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Temperature Polarization Coefficients in Membrane Distillation

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ABSTRACT

Membrane distillation is a membrane process in which two liquid phases at different temperatures are separated by a microporous hydrophobic membrane. The membrane plays the role of a physical support for the vapor–liquid interface. The aim of this paper is to study pure water transport by membrane distillation through a PTFE flat membrane. The dependence of the phenomenon on average temperature and recirculation rate at the membrane sides is investigated. The influence of these operating conditions on water transport is discussed by taking into account mass and heat transfer within the membrane and the adjoining liquid phases. The concept of temperature polarization is introduced into the transport equations and shown to be important in the interpretation of our experimental results.

INTRODUCTION

Membrane distillation is a temperature-driven process in which two liquids or solutions at different temperatures are separated by a microporous membrane. The liquids or solutions must not wet the membrane, so that only vapor (and not liquid) is present in the pores. In this way the imposed transmembrane temperature gradient induces a vapor pressure gradient across the hydrophobic microporous membrane. The vapor molecules will migrate through the mem-

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brane from the high vapor pressure side (where they evaporate) to the low vapor pressure side (where they condense). Therefore, the driving force for mass transfer is the difference in water vapor pressure on either side of the membrane. To avoid wetting, the maximum pore size must be small (<1 μm) and the surface tension of the liquid high. Hydrophobic microporous membranes such as those made from polypropylene (PP), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF) meet these requirements. Extensive information about the state-of-the-art of membrane distillation can be found in the recent review of Lawson and Lloyd (1).

Heat transfer plays an important part in mass transfer through these membranes: the vapor flux varies with the temperature difference between the membrane walls, and this difference depends, to a large extent, on the heat transfer characteristics of the membrane module. In fact, the need to supply heat to the evaporation surface of the membrane means that the temperature gradients must be in the liquid phase adjacent to the membrane. The same occurs in the condensation surface side. In this way the effective temperature difference between the two sides of the membrane is lower than the temperature difference between the bulk solutions.

This loss of driving force brought about by thermal gradients in the fluids bounding the membrane is known as temperature polarization. This concept was introduced by Vink and Chisthi (2) after studying another transport phenomenon (thermal osmosis) through membranes; it is also based on the existence of a temperature gradient between the two sides. The importance of this polarization phenomenon in thermal osmosis has been analyzed by Bellucci (3), but it is frequently ignored when analyzing the distillation process using membranes. Nevertheless, a number of studies have appeared recently in the membrane distillation literature with the main purpose of examining the influence of temperature polarization on membrane distillation performance (4–10). In each of these studies the authors showed that temperature polarization can have a significant effect on the flux. The aim of the present work is to show this effect for the different system we here study. Mass and heat transfer theories are applied to membranes and their adjoining fluids in a way similar to the work of Schofield et al. (4).

EXPERIMENTAL

One PTFE membrane has been studied. This membrane is marketed by Gelman Instruments Co. as TF-1000 with a nominal pore size of 1.0 μm and a porosity of 0.80. This membrane has limited mechanical strength, and in practice it must be supported by a net. It is therefore a composite membrane formed by an actual porous PTFE layer with a thickness of 60 μm on a

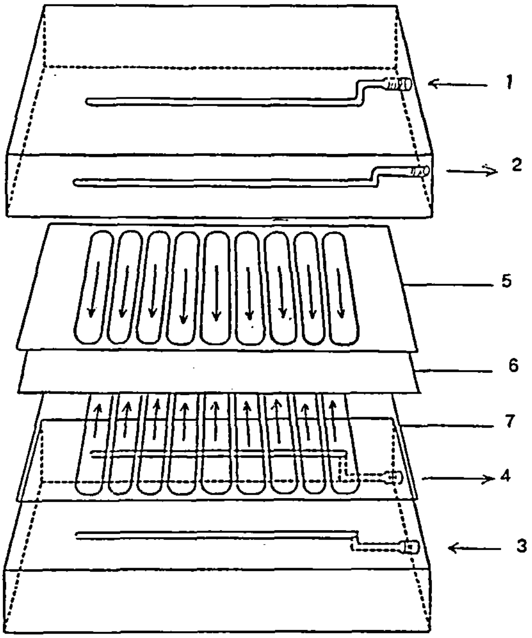

FIG. 1 Membrane holder. Entrance (1) and exit (2) of cold water; entrance (3) and exit (4) of hot water; silicone separators (5) and (7), and membrane (6).

polypropylene screen support which has a pore diameter greater than 500 μm.

The liquid employed in the experiments was pure, doubly distilled, deionized water.

The membrane cell is a tangential filtration cell manufactured by Millipore Corporation as Minitan-S. It is schematically shown in Fig. 1. In this membrane cell a flat sheet membrane separates the distilland and the distillate liquid phases. Both hot (distilland) and cold (distillate) liquid phases are formed by nine prismatic channels (provided by each silicon sheet) of approximately 0.45 × 7.0 × 55.0 mm, giving an effective membrane area of 34.65×10^{-4} m^2. The cold and hot liquids are preheated in each corresponding thermostatic bath and are then pumped across the membrane in countercurrent directions (Fig. 2).

The recirculation rate, temperatures, and pressures were monitored. The pressures were measured at the entrances of the hot and cold liquids. The temperatures of the water were measured at the entrances ($T_{b1\text{-in}}$, $T_{b2\text{-in}}$) and exits ($T_{b1\text{-out}}$, $T_{b2\text{-out}}$) of the membrane cell (Fig. 3) with thermocouples of a

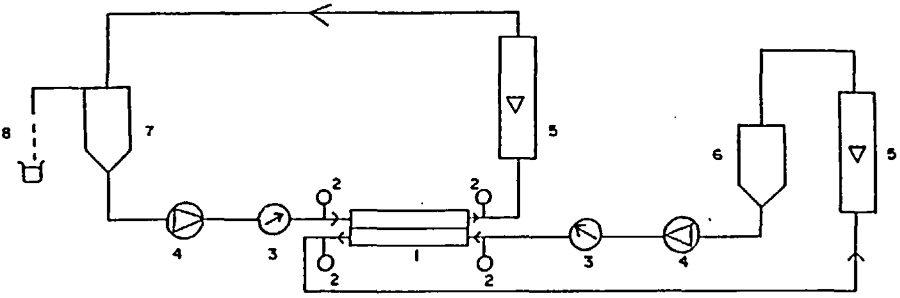

FIG. 2 Experimental device. Membrane cell (1), thermocouple (2), pressure transducer (3), pump (4), flowmeter (5), hot tank (6), cold tank (7), and distillate water (8).

sensitivity of ±0.1°C. The average values of the temperature T_{b1}, T_{b2}, and T_b and of the temperature difference ΔT_b between the bulk phases at both sides of the membrane were calculated as

$$T_{b1} = \frac{T_{b1\text{-in}} + T_{b1\text{-out}}}{2}$$

$$T_{b2} = \frac{T_{b2\text{-in}} + T_{b2\text{-out}}}{2}$$

$$T_b = \frac{T_{b1} + T_{b2}}{2}$$

$$\Delta T_b = T_{b1} - T_{b2}$$

As mentioned in the Introduction, due to the existence of temperature gra-

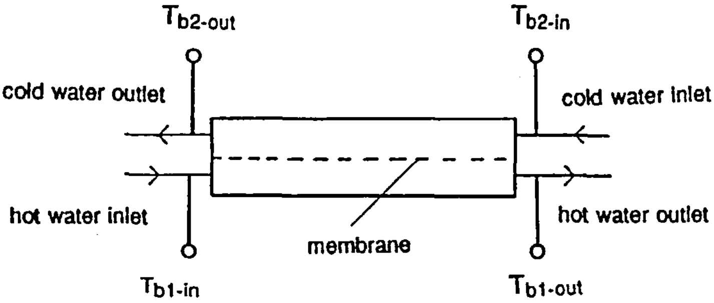

FIG. 3 Fundamental process flow diagram of membrane cell.

dients in the liquid phases adjacent to the membrane, this ΔT_b is higher than the actual temperature difference between both sides of the membrane. Therefore, we have used the following in order to differentiate them:

$$\Delta T_m = T_{m1} - T_{m2}$$

where T_{m1} and T_{m2} are the average temperatures of the hot and cold membrane sides, respectively.

The distillate flux is measured by timing and weighing the water which overflows out of the capillary attached to the top of the cold reservoir.

In the present work a series of experiments was been performed. In each experiment a temperature difference was maintained between the thermostatic baths, and the corresponding mass flux through the membrane was measured for different recirculation rates on both sides of the membrane. Different experiments were carried out for different temperatures.

THEORY

In membrane distillation, coupling between heat and mass transfer arises. The transmembrane temperature difference may not only result in heat transfer but can also lead to mass transfer. In this case a concentration gradient is set up as a result of the nonuniformity of the temperature T, and the water flux is given according to the theory of nonequilibrium thermodynamics (11) as

$$J = \frac{\epsilon}{\chi}\left[D\nabla c + L\frac{\nabla T}{T}\right] \tag{1}$$

where ϵ is the membrane porosity, χ is the tortuosity factor, D is the diffusion coefficient of water vapor at the average temperature in the membrane, c is the water vapor concentration (which for low pressures may change for the expression pM/RT), and L is the coupling coefficient. Therefore, the total flow of water vapor is made up of two terms: the diffusion flow proportional to the concentration gradient and a thermal diffusion flow dependent on the transmembrane temperature gradient. However, as indicated by Katchalsky and Curran (11) and measured by Banat and Simandl (12), the thermal diffusion coefficient is found to be smaller by a factor of 10^2 to 10^3 than the ordinary diffusion coefficient for gases, which causes the thermal diffusion contribution toward the mass flux through the membrane to be minimal. In this way and for sufficiently small transmembrane temperature differences, the following linear relation between flux and vapor pressure difference can be obtained:

$$J = C(p_1 - p_2) \tag{2}$$

This relation is commonly accepted in studies of membrane distillation (1, 4, 13, 14) to show that the vapor pressure difference through the membrane

$(p_1 - p_2)$ determines the J flow rate. In Eq. (2), C is a parameter that has different expresions depending on the transport mechanism which takes place through the membrane. The following transport mechanisms can be considered.

1. When noncondensable gases are contained in the pores of the membrane (e.g., air) as stagnant film, the molecular diffusion model applies approximately:

$$J = C_D(p_1 - p_2)$$

where C_D includes, inter alia, the diffusion coefficient and the mole fraction of air.

2. A convective flow through the pores is possible when the air has been eliminated from the membrane, for instance by vacuum. The Poiseuille flow model applies when the mean free molecular path for the water vapor molecules is small compared with the pore size:

$$J = C_P(p_1 - p_2)$$

In this case C_P includes, for instance, the pore radius and the viscosity.

3. In most cases the pore sizes and the mean free molecular paths in the membrane distillation process are of the same order of magnitude. Here, the Knudsen diffusion model applies:

$$J = C_K(p_1 - p_2)$$

The three models suggest a description of the transport given by Eq. (2), C representing a parameter which is constant only for certain pore radii, membrane thicknesses, combinations of substances, amount of air in the pores, and temperature range.

As vapor pressures within the membrane are not directly measurable, it is convenient to express Eq. (2) in terms of temperatures:

$$J = C\left[\frac{dp}{dT}\right](T_{m1} - T_{m2}) \tag{3}$$

Equation (3) is a good approximation for values of $T_{m1} - T_{m2} < 10°C$. In addition, dp/dT can be evaluated from the Clausius–Clapeyron equation at the average membrane temperature. Since, as opposed to the temperatures T_{b1} and T_{b2}, the temperatures T_{m1} and T_{m2} are difficult to measure, T_{b1} and T_{b2} are, as a rule, inserted in the above equation. In order to do this, we must use the heat-transfer coefficients (h_1, h_2) in the liquid films near the membrane, the latent heat transfer (λ) accompanying the vapor flux, and the thermal conductivity of the membrane (k_m). In this way, for the stationary transmembrane thermal flux across the membrane system we can write

$$h_1(T_{b1} - T_{m1}) = \frac{k_m}{\delta}(T_{m1} - T_{m2}) + J\lambda = h_2(T_{m2} - T_{b2}) \tag{4}$$

where k_m for the porous membrane can be calculated as

$$k_m = \epsilon k_g + (1 - \epsilon)k_s$$

with k_g and k_s the thermal conductivities of the gas phase and of the solid phase, respectively.

Equations (3) and (4) show that the process is characterized by a simultaneous mass and heat transfer in the membrane and in the external liquid phases. In fact, as indicated by Eq. (3), the driving force for a transmembrane mass transfer is related to the temperature difference between the evaporation and condensation surfaces, $T_{m1} - T_{m2}$, which, in turn, as indicated by Eq. (4), depends on the heat-transfer rate in the liquid phases. Here, we introduce the temperature polarization coefficient, τ, defined as (1)

$$\tau = \frac{T_{m1} - T_{m2}}{T_{b1} - T_{b2}}$$

This coefficient represent the fraction of the total thermal driving force ($T_{b1} - T_{b2}$) that contributes to the mass transfer driving force ($T_{m1} - T_{m2}$). The τ coefficient so defined is commonly used as a measure of the relative role played by the mass transfer resistance of the membrane and the heat transfer resistance of the liquid phases. So, in the case of very fast heat transfer in the liquid phases, the T_{m1} temperature approaches the bulk temperature T_{b1}, and T_{m2} to T_{b2}, resulting in $\tau \rightarrow 1$; in this case the process rate is completely controlled by the transmembrane mass-transfer resistance.

On the other hand, for a low heat transfer value and a large C value, the T_{m1} approaches T_{m2} and $\tau \rightarrow 0$; in this case the process rate is completely controlled by the heat transfer resistance in the liquid phases.

In order to calculate τ, we can deduce from Eqs. (3) and (4)

$$T_{m1} - T_{m2} = \frac{1}{1 + \frac{H}{h_1} + \frac{H}{h_2}}(T_{b1} - T_{b2}) = \tau(T_{b1} - T_{b2}) \qquad (5)$$

where

$$H = C\lambda \frac{dp}{dT} + \frac{k_m}{\delta} \qquad (6)$$

and

$$\tau = \frac{1}{1 + \frac{H}{h_1} + \frac{H}{h_2}} = \frac{1}{1 + \frac{H}{h}} \qquad (7)$$

with

$$h = \frac{1}{\frac{1}{h_1} + \frac{1}{h_2}}$$

being the overall film heat transfer coefficient in the liquid boundary layers of the membrane.

From Eqs. (3) and (5)

$$\frac{T_{b1} - T_{b2}}{J\lambda} = \frac{1 + \dfrac{k_m}{\delta h}}{C\lambda \dfrac{dp}{dT}} + \frac{1}{h} \tag{8}$$

Equation (8) may be used for the analysis of experimental results for which T_{b1}, T_{b2}, and J are reported because (dp/dT) is a function of the average temperature in the membrane. As the temperature difference $(T_{b1} - T_{b2})$ is small in all experiments and in spite of the membrane assymetry, we assume that the average temperature in the membrane is $(T_{b1} + T_{b2})/2$. On the other hand, as K_m/δ can be estimated, the only unknowns in Eq. (8) are h and C. A plot of $(T_{b1} - T_{b2})/J\lambda$ vs $1/(dp/dT)$ should yield an intercept of $1/h$ and a slope of $(1/C\lambda)(1 + K_m/\delta h)$, from which C may be obtained. As a consequence, τ may be calculated from Eqs. (6) and (7).

RESULTS AND DISCUSSION

As previously mentioned, experiments were carried out for fixed temperatures in the membrane module. In all the experiments $\Delta T_b = 10°C$, while the average temperatures T_{b1} varied from 20 to 50°C at steps of about 7°C, and T_{b2} from 10 to 40°C, also at steps of about 7°C.

In each experiment the liquid recirculation rate v was the same (except for small fluctuations, always under 5%) on both sides of the membrane. This rate varied in the different experiments from 9.0 ± 0.2 to 15.0 ± 0.6 cm^3/s. Having in mind that the membrane module have nine flow channels each with cross sections of 0.45 mm × 7.0 mm, the average linear velocities of the recirculating fluid varied in the experiments from 31.7 to 52.9 cm/s. At a temperature of 30°C, these values correspond to Reynolds numbers of 334 and 558, respectively.

The pressures measured at the entrances of hot and cold liquids (Fig. 2) were similar in all the experiments and varied from 1.1×10^5 Pa when the lower recirculation rate is used up to 1.3×10^5 Pa for the higher recirculation rate.

In Fig. 4 the distillate fluxes are displayed as function of the imposed average temperatures for different recirculation rates. The maximum error in the flux measurement was 2% of its own value. We can see how the distillate flow monotonically increases with the recirculation rate. Also, the flux increases when the temperature in the membrane increases.

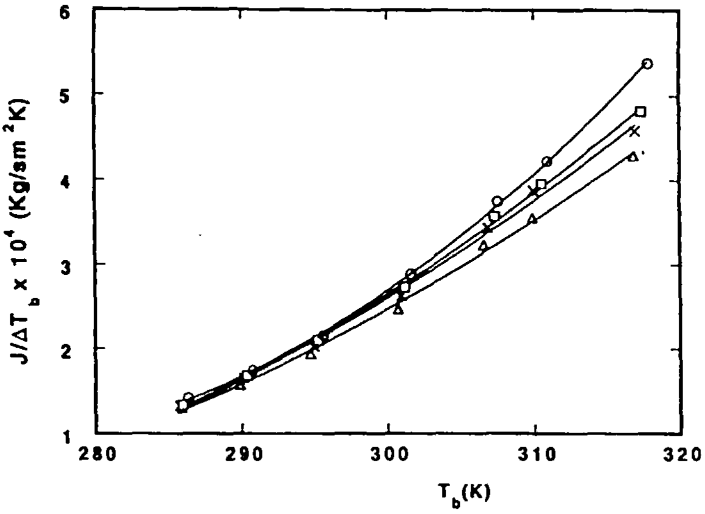

FIG. 4 Water flux through the membrane vs average temperature. The different symbols correspond to different recirculation rates. (Δ) 9 $cm^3 \cdot s^{-1}$, (×) 11 $cm^3 \cdot s^{-1}$, (□) 13 $cm^3 \cdot s^{-1}$; (O) 15 $cm^3 \cdot s^{-1}$.

In order to interpret these flux results and to calculate the temperature polarization coefficients, plots of Eq. (8) for the experimental water flux corresponding to the same recirculation rate and different average temperatures have been carried out. In this equation, dp/dT is evaluated for the T_b average temperature. In order to minimize errors in all the experiments, the overall temperature difference is only 10°C. In the same way, for the different experiments, the measured $T_{b1\text{-in}} - T_{b1\text{-out}}$ and $T_{b2\text{-out}} - T_{b2\text{-in}}$ differences were small (between 0.3 and 0.7°C, depending on the different recirculation rates). The corresponding plots of Eq. (8) are shown in Fig. 5 and have a correlation coefficient >0.99. This linearity of the data provides support for the form of Eq. (8) for average temperatures from 13 to 45°C and for $(T_{b1} - T_{b2})$ equal to 10°C.

The h values obtained from the intercept of plots of Eq. (8) are shown in Table 1 as a function of the recirculation rate. These h values show an important increase with the recirculation rate. They are global heat transfer coefficients that include the individual boundary layer heat transfer coefficients h_1 and h_2 (Eq. 7). As a consequence, the obtained increase of h is due to the increase of h_1 and h_2 in accordance with the theory of heat transfer of liquid films (15).

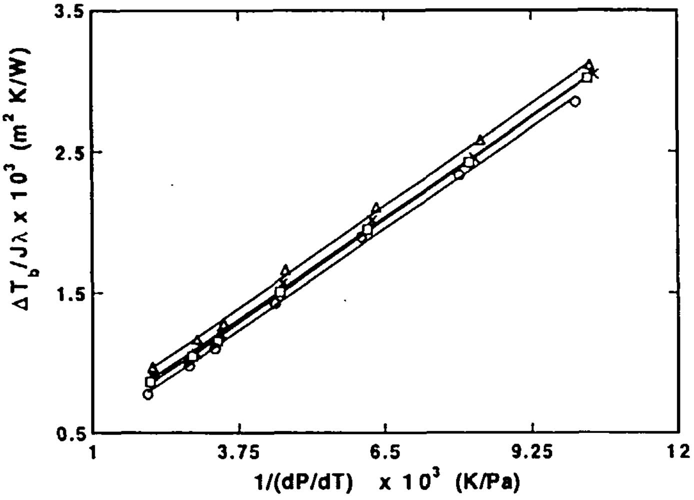

FIG. 5 Plots of Eq. (8). Symbols as for Fig. 4.

In order to evaluate the C coefficients from the slope of plots of Eq. (8), the thermal conductivity of the porous membranes k_m was estimated from the values of $K_g = 0.027$ W·m^{-1}·K^{-1} and $K_s = 0.22$ W·m^{-1}·K^{-1} found in the literature (16, 17). In this way the C values shown in Table 1 were obtained. Because the membrane pore size is 1 μm and taking into account that air is present in these pores, we can expect molecular diffusion to be predominant. This fact would explain why C decreases as the recirculation rate increases, taking into account that when the recirculation rate increases, the air pressure in the pores also increases. As mentioned above, the h and C values allow us to interpret the flux results in Fig. 4 and also to quantify the τ coefficient.

TABLE 1
h and *C* Results for Different Recirculation Rates

v (cm^3·s^{-1})	h (W·m^2·K^{-1})	$C \times 10^7$ (kg·m^{-2}·s^{-1}·Pa^{-1})
9	2512 ± 190	22.4 ± 0.9
11	2880 ± 170	21.8 ± 0.6
13	3340 ± 110	20.7 ± 0.3
15	3864 ± 300	20.2 ± 0.6

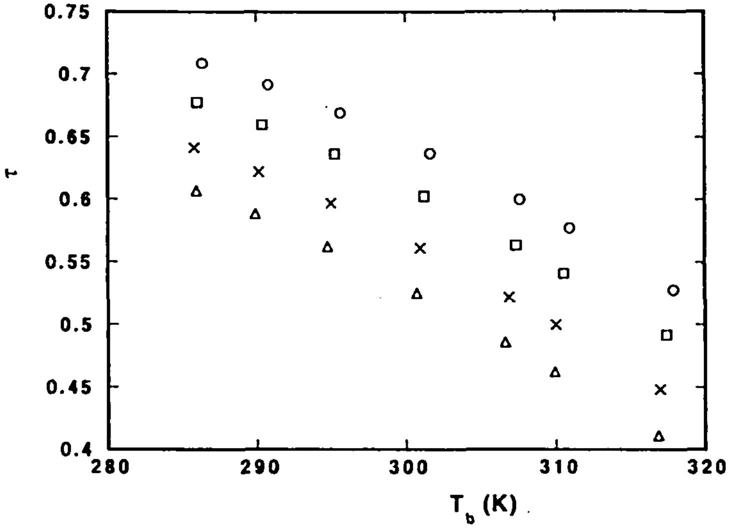

FIG. 6. Temperature polarization coefficient vs temperature. Symbols as for Fig. 4.

In fact, the observed increased of the distillate flux with the recirculation rate corresponds with the obtained increase of the heat transfer coefficient, despite the low decrease of the *C* coefficient. When the recirculation rate is varied from 9.0 to 15.0 cm^3/s, the distillate flux increases by 25% more or less.

On the other hand, we know that the distillate flux increases with temperature because (dp/dT) also increases. Nevertheless, when the temperature is varied from 13 to 45°C, (dp/dT) increases fivefold while the distillate flux increases approximately fourfold. In order to explain this last result, we have calculated the τ coefficient. Figure 6 shows the results obtained, where we can see that τ decreases with temperature. The larger mass fluxes obtained as the temperature increases involve more important heat fluxes through the liquid phases, so that the resistance offered by heat transfer in the liquid phases increases in relation to the resistance to a transmembrane mass transport. As a consequence, τ decreases and the fluxes do not increase proportionally to (dp/dT).

In addition, the τ values obtained (ranging from 0.7 to 0.4) make evident that in the studied system only a fraction (ranging from 7 to 4°C) of the 10°C of temperature difference imposed contributes to the mass transfer driving force $(T_{m1} - T_{m2})$.

On the other hand, as the τ results obtained are significantly different from 0 and 1, we cannot conclude if the mass flux is controlled by the mass transfer resistance through the membrane or by the heat transfer resistance of the liquid phases. It is likely that none of these resistances plays a predominant role.

Finally, we can obtain more important fluxes but with a lower coefficient τ when operating at a high temperature. We can increase this τ value, and therefore the distillate flux, by increasing the recirculation rate.

NOMENCLATURE

C	membrane coefficient ($kg{\cdot}m^{-2}{\cdot}s^{-1}{\cdot}Pa^{-1}$)
c	concentration of water vapor ($kg{\cdot}m^{-3}$)
D	diffusion coefficient of water vapor ($m^2{\cdot}s^{-1}$)
H	membrane heat transfer coefficient ($W{\cdot}m^{-2}{\cdot}K^{-1}$)
h	film heat transfer coefficient ($W{\cdot}m^{-2}{\cdot}K^{-1}$)
J	mass flux ($kg{\cdot}m^{-2}{\cdot}s^{-1}$)
k	thermal conductivity ($W{\cdot}m^{-1}{\cdot}K^{-1}$)
k_m	thermal conductivity of the membrane ($W{\cdot}m^{-1}{\cdot}K^{-1}$)
k_g	thermal conductivity of the air ($W{\cdot}m^{-1}{\cdot}K^{-1}$)
k_s	thermal conductivity of the solid phase of the membrane ($W{\cdot}m^{-1}{\cdot}K^{-1}$)
L	coupling coefficient ($kg{\cdot}m^{-1}{\cdot}s^{-1}$)
M	molecular weight ($kg{\cdot}mol^{-1}$)
p	pressure of water vapor (Pa)
R	gas constant ($J{\cdot}mol^{-1}{\cdot}K^{-1}$)
T	temperature (K)
T_b	mean temperature in the bulk phases (K)
T_m	mean temperature at membrane surface (K)
v	liquid recirculation rate ($m^3{\cdot}s^{-1}$)

Greek Letters

χ	tortuosity factor (—)
ΔT_b	mean temperature difference between the bulk phases (K)
∇c,	concentration gradient ($kg{\cdot}m^{-4}$)
ΔT_m	mean temperature difference between the membrane surfaces (K)
∇T	temperature gradient ($K{\cdot}m^{-1}$)
δ	membrane thickness (m)
ϵ	porosity (—)
λ	latent heat of vaporization ($J{\cdot}kg^{-1}$)
τ	polarization coefficient (—)

Subscripts

in, out	defined in Fig. 3

1	hot-water phase
2	cold-water phase
D	molecular diffusion model
K	Knudsen diffusion model
P	Poiseuille diffusion model

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