q)$ = rate of transfer or exchange of moisture between the pore and fiber phases [mol/(g s)]
T = experimental temperature (K)
z = distance into a paperboard stack measured from the surface of the solution in the diffusion cup (cm)
Z = dimensionless distance into a paperboard stack measured from its lower surface, $(z - L)/H$
Z_j = dimensionless distance of grid point j from the lower surface of a paperboard stack
Z_1, Z_N = dimensionless distances of the first and last grid points, respectively, from the lower surface of a paperboard stack
$\alpha = \rho_{\mathrm{p}} D_1 q_0/(D_{\mathrm{p}} c_0)$
$\beta = m q_0$
$\gamma = D_{\mathrm{w}} H/(D_{\mathrm{p}} L)$
ΔZ = dimensionless grid spacing, $1/(N - 1)$
ρ_{p} = oven-dry density of the paperboard (g of dry fiber/cm^3)
ϵ_{p} = porosity of the paperboard

Appendix

In this section, we provide a theoretical derivation of the expression for the apparent bound-water diffusion coefficient D_{q} (eq 11). Following the work of Topgaard and Söderman,[30] we postulate that bound water diffuses in the thickness direction of paper through channels between and along the microfibrils. Assuming Fick's law, the local flux of bound water, j_{bw}, in one such channel is given by

$$j_{\mathrm{bw}}\ (\text{one channel}) = -\rho_{\mathrm{p}} D_{\mathrm{bw}} \frac{\mathrm{d}q}{\mathrm{d}z} \tag{A1}$$

where D_{bw} is an "intrinsic" diffusion coefficient of bound water in the fiber phase. For n such channels

$$j_{\mathrm{bw}}\ (n\ \text{channels}) = -n \rho_{\mathrm{p}} D_{\mathrm{bw}} \frac{\mathrm{d}q}{\mathrm{d}z} \tag{A2}$$

As MC increases from 10 to 20%, the distance between the microfibrils increases from about one monolayer of water to four such layers.[30] We hypothesize that the number of channels, n, is an increasing function of the local MC, q; let the law describing this growth be given by

$$\frac{\mathrm{d}n}{\mathrm{d}q} = mn \tag{A3}$$

where m is a constant. Integrating eq A3 from reference values n_{init} and q_{init}, we obtain

$$n = n_{\mathrm{init}} \mathrm{e}^{m(q - q_{\mathrm{init}})} \tag{A4}$$

Substituting eq A4 into eq A2 gives

$$j_{\mathrm{bw}} = -n_{\mathrm{init}} \mathrm{e}^{-mq_{\mathrm{init}}} D_{\mathrm{bw}} \rho_{\mathrm{p}} \mathrm{e}^{mq} \frac{\mathrm{d}q}{\mathrm{d}z} \tag{A5}$$

Letting

$$D_1 = n_{\mathrm{init}} \mathrm{e}^{-mq_{\mathrm{init}}} D_{\mathrm{bw}} \tag{A6}$$

transforms eq A5 into

$$j_{\mathrm{bw}} = -\rho_{\mathrm{p}} D_1 \mathrm{e}^{mq} \frac{\mathrm{d}q}{\mathrm{d}z} \tag{A7}$$

Thus, from eqs A7 and 8, it is clear that the apparent diffusivity of bound water D_{q} is given by

$$D_{\mathrm{q}}(q) = D_1 \mathrm{e}^{mq} \tag{A8}$$

which is identical to eq 11.

Literature Cited

(1) Habeger, C. C.; Coffin, D. W. The Role of Stress Concentrations in Accelerated Creep and Sorption-Induced Physical Aging. *J. Pulp Paper Sci.* **2000**, *26* (4), 145.

(2) Liang, B.; Fields, R. J.; King, J. C. The Mechanisms of Transport of Water and *n*-Propanol through Pulp and Paper. *Drying Technol.* **1990**, *8* (4), 641.

(3) Nilsson, L.; Wilhelmsson, B.; Stenström, S. The Diffusion of Water Vapor through Pulp and Paper. *Drying Technol.* **1993**, *11* (6), 1205.

(4) Ahlen, A. T. Diffusion of Sorbed Water Vapor through Paper and Cellulose Film. *Tappi J.* **1970**, *53* (7), 1320.

(5) Hashemi, S. J.; Gomes, V. G.; Crotogino, R. H.; Douglas, W. J. M. In-Plane Diffusivity of Moisture in Paper. *Drying Technol.* **1997**, *15* (2), 265.

(6) Hellén, E. K. O.; Ketoja, J. A.; Niskanen, K. J.; Alava, M. J. Diffusion through Fibre Networks. *J. Pulp Paper Sci.* **2002**, *28* (2), 55.

(7) Yoon, S. H.; Jeon, Y.; Ow, S. K.; Seo, Y. B. Molecular Diffusion of Water in Paper (I). *J. Korea Tappi* **1998**, *30* (1), 59.

(8) Yoon, S. H.; Jeon, Y. Molecular Diffusion of Water in Paper (II). *J. Korea Tappi* **1998**, *30* (3), 46.

(9) Yoon, S. H.; Jeon, Y.; Park, J. M. Molecular Diffusion of Water in Paper (III). *J. Korea Tappi* **1999**, *31* (1), 61.

(10) Lescanne, Y.; Moyne, C.; Perre, P. Diffusion Mechanisms in a Sheet of Paper. Mujumdan, A. S., Ed.; *Drying ′92*; Elsevier Science Publishers: B.V., 1992; p 1017.

(11) Ramarao, B. V.; Chatterjee, S. G.; Eusufzai, A. R. K. Moisture transport and sorption by paper under cyclic variations in humidity. In *Mechanics of Cellulosic Materials*; Perkins, R., Ed.; ASME Press: New York, 1995; AMD - Vol. 209/MD - Vol. 60, p 195.

(12) Foss, W. R.; Bronkhorst, C. A.; Bennett, K. A.; Riedemann, J. R. Transient moisture transport in paper in the hygroscopic range and its role in the mechano-sorptive effect. In *Proceedings of the Third International Symposium: Moisture and Creep Effects on Paper, Board and Containers*; Chalmers, I. R., Ed.; PAPRO: Rotorua, New Zealand, 1997; p 221.

(13) Ramarao, B. V.; Chatterjee, S. G. Moisture sorption by paper materials under varying humidity conditions. In *The Fundamentals of Papermaking Materials: Transactions of the Eleventh Fundamental Research Symposium*; PIRA International: Leatherhead, Surrey, U.K., 1997; Vol. 2, p 703.

(14) Tien, C. Adsorbate Transport: Its Adsorption and Rates. In *Adsorption Calculations and Modeling*; Butterworth-Heinemann: Boston, 1994; p 81.

(15) Bandyopadhyay, A.; Radhakrishnan, H.; Ramarao, B. V.; Chatterjee, S. G. Moisture Sorption Response of Paper Subjected to Ramp Humidity Changes: Modeling and Experiments. *Ind. Eng. Chem. Res.* **2000**, *39* (1), 244.

(16) Hägglund, R.; Westerlind, B.; Gulliksson, M.; Nordstrand, T. Diffusion of water vapor in paper. In *Fundamental Advances and Innovations in the Pulp and Paper Industry: AIChE Symposium Series*; Brogdon, B. N., Ed.; AIChE: New York, 1999; Vol. 95, No. 322, p 71.

(17) Roisum, D. R. Moisture Effects on Webs and Rolls. *Tappi J.* **1993**, *76* (6), 129.

(18) Amiri, R.; Hamel, J.; McDonald, J. D. Moisture Distribution in Paper Rolls: The Effect of Wrapping Materials. *J. Pulp Paper Sci.* **2002**, *28* (5), 143.

(19) Radhakrishnan, H.; Chatterjee, S. G.; Ramarao, B. V. Steady-State Moisture Transport in a Bleached-Kraft Paperboard Stack. *J. Pulp Paper Sci.* **2000**, *26* (4), 140.

(20) Takeuchi, Y.; Furuya, E.; Ikeda, H. On the Concentration Dependency of Intraparticle Effective Diffusivity for Tetrahydrofuran-Activated Carbon System. *J. Chem. Eng. Jpn.* **1984**, *17* (3), 304.

(21) Costa, E.; Calleja, G.; Domingo, F. Adsorption of Gaseous Hydrocarbons on Activated Carbon. *AIChE J.* **1985**, *31* (6), 982.

(22) Yoshida, H.; Maekawa, M.; Nango, M. Parallel Transport by Surface and Pore Diffusion in a Porous Membrane. *Chem. Eng. Sci.* **1991**, *46* (2), 429.

(23) Yoshida, H.; Yoshikawa, M.; Kataoka, T. Parallel Transport of BSA by Surface and Pore Diffusion in Strongly Basic Chitosan. *AIChE J.* **1994**, *40* (12), 2034.

(24) Takatsuji, W.; Yoshida, H. Parallel Transport by Solid-Phase and Macropore Diffusion in a Polyaminated Highly Porous Chitosan Bead in Case of Acetic Acid and Lactic Acid. *J. Chem. Eng. Jpn.* **2001**, *34* (1), 55.

(25) Chatterjee, S. G.; Gupta, H. *Steady-State Moisture Transport in Paper: Part I Theory*; ESPRA Research Report No. 112; Empire State Paper Research Institute: Syracuse, NY, 2000; p 35.

(26) Bandyopadhyay, A.; Ramarao, B. V.; Ramaswamy, S. Transient Moisture Diffusion through Paperboard Materials. *Colloids Surf. A: Physicochem. Eng. Aspects* **2002**, *206*, 455.

(27) Einstein, A. Autobiographical Notes. In *Albert Einstein: Philosopher-Scientist*; Schilpp, P. A., Ed.; The Library of Living Philosophers: Evanston, IL, 1949.

(28) Gupta, H.; Chatterjee, S. G. Parallel Diffusion of Moisture in Paper. Part 2: Transient Conditions. *Ind. Eng. Chem. Res.* **2003**, *42*, 6593−6600.

(29) Lin, S. H. Moisture Absorption in Cellulosic Materials. *Int. J. Eng. Sci.* **1990**, *28* (11), 1151.

(30) Topgaard, D.; Söderman, O. Diffusion of Water Absorbed in Cellulose Fibers Studied with ^{1}H NMR. *Langmuir* **2001**, *17*, 2694.

(31) Bizot, H. Using the GAB Model to Construct Sorption Isotherms. In *Physical Properties of Foods*; Jowitt, R., Esher, F., Hallström, B., Meffert, H. T. Th., Spiess, W. E. L., Vos, G., Eds.; Applied Science Publishers: Essex, U.K., 1983; Chapter 4.

(32) Eagleton, D. G.; Marcondes, J. A. Moisture-Sorption Isotherms for Paper-based Components of Transport Packaging of Fresh Produce. *Tappi J.* **1994**, *77* (7), 75.

(33) Chatterjee, S. G.; Ramarao, B. V.; Tien, C. Water-Vapor Sorption Equilibria of a Bleached-Kraft Paperboard—A Study of the Hysteresis Region. *J. Pulp Paper Sci.* **1997**, *23* (8), 366.

(34) Chatterjee, S. G. Comparison of Domain and Similarity Models for Characterizing Moisture Sorption Equilibria of Paper. *Ind. Eng. Chem. Res.* **2001**, *40* (1), 188.

(35) Gupta, H. Moisture Transport in Paper under Steady and Unsteady Conditions Investigated with a Parallel Diffusion Concept. Ph.D. Thesis, SUNY College of Environmental Science and Forestry, Syracuse, NY, 2003.

(36) Harding, S. G.; Wessman, D.; Stenström, S.; Kenne, L. Water Transport during the Drying of Cardboard Studied by NMR Imaging and Diffusion Techniques. *Chem. Eng. Sci.* **2001**, *56*, 5269.

(37) Bernada, P.; Stenström, S.; Månsson, S. Experimental Study of the Moisture Distribution inside a Pulp Sheet Using MRI. Part I: Principles of the MRI Technique. *J. Pulp Paper Sci.* **1998**, *24* (12), 373.

(38) Bernada, P.; Stenström, S.; Månsson, S. Experimental Study of the Moisture Distribution inside a Pulp Sheet Using MRI. Part II: Drying Experiments. *J. Pulp Paper Sci.* **1998**, *24* (12), 380.

(39) Hojjatie, B.; Abedi, J.; Coffin, D. W. Quantitative Determination of In-Plane Moisture Distribution in Paper by Infrared Thermography. *Tappi J.* **2001**, *84* (5), 71.

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