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Low Temperature Distillation through Hydrophobic Membranes

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ABSTRACT

The use of hydrophobic porous membranes makes it possible to maintain liquid-vapour interfaces localized at a membrane surface. Based on that, thermally driven separation processes were obtained through the membrane and thoroughly analyzed both experimentally and theoretically. Two experimental conditions were used: i) the porous membrane is in direct contact with two liquid aqueous phases on both sides and the vapour phase is trapped inside the pores (capillary distillation); ii) on one side of the porous membrane there is a warm aqueous solution, while an additional gaseous gap is maintained on the opposite side of the porous membrane ; the vaporizing component diffuses through the entire gas phase and condenses at a cold surface confining the gaseous gap (cold wall distillation).

The mathematical model, describing both the separation rate and the energy flux is presented and compared with the experimental results. The influence of the gas membrane thickness is also discussed.

1. INTRODUCTION

Various separation processes based on the use of hydrophobic membranes have been recently proposed. They are all based on the fact that when a non-wetting liquid faces a porous membrane a fixed interface is formed at the pores entrance. Thus a porous membrane may be used for gas absorption (1), or for liquid extraction (2) purposes.

When both sides of the porous membrane are in contact with non wetting liquids, a gasous phase, usually containing air, is entrapped within the pores; thus, under an appropriate driving force, mass transfer across the "gas membrane" occurs.

Gas membranes supported by hydrophobic porous membranes have been used for iodine and for ammonia separation by Imai et al. (3) and for the separation of bromine by Zhang and Cussler (4).

The membrane distillation here considered is a gas membrane separation process in which a temperature difference is the driving force; more precisely the true driving force for mass transfer is a partial pressure gradient across the gas membrane, sustained by an applied temperature difference.

The process may be attractive for ultrapure water production, for desalination of brackish or sea waters or for the concentration of dilute aqueous solutions. The main advantage over traditional distillation processes is associated with the possibility of using low temperature energy sources.

In previous papers (5,6) the present authors presented results on the separation process through flat PTFE porous membranes, as well as the relevant mathemathical model,which proved to be in good agreement with experimental data. In the present work the role played by various parameters is further investigated both experimentally and theoretically. The influence of the membrane thickness on the mass flux is considered in some detail.

Results on evaporation experiments through very thick gas membranes are presented and the theoretical model is suitably extended to account also for the presence of a thick air gap.

2. EXPERIMENTAL

a) Apparatus and procedure

The equipment used in the present investigation is the same detailed in ref. 5: a PTFE membrane separates two cylindrical chambers 6.1 cm in diameter and 1 cm depth; by circulating thermostated fluids through the jakets, the bottoms of the two chambers are maintained at two fixed temperatures ; the temperature values are recorded by two thermocouples sealed at the bottoms of the cells.

Commercial PTFE membranes, manufactured by Gelman Instruments Co. as TF 200, were used. They are composite membranes formed by an actual porous PTFE layer 60 μm thick supported by a polypropylene mesh. The nominal pore size is .2 μm the void fraction nearly .6 and the penetration pressure for water is nearly 3 bar (6).

In all experiments,the warm semicell contained an aqueous solution, kept in direct contact with the membrane; a continuous flow of solution was maintained in order to obtain steady state concentration values.

The following two types of experiments were performed (Fig.1):

i) the cold semicell containes liquid distilled water, therefore the vapour, diffusing through the membrane pores, condenses at the cold membrane surface (simple capillary distillation, CD).

ii) the cold semicell containes an additional air gap in direct contact with the membrane; thus the vapour diffuses through the membrane pores and then through the air gap, while condensation takes place at the cold external walls of the semicell (cold wall distillation

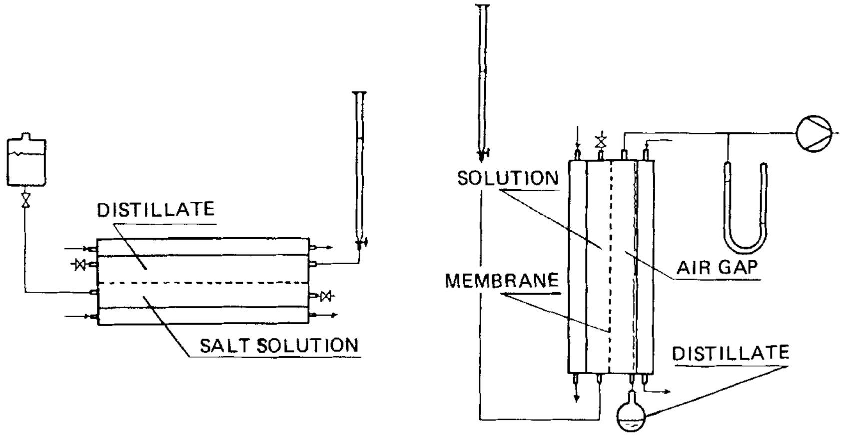

Fig. 1. Experimental Apparatus
left: Capillary Distillation
right: Cold Wall Distillation

CWD). The pressure in the cold semicell is controlled; different pressure values were maintained by connecting the semicell with a vacuum pump. In all cases, however, pressure was always kept at values larger than the water vapour pressure.

Indeed, both operations are membrane distillation processes or gas membrane separations; in the capillary distillation the "gas membrane" is only that immobilized within the pores, while in the cold wall distillation the "gas membrane" is formed by the overall air gap, in addition to the gas contained within the pores. Essentially the two types of experiments differ from each other for the gas membrane thickness (60 µm in CD and 1cm in CWD).

In the capillary distillation experiments three different orientation of the cell were investigated:
- Horizontal cell, Warm Top (WT), in which the higher temperature is maintained in the upper semicell.
- Horizontal cell, Warm Botton (WB), in which the higher temperature is maintained in the lower semicell.
- Vertical cell.

In all the cold wall distillation experiments the cell was placed in vertical position.

The total transmembrane flux was recorded under steady state conditions.

b) Results.

In the capillary distillation the separation rate greatly depends on the orientation of the apparatus.

Results for the Warm Top (WT) case were extensively reported in ref.5; the main features of the WT configuration are as follows:

- The flux is a linear function of the temperature difference (ΔTb) between the semicell bottoms.
- The slopes of the flux vs. ΔTb lines are independent of the concentration and increase by increasing the average temperature.
- The effect of an increase in the solute concentration is an increase in the threshold value, ΔTb°, which must be overcome in order to obtain a flux from the solution towards the pure water; that effect results in an horizontal shift for the flux vs. ΔTb lines.

In the Warm Bottom (WB) case and in the vertical cell position the flux is much larger than in the WT (approximatively 4 to 6 times, for the experimental conditions inspected) and the flux is no longer linear in ΔTb. Extensive results for WB are reported in ref. 6. It was shown that the larger flux observed in the WB case and in the vertical cell position is clearly due to the effect of free convection which enhances the heat transfer rate; as a consequence, the temperature difference across the membrane , ΔT , which is the true driving force for mass transfer, is increased with respect to the WT case, in which only pure conduction of heat takes place through the liquid phases.

In Fig. 2 the typical results for Cold Wall Distillation are reported and compared with the flux observed in capillary distillation experiments under the same conditions (vertical cell).

It is worth observing that the flux in CWD is smaller than in CD, but not so drammatically as one could expect.

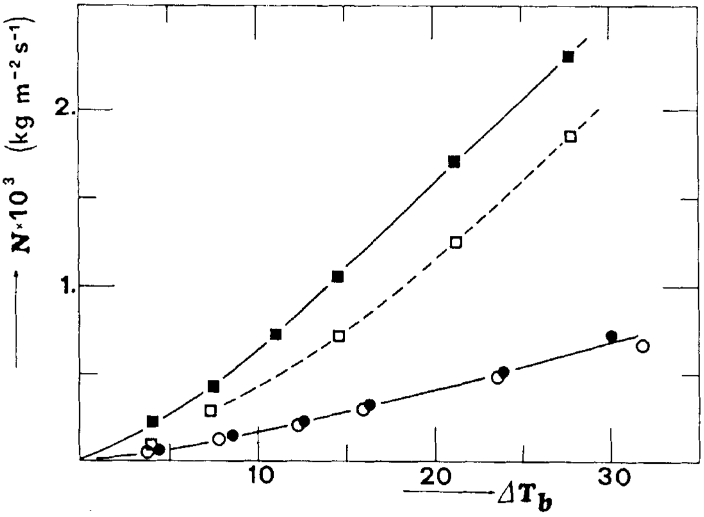

Fig. 2. Water flux vs. ΔTb at Tm=50°C and P=1 bar for Capillary Distillation (■ water, □ NaCl .5 M) and for Cold Wall Distillation (● water, o NaCl .5 M)

Indeed the ratio between the thickness of the gas membranes is nearly 170, while the two fluxes differ from each other only by a factor of nearly 4. Thus the membrane thickness does not seem to play a crucial role in the membrane distillation performance. It is noteworthy to point out, in addition, that while for very thin gas membranes, as those used in CD, the flux depends on the salt concentration , for very thick membranes, as those used in CWD, nearly the same values of the flux are observed both from pure water and from salt solutions.

In Figs. 3 and 4 the flux data are reported vs. ΔTb for the cold wall distillation experiments, at various pressures and average temperatures.

3. MODEL DESCRIPTION FOR HEAT AND MASS TRANSFER ACROSS GAS MEMBRANES.

Let us consider two aqueous solutions kept at different temperatures and separated by a gas membrane. At

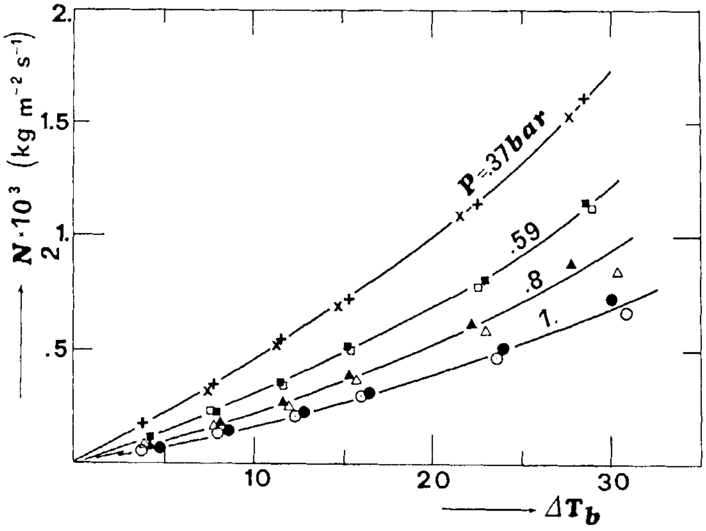

Fig 3. Cold Wall Distillation: Water flux vs. ΔTb at Tm = 50°C (●,▲,■,+ water, ○,△,□,x NaCl .5 M)

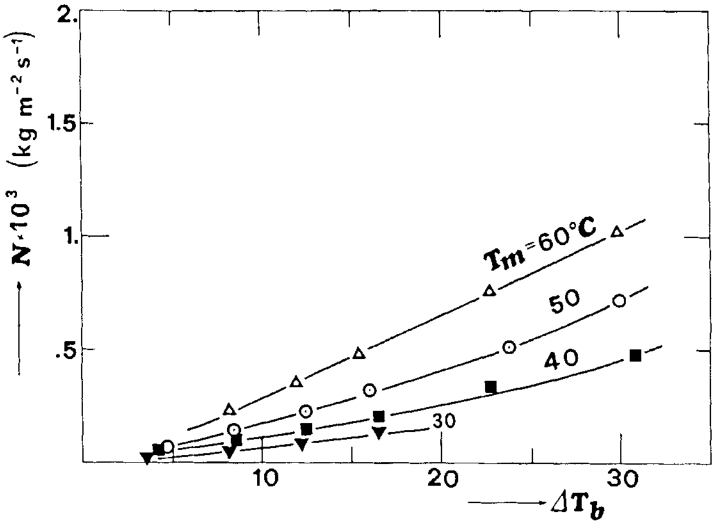

Fig. 4. Cold Wall Distillation: Water Flux vs ΔTb at P = 1 bar, pure water.

the opposite sides of the membrane, liquid-vapor equilibria hold at different temperatures and different activities; as a consequence, a temperature and concentration gredient is maintained through the membrane. The mass flux of water, N, and the energy flux, E, are given by (7):

$$N = -\frac{\varepsilon M}{\varkappa R}\left(\frac{P\mathcal{D}}{T^b}\right)\frac{T^{b-1}}{1-y}\frac{dy}{dz} \tag{1}$$

$$E = -k_p\frac{dT}{dz} + N\hat{H}_v \tag{2}$$

In Eq. 1 the term $(P\mathcal{D}/T^b)$ for a given gas pair is a constant. The exponent b is 1.5 for perfect gases, while is 1.75, after Fuller (8) and is 2.334 according to Bird-Slattery's equation (7). In any case, in the range of temperatures here investigated both Fuller's and Bird-Slattery's equations give rise to essentially the same flux, as shown in ref. 6; thus, for simplicity sake, the value of b=2 is assumed in all the calculations below.

The mass and energy fluxes are coupled through Eq. (1) and (2); however, the coefficients entering Eq. (1) can be calculated at the average temperature Tm with negligible error. Therefore, use of Eq. (1) into the mass balance equation leads to:

$$N = M\frac{\varepsilon}{\varkappa}\left(\frac{P\mathcal{D}}{T^b}\right)\frac{T_m^{b-1}}{R\delta}\ln\frac{P_{l_2}}{P_{l_1}} \tag{3}$$

The energy flux can then be evaluated. The specific enthalpy of the diffusing water vapor can be expressed as :

$$\hat{H} = \hat{\lambda} + C\,(T - T_m) \tag{4}$$

By simple integration of Eq. 2 one has:

$$E = \frac{k_p}{\delta}(T_1 - T_2) + N\left[\hat{\lambda}_m + C\frac{1}{\delta}\int_0^{\delta}(T - T_m)\,dz\right] \qquad (5)$$

The temperature profile can be evaluated in a straighforward way from the energy balance equation and put into Eq. (5). We finally obtain:

$$E = \frac{k_p}{\delta}(1 + \alpha Pe)(T_1 - T_2) + N\hat{\lambda}_m \qquad (6)$$

in which:

$$\alpha = .5 - \frac{1}{1 - Exp(Pe)} - \frac{1}{Pe} \qquad (7)$$

and

$$Pe = \frac{N\,C\,\delta}{k_p} \qquad (8)$$

The quantity Pe has the usual structure of a Peclét number, in which the bulk velocity is substituted with the velocity of the water vapour only.

It can be easily shown that $0 < \alpha < .5$; the term αPe in Eq.(7) becomes important for Peclét numbers of the order of unity. Based on the experimental results reported, the Pe number may reach values close to unity in the cold wall experiments; in that case the term αPe is as small as few percents only. On the contrary in the capillary distillation experiments the Peclet number does not exceed .01, so that α is well below .001 and the product αPe can be definitely disregarded, as has been made in ref. 5.

Steady state heat transfer considerations lead to expressions for the temperatures values T1 and T2 at the membrane interfaces , in terms of the bulk temperatures, Tb_1, Tb_2:

$$T_1 = T_{b1} - \frac{U}{h_1}\left[\Delta T_b + N\hat{\lambda}_m \frac{\delta}{k_p(1+\alpha Pe)}\right] \qquad (9)$$

$$T_2 = T_{b2} + \frac{U}{h_2}\left[\Delta T_b + N\hat{\lambda}_m \frac{\delta}{k_p(1+\alpha Pe)}\right] \qquad (10)$$

in which:

$$\frac{1}{U} = \frac{1}{h_1} + \frac{1}{h_2} + \frac{\delta}{k_p(1+\alpha Pe)} \qquad (11)$$

Linear model

For dilute solutions and for sufficiently small temperature differences across the membrane, ΔT, the model above may be simplified. Indeed, by making use of Raoult's law and of Clausius - Clapeyron equation, Eq. 3 can be written as:

$$N = K\ (\Delta T - \Delta T^{\circ}) \qquad (12)$$

in which:

$$K = M\,\frac{\varepsilon}{\chi}\left(\frac{P\mathcal{D}}{T^{b}}\right)\frac{T^{b-3}}{R^{2}\delta}\,(1 - x_m)\,\frac{P_m^{*}}{P - P_m^{*}(1 - x_m)} \qquad (13)$$

and

$$\Delta T^{\circ} = \frac{R\ T_m^{2}}{\tilde{\lambda}_m}\ \frac{\Delta X}{1 - X_m} \qquad (14)$$

is the boiling point elevation.

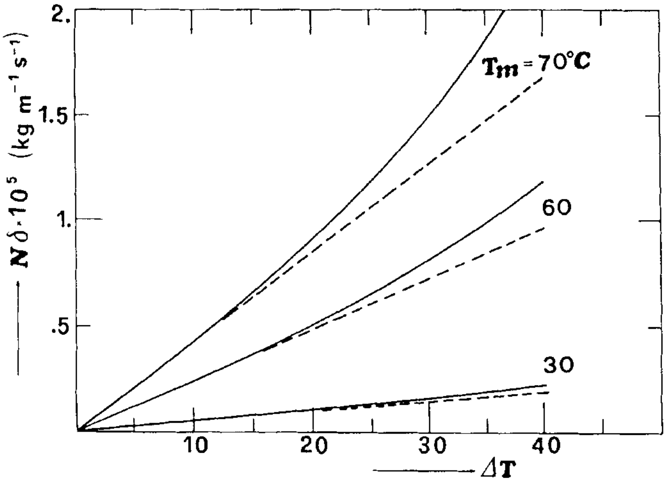

Fig. 5. Theoretical values of the water flux vs. the temperature difference across the membrane at P = 1 bar. Exact values (continuous lines) compared with the linear model predictions (dashed lines).

The use of the linear model, embodied by Eqs. (12)-(14), leads to underestimate values of the flux, but the error becomes appreciable only for membrane temperature differences larger than 15°C, as shown in Fig. 5.

The linear model thus appears to be adequate for the description of capillary distillation processes; in that case indeed, due to the low membrane thickness, the temperature difference across the membrane is certainly rather small.

Finally, the explicit dependance on the bulk temperature difference can be introduced. By making use of Eqs. (9) and (10) the water flux can be expressed as:

$$N = K_{eff}\left(\Delta T_b - \Delta T_b^{\circ}\right) \tag{15}$$

in which K_{eff} is a sort of overall effective mass transfer coefficient, calculated as:

$$\frac{1}{K_{eff}} = \frac{k_p}{K\,U\delta} - \frac{\hat{\lambda}_m}{U_L} \tag{16}$$

and the symbol $\Delta Tb°$ indicates the threshold value for the bulk temperature difference which must be overcome in order to have a positive water flux. Apparently, $\Delta Tb°$ is influenced by both heat transfer coefficient and boiling point elevation.

$$\Delta Tb° = \frac{k_p}{U\delta}\,\Delta T° \tag{17}$$

4. DISCUSSION

A direct comparison of the linear model predictions and the experimental data for capillary distillation, Warm Top case, has been presented in refs. 5,6. In that case the quantitative agreement between the theory and experiments is quite satisfactory.

In the present work Eq.(3) is synthetically compared with experimental data by plotting all the flux data for capillary distillation, WT, against $\ln(P_{I2}/P_{I1})$ (Fig.6). The interfacial temperatures T1 and T2 were calculated by assuming pure heat conduction through the liquid phases. The data refer to pure water and NaCl solutions with molar concentrations ranging from 0 to .5 mol/l, temperature differences from 0 to 20°C and average temperatures from 30 to 50°C.

It is interesting to observe that all the data reduce to a unique straight line,as Eq.(3) demands. Actually Eq.(3) predicts an explicit dependance of the slope on the average absolute temperature; however, the latter quantity only changes to within few percents in the temperature range experimentally investigated, so that no slope difference was experimentally observable.

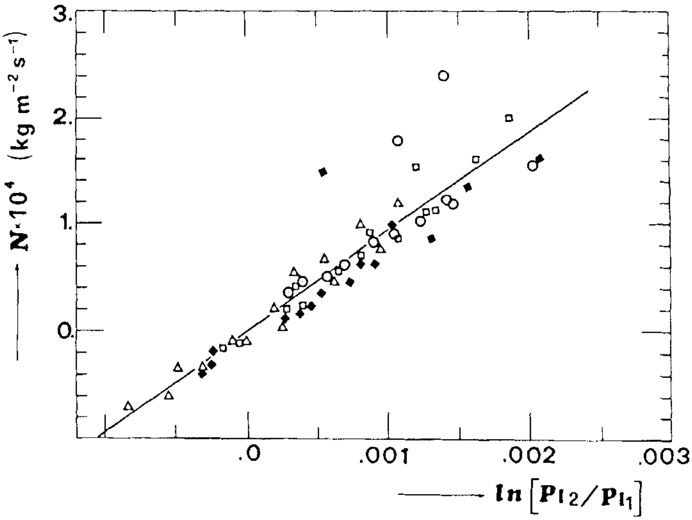

Fig. 6. Capillary Distillation, Warm Top Case: The water flux vs. $\ln(P_{I2}/P_{I1})$, ○ water, □ NaCl .1 M, ◆ NaCl .25 M, △ NaCl .5 M, The temperature difference, ΔTb, ranges from 0 to 20°C and the average temperature from 30 to 50°C

In Fig. 7 all the data for Cold Wall Distillation are replotted in similar way, again all the data at different pressures, temperatures and temperature differences, reduce to a unique straight line.

The slope of the straight line in Fig. 7 which best fits the data, is nearly twice as much as the value predicted by Eq. (3). That discrepancy, however, is not due to a failure in the underlying physical model, but rather is associated to some geometrical considerations. The theory presented is one dimensional as are indeed the experimental conditions in capillary distillation. In cold wall distillation tests, on the contrary, the membrane cross sectional area and the area of the external surface on which condensation takes place are significantly different from each other and their ratio is close to one half. That explaines the above mentioned slope difference.

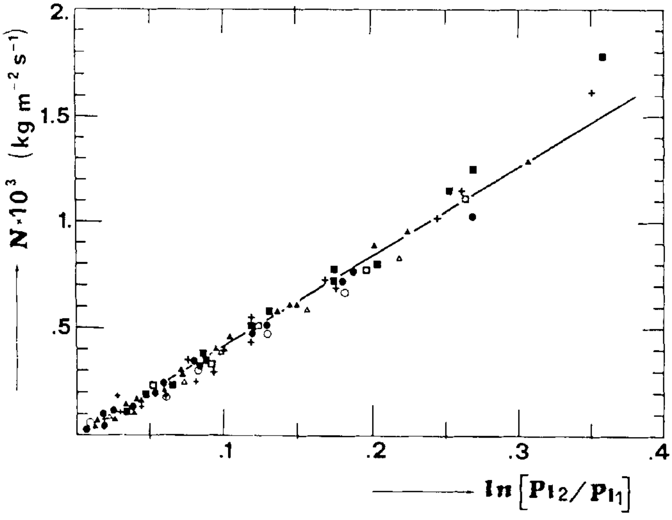

Fig. 7. Cold Wall Distillation: The water flux vs. ln(P_{l2} /P_{l1}) for pure water at P = 1 bar (●), .8 bar (▲), .59 bar (■), .37 bar (+) and for .5 mol/l NaCl solutions at the same pressures (open symbols). The temperature difference ranges from 0 to 30°C and the average temperature from 30 to 60°C.

Some comments are now in order about the calculations involved in Fig. 7. The heat transfer coefficient through the condensed liquid film, h2, has been taken as infinity, i.e. T2 = Tb2, while instead the heat transfer coefficient in the warm liquid phase, h1, has been calculated accounting for free convection. For a vertical box enclosure of thickness l and height d one has (9):

$$\frac{h\ l}{k_w} = .22 \left(\frac{Ra\ Pr}{.2 + Pr}\right)^{0.28} \left(\frac{l}{d}\right)^{0.25} \qquad (18)$$

The height d was assumed to be equal to the cell diameter. In spite of the fact that Eq.(18) can be applied only for approximate estimate purposes, due to the cylindrical shape and to the effect of the lateral surfaces, we can nevertheless accept using Eq.(18) since in cold wall distillation experiments the largest resistance to heat transfer is given by the gas membrane.

The above results clearly show that the basic mechanism of capillary distillation and of cold wall distillation is the same and it is well described by the already reported theory.

The influence of the relevant parameters in membrane distillation is now considered. The role played by some membrane properties, such as the void fraction and the thermal conductivity are obvious. Less obvious is the influence of the membrane thickness; indeed two competing effects are present: an increase in the thickness leads to a greater diffusion resistance, but the effective temperature difference ΔT is also increased. The latter effect depends on the value of the heat transfer coefficient U_L.

For very low values of the membrane thickness, say $\delta \ll k_p/U_L$, we have $U = U_L$, and Eq. (16) shows that K_{eff} becomes indipendent of δ, and so does the flux for pure water case.

Under the same operating conditions, the flux from a salt solution may increase by increasing δ due to the lowering of $\Delta Tb°$ (see Eq. 17).

For large values of the membrane thickness, say $\delta \gg k_p/U_L$, the thermal resistance of the gas membrane dominates and $\Delta T = \Delta Tb$; under these conditions the transmembrane water flux becomes proportional to $1/\delta$, according to Eq. (3).

Interestingly, while for very thick membranes the flux from a salt solution is much lower than the flux from pure water, such a difference decreases by using thicker membranes. Indeed in the former case ΔT is comparable with $\Delta T°$, while in the latter case ΔT is quite close to ΔTb, and much larger than $\Delta T°$.

The influence of the thickness and of the heat transfer characteristics, discussed above, are shown in Fig. 8. For the sake of simplicity, reference is made

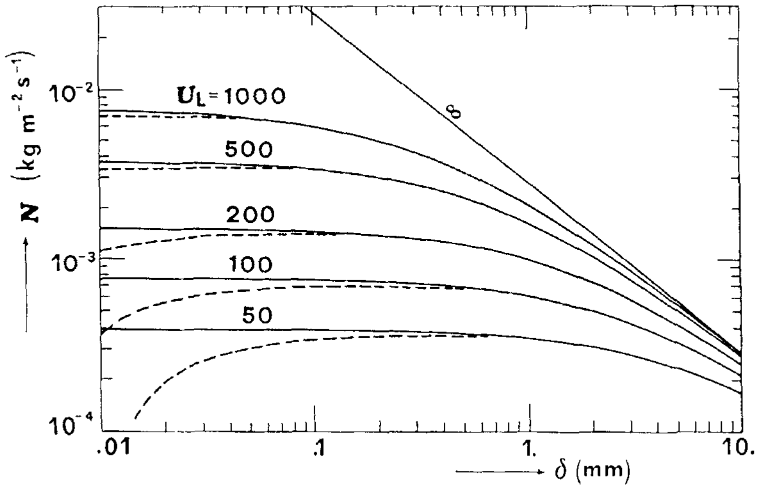

Fig. 8. The water flux vs. the gas membrane thickness at various liquid phase heat transfer coefficient, U_L(W/m K). Tm = 50°C, ΔTb = 20°C, ε = 1, χ = 1, k_p = .027 W/mK

to a hypothetical gas membrane with $\varepsilon = \chi = 1$ and k_p = .027 W/m K (the thermal conductivity of air). In addition use has been made of the following assumptions: $h_1 = h_2 = 2\ U_L$, T_m = 50°C, ΔT_b = 20°C.

Acknowledgements

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NOTATIONS

C	heat capacity
E	energy flux
H	enthalpy
h	heat transfer coefficient
K	Mass transfer coefficient, Eq. 13
K_{eff}	Overall mass transfer coefficient, Eq. 16
k	Thermal conductivity
M	Molecular weight

N	Mass flux
P	Pressure
P^*	Vapor pressure of pure water
ΔT°	Boiling point elevation
ΔTb°	Defined by Eq. 17
T	Temperature
Pe	Peclét Number
Pr	Prandl Number
Ra	Rayleigh Number
U	Overall heat transfer coefficient, Eq.11
U_L	1/(1/h1 +1/h2)
x	Ionic mole fraction
y	Mole fraction of water vapor
z	Distance along the gas membrane
α	Defined by Eq. 7
δ	Membrane thickness
ε	Void fraction
χ	Tortuosity factor
λ	Latent heat

Subscripts

1	Warm side
2	Cold side
b	Bulk
I	Inert gas (air)
ln	Logarithmic mean
m	Average value
p	Membrane
v	Vapor
w	Water
^	Specific value
~	Molar value

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