Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Swollen-Dry-Layer Model for the Pervaporation of Ethanol-Water Solution through Hydrophilic Membranes

A. Ito[a]; K. Watanabe[a]; Y. Feng[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, NIIGATA UNIVERSITY, NIIGATA, JAPAN

To cite this Article Ito, A. , Watanabe, K. and Feng, Y.(1995) 'Swollen-Dry-Layer Model for the Pervaporation of Ethanol-Water Solution through Hydrophilic Membranes', Separation Science and Technology, 30: 15, 3045 — 3060
To link to this Article: DOI: 10.1080/01496399508013127
URL: http://dx.doi.org/10.1080/01496399508013127

SEPARATION SCIENCE AND TECHNOLOGY, 30(15), pp. 3045–3060, 1995

Swollen–Dry-Layer Model for the Pervaporation of Ethanol–Water Solution through Hydrophilic Membranes

A. ITO, K. WATANABE, and Y. FENG
DEPARTMENT OF CHEMICAL ENGINEERING
NIIGATA UNIVERSITY
IKARASHI 2-8050, NIIGATA 950-21, JAPAN

ABSTRACT

A swollen–dry-layer model is presented for the pervaporation of ethanol–water solution through hydrophilic polymer membranes: poly(vinyl alcohol) and carboxymethyl cellulose. Independent measurements were conducted of the sorption equilibrium, the hydraulic permeation rates through the swollen membranes, and the permeabilities of ethanol and water vapors. The hydraulic permeabilities were estimated from the mutual diffusion coefficients of solution in the swollen membrane. Sorption behavior and hydraulic permeabilities showed a dependence on feed concentration. Vapor permeabilities of water and ethanol through dry membranes differ by a factor of about 20. Comparisons between the experimental data from the pervaporation run and the results calculated from the model were made. The model offers a quantitative explanation for the dependency of selectivity and flux on feed concentration. The model explained that the flux dependency caused by a change in the swollen–dry-layer ratio, and that the selectivity is governed by vapor permeabilities through the dry layer.

INTRODUCTION

The pioneering study of pervaporation for the separation of liquid mixtures was conducted by Binning and coworkers (1). At present, the pervaporation process is becoming recognized as an energy efficient alternative to distillation. A solution–diffusion mechanism has been widely accepted to describe the separation performance of pervaporation (2–4). Binning and coworkers (1), however, originally assumed that a membrane under the pervaporation condition consists of a solution phase zone (swollen layer) and a vapor phase zone (dry layer). This swollen–dry-layer model could be an alternate approach to describe the pervaporation process. But little attention has been paid in the past to the description of pervaporation by the swollen–dry-layer model.

Thomas and coworkers (5) studied pervaporation of water through a hydrophilic membrane by small-angle neutron scattering experiments. They reported the existence of the first layer containing water in a swollen state on the upstream side of the membrane and another layer with low water concentration on the downstream side. Recently Wijmans and Baker (6) presented a new simple predictive treatment of the permeation process in pervaporation. They expressed the drive for pervaporation as a vapor pressure difference rather than a concentration difference. Their permeation equations were based to a large extent on gas permeation experiments.

For pervaporation of aqueous solution through a hydrophilic membrane, the upstream surface of the membrane appears to be in a swollen state, and the downstream side, under equilibrium vapor pressure, seems to be in a dry state. If we assume that a membrane consists of a swollen layer and a dry layer, the transport mechanisms in these layers should be related to the liquid permeation process through a swollen membrane and the vapor permeation process through a dry polymer membrane, respectively. Vapor or gas permeation through a dry membrane has been well established.

This study deals with the pervaporation of ethanol–water solution through hydrophobic and hydrophilic polymer membranes from the standpoint of the swollen–dry-layer model. The mechanism of the pervaporation process is described as involving: 1) dissolution of the feed liquid into the membrane, 2) transport through the swollen layer, 3) evaporation of the penetrant molecules in the membrane, and 4) vapor permeation through the dry layer. Independent measurements have been made of the sorption equilibrium between solution and membrane, the hydraulic permeation rate in the swollen layer, and mixed vapor permeation. The swollen–dry-layer ratio in a pervaporation run was visualized with a dye solution. The present model could provide a simple explanation of the selectivity and the concentration dependency of flux.

EXPERIMENTAL

Membrane Preparation

The hydrophilic polymers used in this study were polyvinyl alcohol with a nonionic hydroxyl group and carboxymethyl cellulose sodium salt with a carboxyl group. The polyvinyl alcohol had a molecular weight of 600 and was photocrosslinkable, containing 1–2% of a styrylpyridinium group (Toyo Gousei Co.) (7). The carboxymethyl cellulose membrane was prepared from a mixture of 75 wt% carboxymethyl cellulose (degree of polymerization, 300–500), 20 wt% poly(acrylic acid sodium salt) (degree of polymerization, 2200–7000) as the crosslinking agent according to Reineke (8), and 5 wt% glutaraldehyde. The membranes were prepared by casting aqueous solutions (5–7 wt% solids) on hydrophilic-treated polypropylene microporous membranes of 25 μm thickness [Celgard 3501 (Daisel Chem. Ind., Ltd.)]. Evaporation of water was allowed to occur, and the films were stored under ambient conditions before use. The thicknesses of the polyvinyl alcohol or carboxymethyl cellulose dense layers were 9–60 μm.

A silicone rubber membrane was also prepared by casting a solution of silicone RTV rubber (Shinetu Chemical, Japan) in chloroform.

The membrane thickness, δ, in this study refers to the dense layer of the cast polymer and is defined in a dry state for all further experiments. Since the porosity of the support membrane was 40%, its mass transfer resistance was small enough to ignore throughout this study.

Vapor Permeability Measurement

Permeabilities of water and ethanol vapor through nonswollen or dry membranes were measured by permeation experiments with mixed vapors. The measurement system consisted of a membrane cell of 0.00235 m^2 permeation area, a gas flow system which delivered a mixture of carrier gas (helium) and binary vapor to the cell, two cold traps for the collection of permeated vapor and residual vapor, and a vacuum pump. The gas stream saturated with ethanol and water vapor was fed to the membrane cell. The vapor permeation rates were measured from the weights and concentrations of trapped permeates. Permeabilities were calculated by dividing the thickness-normalized fluxes by the vapor pressure differentials across the membrane. A heating bath surrounding the cell and saturator allows change in the ambient temperature, which was changed between 298 and 308 K to vary the driving force of vapor permeation.

Sorption Equilibrium and Diffusion Coefficients of Ethanol–Water Solution through Swollen Membrane

Sorption equilibrium of the swollen-state polymer was measured with an ethanol–water solution for the polyvinyl alcohol and carboxymethyl cellulose membrane. The liquid content of the swollen membrane was measured by weighing after it was blotted free of surface liquid. The concentration of absorbed liquid, x_m, in equilibrium with the feed concentration, x_f, was analyzed by direct sampling of absorbed liquid for $x_f < 0.65$. Absorbed liquid in the membrane was evaporated into a carrier gas and collected in a cold trap. For $x_f > 0.65$, dry pieces of membrane were immersed into a solution of known concentration. After sorption equilibrium was reached, the change in concentration was measured, and x_m was evaluated from the mass balance.

The hydraulic permeability is defined from the permeation rate of a liquid through a membrane in the swollen state, and the driving force is the pressure difference between the liquids on both sides of the membrane. For a binary solution, however, direct measurement by applying hydrostatic pressure on the feed liquid is difficult because of osmotic pressure. The mutual diffusion coefficients of a solution adsorbed in the swollen membrane were measured instead of the hydraulic permeability. A membrane was clamped between two halves of a cell with no support. Compartments of equal volume ($0.02\ m^3$) were filled with ethanol–water solutions, which had about 5 mol% difference in concentration. Samples were withdrawn from both sides of the cell at selected time intervals and analyzed to follow the concentration changes. Since no change in the level of both cells was found throughout these measurements, the effect of osmotic pressure on the diffusion process was negligible in these conditions.

Pervaporation Experiment

Pervaporation runs of ethanol–water solution were carried out with a vacuum at the downstream side below 0.4 kPa. The pervaporation apparatus was the same as that for the vapor permeation run: a feed storage tank, a circulation pump, a cold trap for permeated vapor, and a vacuum pump. All measurements were made under ambient conditions (room temperature, 295 ± 2 K). The vapor concentration and the flux were derived from the concentration and weight of the permeate collected in the trap.

Swollen/Dry Layer Ratio under Pervaporation Condition

Since the upstream surface of a hydrophilic membrane appears to be swollen by an aqueous feed solution, quantitative observation of the thickness of the swollen layer was done by a staining method. Pervaporation runs were made using a feed solution containing stain, which was amido black for the polyvinyl alcohol membrane and iron(II) chloride for the carboxymethyl cellulose membrane. After a permeation run of 5 hours, we observed the cross section of the membrane. In the case of runs with iron chloride solution, the cross section was stained with a solution of potassium ferrocyanide.

RESULTS AND DISCUSSION

Vapor Permeability

Figures 1 and 2 shows the vapor permeabilities in mixed vapor permeation runs. Permeabilities of water and ethanol vapor are plotted vs the partial pressure difference, Δp_i. The downstream partial pressures, p_{pi}, were negligibly small in all runs.

Silicone rubber is a hydrophobic membrane material, but the observed permeability of water vapor through silicone rubber is larger than that of ethanol vapor (Fig. 1). In Fig. 1 the values are compared with the data by Baker and coworkers (9), which were measured by using the Toepler pump method. For the hydrophilic membranes (Fig. 2), the permeabilities for ethanol vapor and water vapor differ by a factor of about 20.

The permeabilities presented in the figures are the values which include the mutual effects induced by mixed vapor permeation and may be different from those of pure vapor permeation. The lines in the figures were used in later calculations.

Sorption Equilibrium

Figure 3 shows the results of ethanol–water mixtures sorption experiments for the hydrophilic membranes. The concentration of absorbed liquid and the liquid content in the swollen membranes are plotted with the

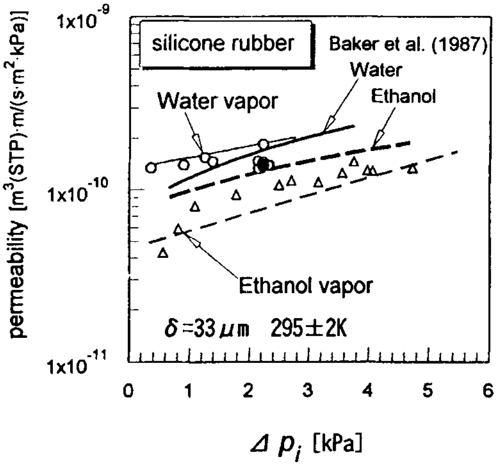

FIG. 1 Permeabilities of ethanol and water vapor through silicone rubber.

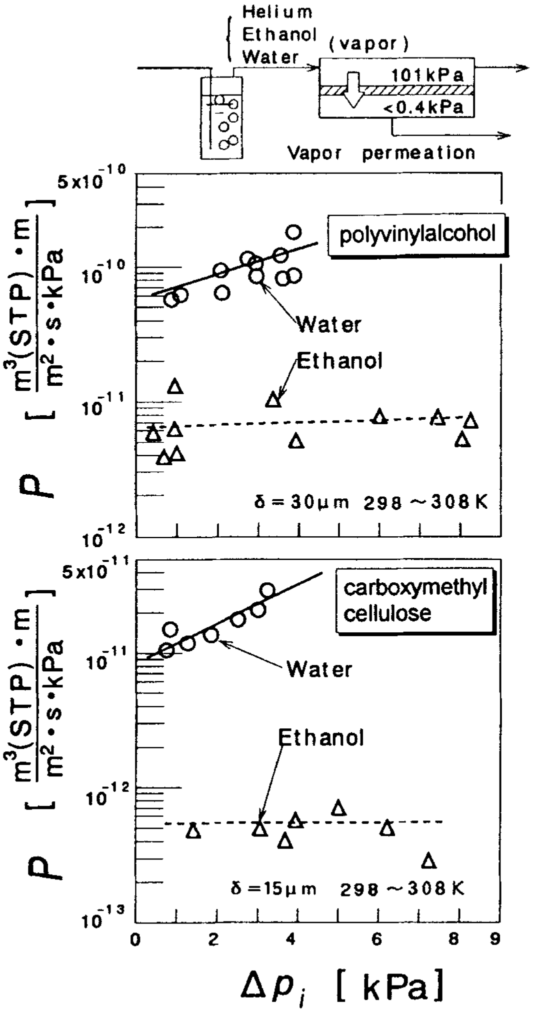

FIG. 2 Permeabilities of ethanol and water vapor through hydrophilic membranes.

feed liquid concentration, x_f. The concentration of liquid absorbed in the swollen membrane tends to be water-rich but its selectivity is not large in comparison with the selectivity of vapor mixture permeation. The degree of swelling liquid content of the swollen membrane, C_g, greatly increases with the water content in the feed solution. This large change in the degree of swelling is an important characteristic of hydrophilic polymers.

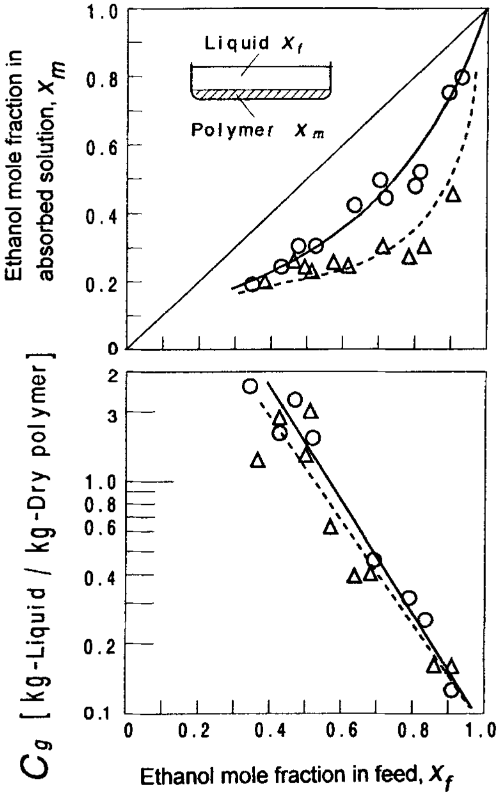

FIG. 3 Sorption equilibrium of polyvinyl alcohol and carboxymethyl cellulose in ethanol–water solution.

Diffusion of Ethanol–Water Solution through Swollen Membrane

Figure 4 is an example of the measurement of the diffusion coefficient in a swollen polyvinyl alcohol membrane. The concentration changes of solutions in both sides of the cell are shown vs time. The dashed curves are integrated values from the differential equations:

$$M_1 \frac{dx_1}{dt} = -M_2 \frac{dx_2}{dt} = -ACD\,(x_{m1} - x_{m2})/\delta \qquad (1)$$

where M is the total number of moles of the solution in each compartment and C is the mole number of the liquid per unit volume in the swollen

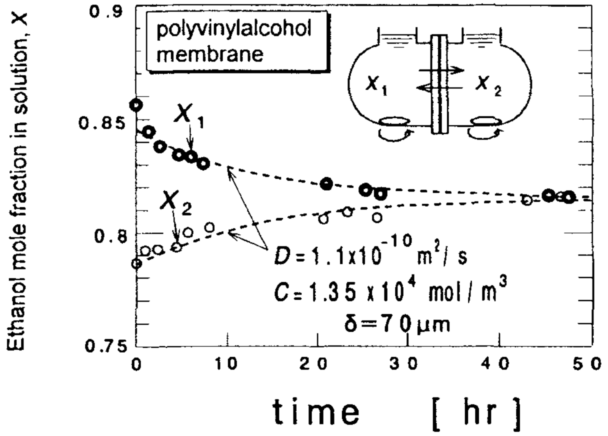

FIG. 4 An example of the diffusion coefficient measurements in swollen polymers.

polymer. The relation between the liquid concentration in the swollen membrane, x_m, and the feed solution, x_1, x_2, is given in Fig. 3. A fitting routine between the experimental data and calculated curves provides the diffusion coefficient, D.

Figure 5 shows the evaluated mutual diffusion coefficients of an absorbed ethanol–water solution in the swollen membrane in relation to the feed concentration, x_f. The solid curve in Fig. 5 is the diffusion coefficient for an ethanol–water solution, D_l, as measured by Hammond and Stokes (10). The difference between D and D_l increases markedly with an increase of ethanol concentration. This dependency of D on feed concentration corresponds with the degree of swelling, as shown in Fig. 3.

Paul (11) derived a general relation between the hydraulic permeability, K_0, and the mutual diffusion coefficient, D, for a swollen membrane:

$$(1/V_l)K_0 = \frac{v_{l0}}{(1 - v_{l0})RT} D \tag{2}$$

where V_l is the molar volume of liquid in a membrane and R is the gas constant. Using this relation, we can convert the measured diffusion coefficients to the hydraulic permeabilities through swollen membranes. The right axis of Fig. 5 shows the converted values of K_0 for polyvinyl alcohol and carboxymethyl cellulose.

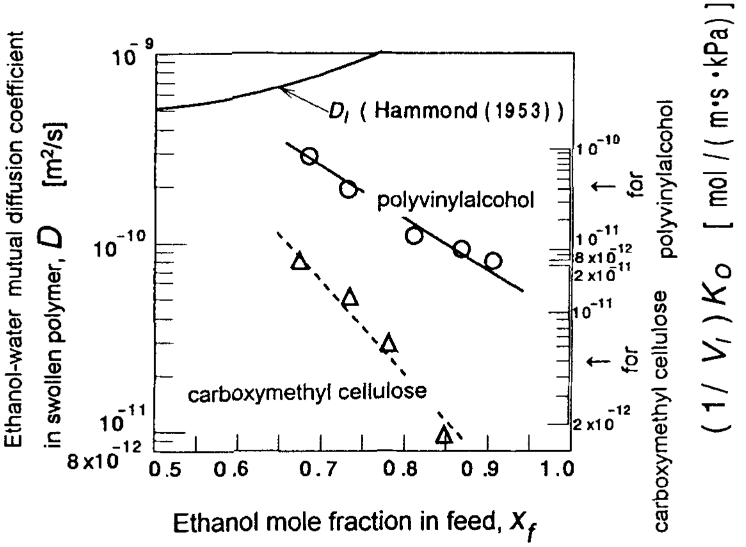

FIG. 5 Hydraulic permeabilities of ethanol–water solution through swollen polymers.

Dry Layer Model for Pervaporation through Silicone Rubber

Figure 6 shows the results of pervaporation runs with a silicone rubber membrane. Permeate vapor concentrations, y_p, and fluxes are plotted vs feed concentration. The lines in the figures are the results calculated from a dry layer model. This model is based on the vapor permeabilities through a silicone rubber membrane, P_E, P_W, and the partial vapor pressures of ethanol and water in a feed solution, p_E^*, p_W^*. Permeate concentration, y_p, and fluxes, N, are given by the following equations:

$$y_p = \frac{N_E}{N_E + N_W} = \frac{p_{p,E}}{p_p} \tag{3}$$

$$N = N_E + N_W = \frac{P_E}{V_v \delta}(p_E^* - p_{p,E}) + \frac{P_W}{V_v \delta}(p_W^* - p_{p,W}) \tag{4}$$

where N_E and N_W are the fluxes of ethanol and water vapors, p_p is the downstream pressure, and $p_{p,E}$ and $p_{p,W}$ are downstream partial pressures. In Fig. 6 the solid line shows the model for zero downstream pressure, $p_p = 0$, and the broken line shows the model for the actual down-

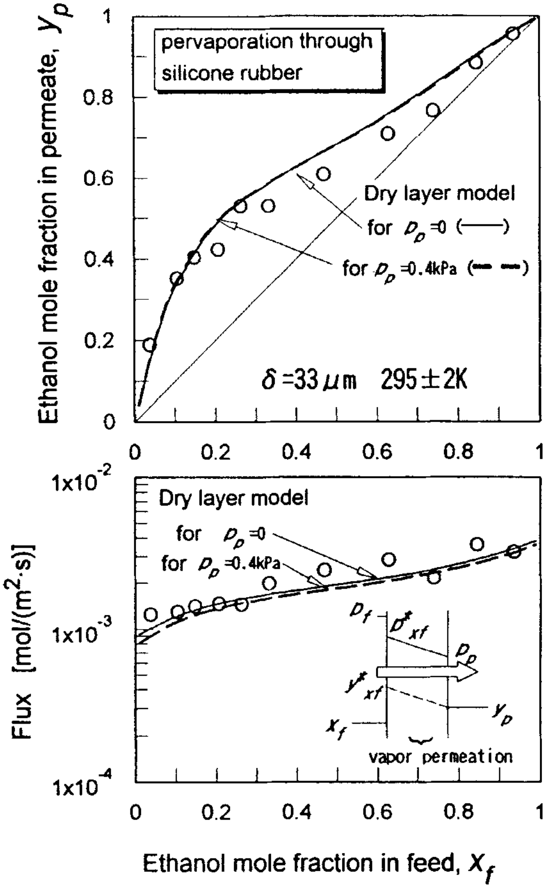

FIG. 6 Comparison between dry-layer model and pervaporation experiments for silicone rubber membrane.

stream pressure, p_p = 0.4 kPa, which is the maximum value measured in the experiments. The effect of downstream pressure is small in this case.

The dry layer model based on vapor permiabilities simultaneously explains the separation performance and the concentration dependency of the pervaporation process through a silicone rubber membrane. For hydrophobic membranes, vapor permeabilities are closely related to the separation performance as well as flux in the pervaporation process.

Swollen–Dry-Layer Model for Permeation through Hydrophilic Membranes

Figure 7(a) is a photomicrograph of the cross section of a polyvinyl alcohol membrane after a pervaporation run with the stain-containing feed solution. This sectional view shows a dark layer on the upstream side and a nonstained layer on the downstream side. The observed dark stained layer could result from feed solution penetration into the membrane and swelling of the polymer. The ethanol–water solution penetrated in the liquid state through the layer. The nonstained layer at the downstream side of the membrane in Fig. 7(a) can be interpreted as the nonswollen

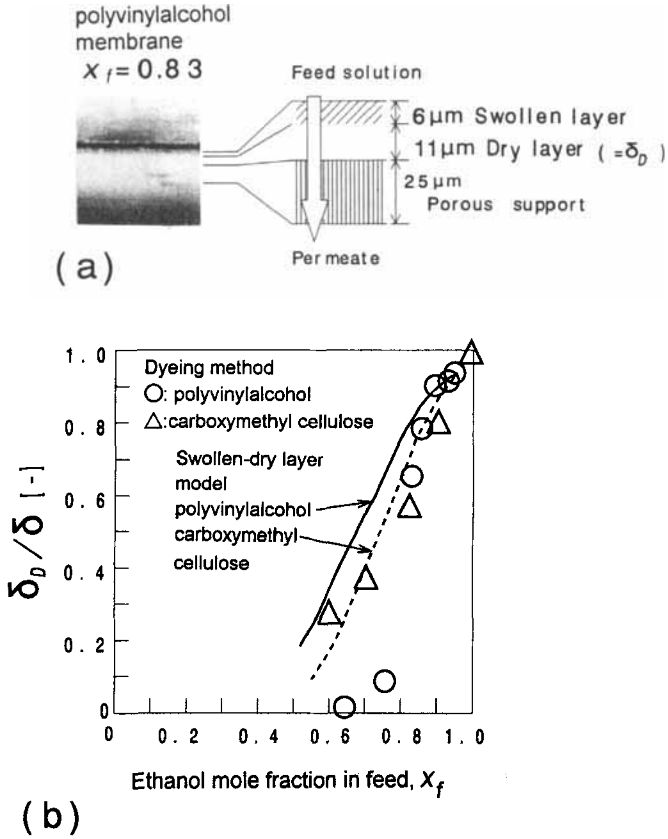

FIG. 7 Swollen layer and dry layer ratio under pervaporation condition for hydrophilic membranes.

layer through which the penetrant permeated in the vapor state. These two layers are thought to be the swollen layer and the dry layer.

In Fig. 7(b) the ratio of dry layer thickness, δ_D, to membrane thickness, δ, is plotted as a function of feed concentration, x_f. The ratio of the dry layer largely depends on the feed concentration. As the ethanol concentration increases, the ratio of the dry layer approaches unity, where the whole membrane is in the dry state and the swollen layer is not observed.

A swollen–dry-layer model is composed of the measured properties of sorption equilibrium, hydraulic permeability, and vapor permeability, as shown in the preceding sections. The swollen–dry-layer model is based

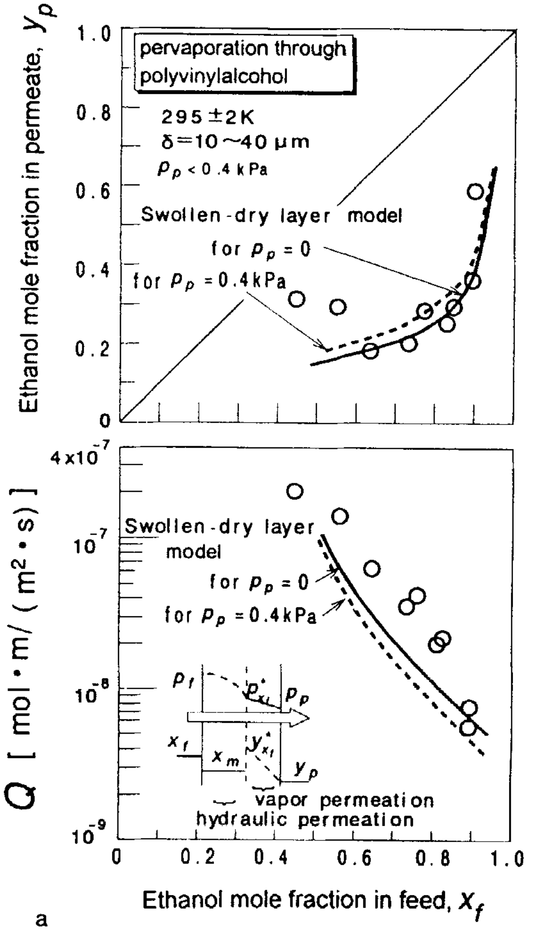

FIG. 8 Comparison between swollen–dry-layer model and pervaporation experiments for hydrophilic membranes.

on the following assumptions. (The membrane thickness is measured in the dry state.)

1. A membrane of thickness δ consists of a swollen layer and a dry layer of thickness δ_D ($= \epsilon\delta$) under pervaporation conditions.
2. The solution absorbed in the swollen layer is in equilibrium with the feed solution, x_f (Fig. 3).
3. Permeation of liquid through a swollen layer of thickness $(1 - \epsilon)\delta$ is

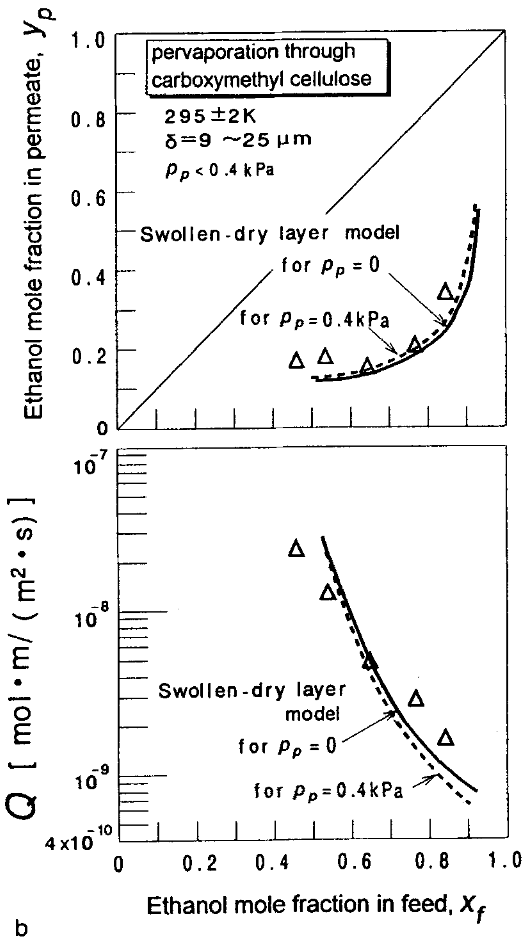

FIG. 8 Continued

induced by a hydrostatic pressure difference ($p_f - p^*_{xf}$) and the diffusion coefficients (Fig. 5). The flux through the swollen layer is given by

$$N_{\text{Swollen}} = \left(\frac{1}{V_l}\right) K_0 \frac{(p_f - p^*_{xf})}{(1 - \epsilon)\delta} \tag{5}$$

Changes in concentrations for liquid permeation through swollen membranes are negligible because the mutual diffusion coefficients of the liquid phase are relatively large.

4. The adsorbed solution vaporizes at the interface between the swollen layer and the dry layer. Postulated partial vapor pressures of ethanol and water, p^*_E and p^*_W, are in equilibrium pressures with the ternary state of the polymer and the adsorbed solution. This ternary state of swollen polymer, in turn, is in equilibrium with the feed solution. Then, when ethanol and water vaporize in the membrane, the partial vapor pressures of ethanol and water are the equilibrium vapor pressures with the feed concentration, x_f, and the operating temperature.
5. Passage of the vapors of ethanol and water through a dry layer of thickness $\epsilon\delta$ depend on the vapor permeabilities (Fig. 2). The driving force of vapor permeation is the difference between the equilibrium vapor pressure of the feed solution and the downstream partial pressure. The concentration of permeated vapor and fluxes through the dry layer are given by

$$y_p = \frac{N_{\text{E,Dry}}}{N_{\text{E,Dry}} + N_{\text{W,Dry}}} = \frac{p_{\text{p,E}}}{p_p} \tag{6}$$

$$N_{\text{Dry}} = N_{\text{E,Dry}} + N_{\text{W,Dry}} = \frac{P_E}{V_v\epsilon\delta}(p^*_E - p_{\text{p,E}}) + \frac{P_W}{V_v\epsilon\delta}(p^*_W - p_{\text{p,W}}) \tag{7}$$

Noting that $N_{\text{Dry}} = N_{\text{Swollen}}$, the dry layer ratio, ϵ, is evaluated by Eqs. (5) and (7). These equations then allow estimation of the total flux and the separation performance of pervaporation.

The pervaporation results for polyvinyl alcohol and carboxymethyl cellulose membranes were compared with the swollen–dry-layer model. The dry layer ratio, ϵ, calculated from the above model for $p_p = 0$ vs the feed concentration, are shown in Fig. 7(b). The calculated results show a trend similar to that observed for the dying method.

Figures 8(a) and 8(b) show comparisons between the experimental results and the theoretical calculations for the permeate concentrations, y_p, and the fluxes, Q ($= N_{\text{dry}}/\delta$), for pervaporation through polyvinyl alcohol and carboxymethyl cellulose membranes. In Fig. 8 the solid line shows the model for zero downstream pressure, $p_P = 0$, and the broken line shows the model for the actual downstream pressure, $p_P = 0.4$ kPa, which is the minimum value used in the experiments. The downstream pressure has appreciable effects on the permeate concentration and the flux. Pervaporation fluxes through hydrophilic membranes decrease one or two orders of magnitude as the feed ethanol concentration is increased (12). The present model provides a good explanation for this trend.

There are some deficiencies in the theory regarding the permeate vapor concentration in the low concentration region. This is attributed to the mutual effect of vapor permeation ignored in the model, or the assumption about partial vapor pressures being in equilibrium at the swollen–dry-layer interface.

According to the swollen–dry-layer model, the vapor permeabilities, P_E and P_W, through the dry layer control the overall selectivity of the pervaporation process, which is formulated by Eqs. (6) and (7). The sorption property between feed solution and swollen membrane makes only a small contribution to the selectivity of the process. On the other hand, the total flux of the pervaporation process through a hydrophilic membrane is strongly affected by the sorption behavior. The large change of degree of swelling with feed concentration controls the ratio of the swollen layer and dry layer, ϵ, and it is caused primarily by the concentration dependency of the total flux.

NOMENCLATURE

A	membrane area (m^2)
C	liquid content in swollen membrane (mol liquid/m^3 dry polymer)
C_g	liquid content in swollen membrane (kg liquid/kg dry polymer)
D	mutual diffusion coefficient of liquid through the swollen membrane (m^2/s)
D_l	mutual diffusion coefficient of ethanol–water solution (m^2/s)
K_0	hydraulic permeability [m^2/(s·kPa)]
M	number of moles (mol)
N	flux [mol/(m^2·s)]
P	permeability of vapor [m^3(STP)·m/(m^2·s·kPa)]
p	pressure (kPa)
p^*_{xf}	equilibrium vapor pressure of feed solution (kPa)
p^*_i	partial vapor pressure of i-component of feed solution (kPa)
Q	flux normalized by thickness [mol·m/(m^2·s)]
R	gas constant [$= 8.312 \times 10^{-3}$ kPa·m^3/(mol·K)]
T	temperature (K)

t	time (s)
V_v	molar volume of ideal gas [= 0.0224 m^3(STP)/mol]
V_l	molar volume of liquid absorbed in membrane (m^3 liquid/mol liquid)
v_{l0}	liquid content in the membrane as volume fraction (—)
x	ethanol mole fraction of liquid (—)
y_p	ethanol mole fraction of permeated vapor (—)
δ	membrane thickness in dry state (m)
ϵ	dry layer ratio (—)

Subscripts

D, Dry	dry layer
E	ethanol
f	feed liquid or upstream
i	component: ethanol or water
m	absorbed liquid in membrane
p	permeated vapor or downstream
Swollen	swollen layer
W	water
1, 2	halves of the cell

REFERENCES

1. R. C. Binning, R. J. Lee, J. F. Jennings, and E. C. Martin, *Ind. Eng. Chem.*, *53*, 45 (1961).
2. H. L. Fleming and C. S. Slater, *Membrane Handbook*, Van Nostrand Reinhold, 1992, p. 117.
3. R. Y. M. Huang and J. W. Rhim, "Separation Characteristics of Pervaporation Membrane Separation Process," in *Pervaporation Membrane Separation Process*, Elsevier Science Publishers, 1991, p. 111.
4. C. K. Yoen and R. Y. M. Huang, *J. Membr. Sci.*, *67*, 39 (1992).
5. M. Thomas, M. Escoubes, P. Esnault, and M. Pineri, *Ibid.*, *48*, 57 (1989).
6. J. G. Wijmans and R. W. Baker, *Ibid.*, *79*, 101 (1993).
7. T. Hirotsu, K. Ichimura, K. Mizoguchi, and E. Nakamura, *J. Appl. Polym. Sci.*, *36*, 1717 (1988).
8. C. E. Reineke, J. A. Jagodzinski, and K. R. Denslow, *J. Membr. Sci.*, *32*, 207 (1987).
9. R. W. Baker, N. Yoshioka, J. M. Mohr, and A. J. Khan, *Ibid.*, *31*, 259 (1987).
10. B. R. Hammond and R. H. Stokes, *Trans. Faraday Soc.*, *49*, 890 (1953).
11. D. R. Paul, *Sep. Purif. Methods*, *5*, 33 (1976).
12. Q. T. Nguyen and R. Clement, *J. Membr. Sci.*, *55*, 1 (1991).

Received by editor May 26, 1994
First revision received September 13, 1994
Second revision received November 22, 1994