

A Study on Desorption Resistance in Pervaporation of Single Component Through Dense Membranes

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SYNOPSIS

Desorption resistance taking place between a membrane surface and a permeate vapor phase, which had not accounted for an overall mass transfer resistance in pervaporation, was studied. The resistance-in-series concept and Flory-Huggins thermodynamics were used to establish model equations for evaluating the desorption resistance in the permeation of a single component. In order to exclude any possible concentration polarization of permeants occurring in feed adjacent to a membrane surface, the permeations of pure water through polyether imide membranes with various thicknesses were observed at different permeate pressures. From the permeation data of pure water through the membranes with help of the model equations, both the permeability coefficient based on a general flux equation expressed in terms of the chemical potential driving force and the desorption resistance were determined quantitatively. According to the model equations, the desorption resistance could be affected by two factors: membrane thickness and permeate pressure. The magnitude of the desorption resistance was dependent mainly on permeate pressure, and the importance of the resistance relative to diffusion resistance in the membrane for the overall process became more significant with decreasing membrane thickness at a given permeate pressure. As the membrane thickness decreased and/or the permeate pressure increased, the desorption resistance was observed to be more significant, causing higher chemical activity and a higher concentration of the permeant at the downstream interface of the membrane. In some cases, the desorption resistance was predominant over the diffusion resistance in very thin membrane thicknesses. This study seeks to emphasize the importance of the desorption resistance on the transport of components at small membrane thicknesses or high permeate pressure. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

In pervaporation, the solution-diffusion model for the permeation of permeants through a dense membrane assumes that equilibrium is established across both the upstream and the downstream interfaces of the membrane. A boundary layer resistance in feed adjacent to a membrane surface has been considered to contribute signifi-

cantly to overall mass transport on the pervaporation separation of dilute organic aqueous solutions, while an interface resistance on the membrane surface on the permeate side has been excluded when accounting for the overall mass transfer resistance.¹⁻⁵ This can be especially true for pervaporation at low permeate pressure or a sufficiently thick membrane in which the permeation is governed by diffusion alone. Thus, the permeability of a permeant through a membrane should be independent of membrane thickness, and hence, the flux is inversely proportional to membrane thickness. However, under some extreme conditions, such as a very small membrane thickness or high permeate pressure, deviations

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from the normal solution-diffusion model have been observed in pervaporation. Bode and associates^{6,7} reported that the permeability decreased with decreasing membrane thickness in the permeation of pure water through polyether block amide and that the chemical potential moved across the downstream interface of a thin membrane while it was continuous across the upstream interface in the pervaporation process. The decrease of the permeability and the chemical potential step at the downstream interface were explained to be the result of the membrane interface resistance of the membrane developed at the downstream side. Côté and Lipski¹ postulated that there may be a resistance to mass transfer at the permeate film formed just adjacent to the downstream interface at high permeate pressure. It is widely accepted that the upstream interface of the membrane is in an equilibrium state with feed liquid; this is confirmed by experiments.⁶ However, the downstream interface of the membrane contacting with the vapor phase presumably has many chances to be exposed to nonequilibrium situations, depending on permeate pressure, membrane structure, and others. It is also reported that when feed is in vapor phase instead of liquid phase, concentration profiles show nonequilibrium and reduced concentrations at the upstream interfaces of membranes as a result of a resistance developed at the interfaces.^{6,12} In real applications, membranes with very thin effective thickness have been used in order to enhance the flux by reducing the diffusion resistance, and relatively high permeate pressures have been used because of economical considerations. In this case, the desorption resistance might become of importance in the pervaporation process.

The purpose of this study is to establish model equations to quantitatively determine the desorption resistance and the concentration and activity of the permeant at the downstream interface of the membrane for single-component permeation and to examine the effect of the desorption resistance on the pervaporation performance, by using pure water permeation data through dense polyether imide (PEI) membranes which have thicknesses controlled precisely. Mass transport coefficients in the permeation of the permeant will be determined from the experimental data with the help of the model equations. The desorption resistance will be estimated through an analysis of the determined coefficients, and the important role that the desorption resistance plays in the overall

process of pervaporation under some conditions will be discussed. The influence of the desorption resistance on the characteristics of the membrane surface on the permeate side will also be discussed.

THEORY

Mass Transfer Resistance in Single Component Permeation

A chemical potential gradient rather than a concentration gradient should be used as a driving force in a general transport theory to reduce any limiting or special cases for which the answer is known. In this study, in order to rule out any possible concentration polarization, the permeation of a single component will be used. In this case, the possible factors taken into account for describing the overall permeation are membrane resistance and desorption resistance. The former is related to the physicochemical interaction of the permeant molecule with the molecules within the membrane structure, and the latter is related to the surface layer molecules of the membrane with adhering permeant molecules.⁷ As a result, the chemical potential profile of the permeant across the system can be simplified, as shown in Figure 1. For the overall process, the flux can be described as

$$J = K_t(\mu_F - \mu_P) \quad (1)$$

From pervaporation experiments, the so-called overall mass transfer coefficient, K_t , can be determined. It is reported that a difference in chemical potential appears at the downstream interface of the membrane, while the upstream interface is in equilibrium state, because the exchange fluxes across the upstream interface is much larger than that across the downstream interface.^{6,7} Thus, the chemical potential of the permeant dissolved in the upstream interface of the membrane equals that of feed: $\mu_F = \mu_{m1}$. The flux through the membrane can be written in terms of the chemical potential at constant temperature as

$$J = -L_\mu \frac{d\mu}{dx} \quad (2)$$

In a scarcely swollen membrane in which the equilibrium solubility of the permeant is small,

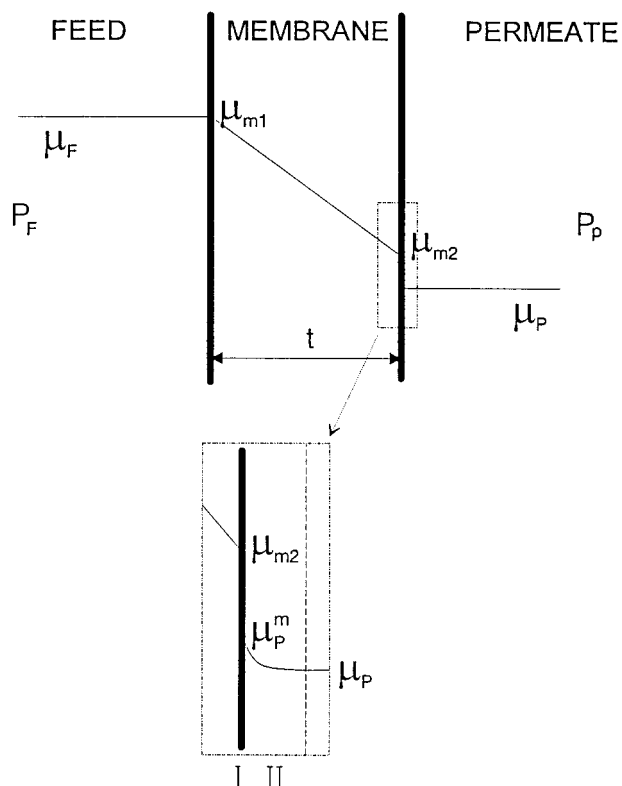


Figure 1 Chemical potential profile across a system in the permeation of a single component.

the chemical potential profile in the membrane can be assumed to be linear.¹³ Thus, L_μ , the phenomenological coefficient which is equivalent with the permeability coefficient, can be constant; then, the flux can be expressed as

$$J = \frac{L_\mu}{t} (\mu_{m1} - \mu_{m2}) \quad (3)$$

where t is the membrane thickness. On the basis of the published research,^{1,6,7} two possible zones for the desorption resistance may be taken into account, as shown in Figure 1: zone I, desorption interface^{6,7}; zone II, boundary layer adjacent to the downstream interface of the membrane.¹

In zone I, mass transfer resistance can be related to the diffusion of a permeant molecule through the outer layer molecules of the membrane with the permeant molecules adhering. It can be significant when membrane thickness is so small that enhanced net flux could become comparable to the exchange flux across the permeate side interface of the membrane. In zone II, the formation of a permeate film, i.e., the hydrody-

amic boundary layer in the permeate adjacent to a membrane surface, in which mass transfer occurs only by diffusion, may be influenced by permeate pressure. With increasing permeate pressure, the thickness of the film increases, causing more significant mass transfer resistance in the permeate phase adjacent to the membrane surface. When the permeate pressure is well below the saturated vapor pressure of the permeant, zone II may not be important to account for the desorption resistance¹ because the thickness of the boundary layer is too small and the permeant is in a vapor phase to such an extent that the mass transfer coefficient in zone II can be much higher than any other step. The flux equation in these zones can be expressed by eq. (4).

$$J = K_d (\mu_{m2} - \mu_P) \quad (4)$$

where K_d is a mass transfer coefficient in the desorption step. Mass transport resistance in each step can be expressed in terms of each reciprocal mass transfer coefficient, respectively. Because the overall chemical potential difference in eq. (1) is expressed as the sum of the chemical potential differences in each step, eqs. (1)–(4) can yield the following relationship:

$$\frac{1}{K_t} = \frac{t}{L_\mu} + \frac{1}{K_d} \quad (5)$$

The reciprocal overall mass transfer coefficient, that is, an overall mass transfer resistance, can be considered as the sum of a membrane resistance (t/L_μ) and a desorption resistance ($1/K_d$). This equation describes a connection of the resistances in series, that is, a so-called resistance-in-series concept.¹

To relate the overall mass transfer coefficient to the permeate pressure, the chemical potential of the single component in each step can be described in terms of a thermodynamic related equation. The relevant equations in each step are the following:

- For the pure liquid feed at pressure P_F and the dissolved liquid at the upstream face of a membrane, because there is no concentration polarization at the feed side and the membrane-liquid interface is in equilibrium, assuming constant molar volume V_F , the following relationships are given: $\mu_F = \mu_{m1}$, a_F

$$= a_{m1} = 1.$$

$$\begin{aligned}\mu_F &= \mu_0 + RT \ln a_F + \int_{P^*}^{P_F} V_F dP \\ &= \mu_0 + V_F(P_F - P^*) \\ &= \mu_{m1}\end{aligned}\quad (6)$$

- For the dissolved liquid permeant at the downstream face, assuming the pressure in the membrane is constant at P_F ,

$$\mu_{m2} = \mu_0 + RT \ln a_{m2} + \int_{P^*}^{P_F} V_F dP \quad (7)$$

- For the permeate at the downstream side ($P_p < P^*$), assuming the vapor is considered to be an ideal gas because of low pressure,

$$\begin{aligned}\mu_P &= \mu_0 + \int_{P^*}^{P_P} V_P dP \\ &= \mu_0 + \int_{P^*}^{P_P} \frac{RT}{P} dP \\ &= \mu_0 + RT \ln \left(\frac{P_P}{P^*} \right)\end{aligned}\quad (8)$$

where μ_0 and P^* are the chemical potential and pressure of the permeant at a saturation state as a reference state, respectively; a_F and a_P are the activities of the permeant at feed and permeate, respectively; and V_P is the molar volume of the permeant in permeate. The overall chemical potential difference, $\Delta\mu$, is given from eqs. (6) and (8),

$$\Delta\mu = V_F(P_F - P^*) + RT \ln \frac{P^*}{P_P} \quad (9)$$

By combining eqs. (1) and (9), the overall mass transfer coefficient K_t can be given as follows:

$$\begin{aligned}K_t &= \frac{J}{RT \ln \frac{P^*}{P_P} + V_F(P_F - P^*)} \\ &= \frac{J}{\Delta\mu}\end{aligned}\quad (10)$$

The overall mass transfer coefficient K_t can simply

be determined from the measurement of the steady-state flux of the component in pervaporation experiments and the permeate pressure used. Equation (5) can be rewritten as

$$\frac{1}{K_t} = \frac{\Delta\mu}{J} = \frac{t}{L_\mu} + \frac{1}{K_d} \quad (11)$$

If the overall mass transfer resistance is plotted against the membrane thickness, a straight line is obtained for which the intercept is equal to the desorption resistance and the slope is equal to the membrane resistance.

Determination of Characteristics at the Downstream Interface of Membrane

In order to characterize the downstream interface of the membrane, the concentration and activity of the permeant at the downstream side interface of the membrane can be obtained by two ways when the two mass transfer coefficients, K_d and L_μ , are known. One is to use eq. (3), the flux equation across the membrane, and the other is to use eq. (4), the flux equation through the desorption step:

- *Using eq. (3)*: from eqs. (6) and (7), the difference in chemical potential inside a membrane is obtained as the difference in permeant activity, as described in eq. (12).

$$\begin{aligned}\Delta\mu_m &= \mu_{m1} - \mu_{m2} \\ &= RT(\ln a_{m1} - \ln a_{m2}) \\ &= -RT \ln a_{m2}\end{aligned}\quad (12)$$

Combining eqs. (3) and (12) yields

$$\ln a_{m2} = \frac{-Jt}{RTL_\mu} \quad (13)$$

- *Using eq. (4)*: from eqs. (7) and (8), the following equation can be obtained:

$$\begin{aligned}\mu_{m2} - \mu_P &= RT \ln a_{m2} \\ &+ RT \ln \frac{P^*}{P_P} + V_F(P_F - P^*)\end{aligned}\quad (14)$$

Combining eqs. (4) and (14) gives

$$\ln a_{m2} = \frac{J}{RTK_d} + \ln \frac{P_P}{P^*} + \frac{V_F}{RT}(P^* - P_F) \quad (15)$$

The relationship between $\ln a_{m2}$ and the volume fraction of the permeant at the downstream interface of the membrane can be expressed by Flory-Huggins thermodynamics as

$$\chi_p = - \frac{\ln v_{m1} + (1 - v_{m1})}{(1 - v_{m1})^2} \quad (16)$$

$$\begin{aligned} \ln a_{m2} &= \ln v_{m2} + \left(1 - \frac{V_F}{V_{pp}}\right)(1 - v_{m2}) \\ &+ \chi_p(1 - v_{m2})^2 \\ &\cong \ln v_{m2} + 1 - v_{m2} + \chi_p(1 - v_{m2})^2 \quad (17) \end{aligned}$$

where v_{m1} and v_{m2} are the volume fractions of the permeant at the upstream side surface and downstream side surface of the membrane, respectively, and χ_p is the interaction parameter between the permeant and the membrane. Therefore, the chemical activity of the permeant at the downstream side interface can be calculated from eq. (13) or (15) and then the permeant concentration can be determined from eq. (17).

Effect of Desorption Resistance on Permeability

It can be seen from eqs. (13) and (15) that the downstream side interface characteristics can be affected by the permeate pressure and the membrane thickness. Bode⁶ investigated the effects of membrane thickness and permeate pressure on the chemical potential step which was used as a measure of mass transfer resistance occurring on the downstream side interface of the membrane in the permeation of pure water through NAFI-ON®117. He reported that smaller membrane thickness or higher permeate pressure gives higher activity of the permeant at the downstream side interface of the membrane, resulting from more significant desorption resistance. If the permeation follows Fick's diffusion equation completely at constant temperature and permeate pressure, no chemical potential step is formed at the downstream side interface of the membrane, that is, the chemical potential difference, $\mu_{m2} - \mu_p$ in eq. (14) is zero because of no significant

desorption resistance, and the following equation can be given from eqs. (13) and (14):

$$Jt = L_\mu RT \ln \frac{P^*}{P_P} + V_F L_\mu (P_F - P^*) \quad (18)$$

where L_μ and K_d can be tentatively assumed to be constant at a given temperature and permeate pressure. In this case, the left side of eq. (18) must be constant with membrane thickness because the right side is always constant at a given permeate pressure and temperature. However, it has been observed from the published research⁷ that the product of flux and membrane thickness decreases with decreasing membrane thickness. This can be explained by eq. (19), which is derived by combining eqs. (13) and (15).

$$\begin{aligned} Jt \left(1 + \frac{L_\mu/t}{K_d}\right) \\ = L_\mu RT \ln \frac{P^*}{P_P} + V_F L_\mu (P_F - P^*) \quad (19) \end{aligned}$$

With decreasing membrane thickness, the ratio, $(L_\mu/t)/K_d$, of mass transfer coefficients in the membrane and the desorption zone increases to the same extent as the product (Jt) decreases, so that the left side of eq. (19) can stay constant. An increase of the ratio with decreasing membrane thickness reflects that the desorption resistance can contribute increasingly to the overall process, causing the resulting flux to be depressed correspondingly. When membrane thickness is large enough, the bracket term on the left side of eq. (19) disappears and then eq. (19) becomes identical with eq. (18). On the other hand, the ratio of the coefficients may be changed with permeate pressure because the K_d value is strongly dependent on permeate pressure; this will be discussed in the next section.

EXPERIMENTAL

Materials

Polyether imide (Ultem, 1000/2000 grade) was purchased from GE Plastics (Mount Vernon, Indiana, USA). Before use, it was dried in a circulat-

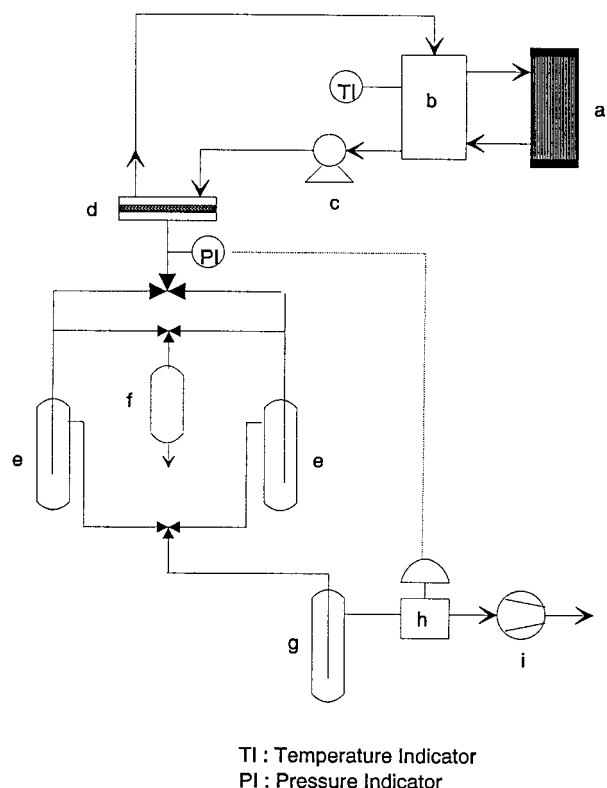


Figure 2 Schematic presentation of pervaporation apparatus: (a) water bath, (b) feed tank, (c) pump, (d) membrane cell, (e) and (g) cold trap, (f) vent to atmosphere, (h) vacuum controller, and (i) vacuum pump.

ing oven for 6 h at 80°C and then dried further at room temperature in a vacuum oven for a day to remove any humidity. Ultrapure deionized water was used.

Membrane Preparation

Casting solutions were prepared by dissolving PEI in dichloromethane. The casting solution was poured into a plastic petri dish of which the coating area was known; it was then allowed to dry in a fume hood at room temperature. The membrane dried further in vacuum oven for a day. Membrane thickness was controlled by the concentration and amount of the casting solution introduced on the known coating area. Scanning electron microscopy confirmed that this method could provide a good control of membrane coating thickness. All of the membranes prepared were dense, and their thicknesses ranged from 2 to 50 μm . The smallest membrane thickness that we could get without defect was 2 μm .

Swelling Measurement

Dry membrane strips were immersed in water thermostated at 70°C for 48 h to allow the strips to reach an equilibrium sorption. After the swollen length, l , of a strip at equilibrium sorption was measured, the strip dried for 30 h at room temperature under a vacuum and then the dry length, l_0 , was measured. The dense membranes used in this study can be assumed to have an isotropic membrane structure. The swelling ratio, R , is defined as¹¹

$$R = \frac{l}{l_0} \quad (20)$$

The volume fraction, v_m , of water in the swollen membrane can be expressed in the following form:

$$v_m = \frac{R^3 - 1}{R^3} \quad (21)$$

The determined v_m can be used as the volume fraction, v_{m1} , of the permeant at the upstream side surface of the membrane in eq. (16).

Pervaporation Experiment

Pervaporation tests of water through different thicknesses of dense PEI membranes were performed at 70°C. A schematic diagram of the pervaporation apparatus used is shown in Figure 2. Feed was kept at the selected temperature by a thermostated water bath. The feed was continuously circulated from the feed tank through a membrane cell by a pump (Iwaki Magnetic Gear Pump, Iwaki Co., Ltd., Tokyo, Japan). The membrane cell was designed to allow high fluid velocity parallel to the membrane surface, as depicted in Figure 3. The effective membrane area in the

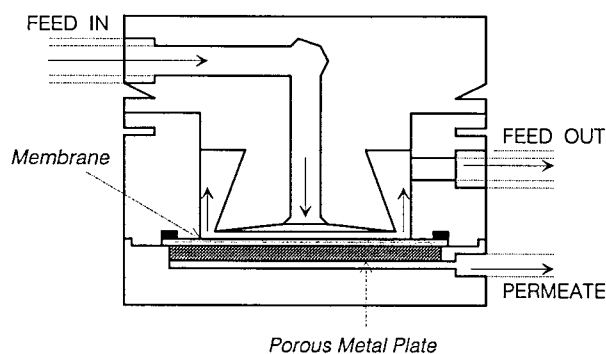


Figure 3 Details of membrane cell.

membrane cell was 19.63 cm². The pressure indicator (Datametric 1450; Edwards, Wilmington, MA) was connected with the membrane cell by a $\frac{1}{4}$ inch SUS tube that was 10 cm long, along which the pressure drop that developed was very small or negligible. The pressure displayed at the pressure indicator was controlled by a vacuum controller (model VC-30S; Okano Works, Ltd., Osaka, Japan) from 0.133 to 2.666 KPa with an accuracy of ± 0.01 KPa. The vacuum pump (Welch vacuum pump, model 8920, pumping speed = 210 L/min) had a capacity enough to control the permeate pressure under the range of fluxes formed in this study. Permeate was condensed in a cold trap by liquid nitrogen. The line from the membrane cell to the cold trap was wrapped with a heating band and kept the same temperature as the permeate in the membrane cell to prevent the permeate from condensing. The condensed permeate in the cold trap was warmed to ambient temperature to weigh.

RESULTS AND DISCUSSION

In this study, the permeation of pure water through a scarcely swollen dense membrane (PEI membrane) was taken as a system in order to simplify the model by which the desorption resistance can be quantitatively determined. The chemical potential profile of the permeant across the system can be considered to be simple in the permeation of water, as shown in Figure 1.

Figure 4 shows the plots of water fluxes through the dense PEI membranes, with thicknesses ranging from 2 to 50 μm at 70°C of feed temperature and various permeate pressures. If membrane resistance is a factor controlling the permeation, the flux must be inversely proportional to the membrane thickness, according to Fick's equation:

$$J = -D \frac{dC}{dx} \quad (22)$$

where D is the concentration-dependent diffusion coefficient of the permeant and dC/dx is the concentration gradient of the permeant across the membrane. In the range of large membrane thicknesses, the fluxes show a linearity, but in the range of small membrane thicknesses it is of interest to find that the water fluxes were de-

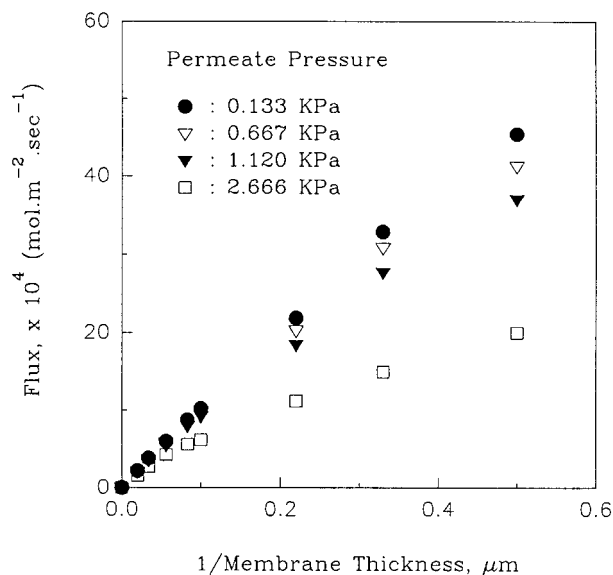


Figure 4 Plots of water fluxes against inverse membrane thickness through dense PEI membranes; operating temperature = 70°C.

pressed, showing lower values than those calculated from the linear relationship of flux and reciprocal membrane thickness, and that the depression of flux was more significant as membrane thickness decreased or permeate pressure increased. This reflects that other resistance besides the diffusion resistance obviously exists to depress the water permeation. In this study, the concentration polarization of permeant in feed and pressure drop in support layer could be excluded by adopting the permeation of pure water through the dense nonporous membrane. Also, a widely accepted assumption in pervaporation is that the feed side interface of the membrane is in equilibrium state. Therefore, the other resistance must be the resistance developed in the desorption zones, as depicted in Figure 1.

The desorption resistance can be evaluated quantitatively by using the model equations proposed in the previous section. The overall mass transfer coefficient K_t for various membrane thicknesses could be determined from eq. (10) using experimental water flux data at a given permeate pressure; then, the determined coefficients were plotted with membrane thickness to evaluate coefficients L_μ and K_d from the slope and intercept, respectively, as presented in eq. (11). The results are shown in Figure 5. The plots in Figure 5 yielded good linearity at a given permeate pressure and given range of membrane thicknesses.

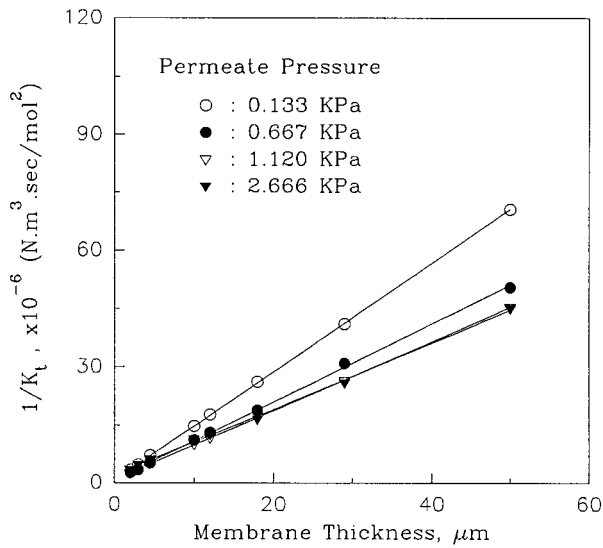


Figure 5 Inverse overall mass transfer coefficient of water against membrane thickness through dense PEI membrane at 70°C.

Figure 6 presents the plots of the determined L_μ and K_d values versus permeate pressure. The L_μ slightly increased with permeate pressure while the K_d decreased more significantly. Basically, the L_μ is a function of diffusion coefficient and permeant concentration in the membrane, which can be changed with permeate pressure. By the use of eq. (2) and the differential form of Equation (12), water flux through the polymeric membrane can be expressed in terms of the chemical activity and concentration of water in the membrane instead of as chemical potential, as follows:

$$J = -L_\mu RT \frac{d(\ln a)}{dC} \frac{dC}{dx} \quad (23)$$

The comparison of eq. (23) with Fick's equation gives the following relationship between the coefficient L_μ and the diffusion coefficient D ,

$$L_\mu = \frac{D}{RT} \frac{dC}{d(\ln a)} \quad (24)$$

Usually, the permeant concentration in the membrane tends to increase with permeate pressure, which may cause the diffusion coefficient to increase. From eq. (24), therefore, it can be seen that an increase in permeate pressure leads to increases in the coefficient L_μ . The reason for the decrease of

K_d with permeate pressure is not clear because no study has been done on this area so far, but it may be postulated as follows: When permeate pressure is higher, the evaporation of the permeant at the downstream side interface of the membrane can slow down, and then the permeant concentration at the membrane surface increases. As both the permeate pressure and the permeant concentration on the membrane surface increase, a layer or film consisting of permeant vapor may be formed on the membrane surface to act as a resistance layer to mass transport. The layer can have characteristics very similar to one described in the film theory.^{1,2} According to the film theory, a boundary layer or film through which permeant molecules are transported only by diffusion can be created in feed adjacent to the membrane surface at the feed side and cause a resistance to mass transport, depending on the hydraulic dynamics in feed. Applying this theory to this process, the thickness of the boundary layer adjacent to the permeate side surface of the membrane can be presumably dependent on the hydraulic dynamics in the permeate, such as permeate pressure: the higher the permeate pressure, the thicker the layer, similar to the boundary layer developed in feed. Hence, the mass transfer coefficient in the layer can be defined as the diffusivity in the layer divided by the layer thickness. That is why the coefficient K_d decreases with permeate pressure.

The fluxes with membrane thickness were back-calculated by eq. (11), with all of the coefficients determined, and compared with experi-

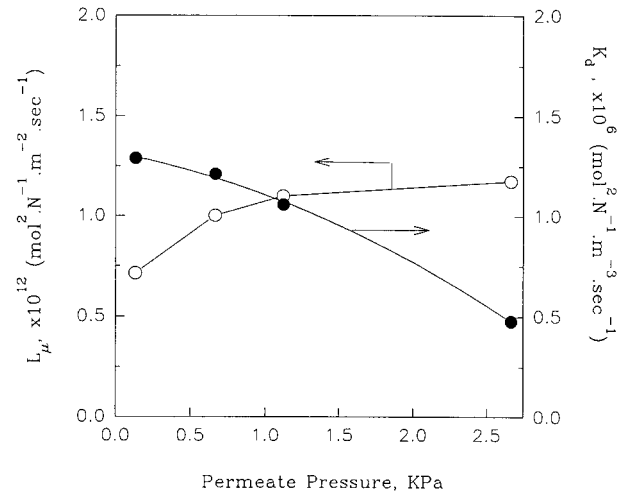


Figure 6 Determined coefficients L_μ and K_d with permeate pressure for water permeation through PEI at 70°C.

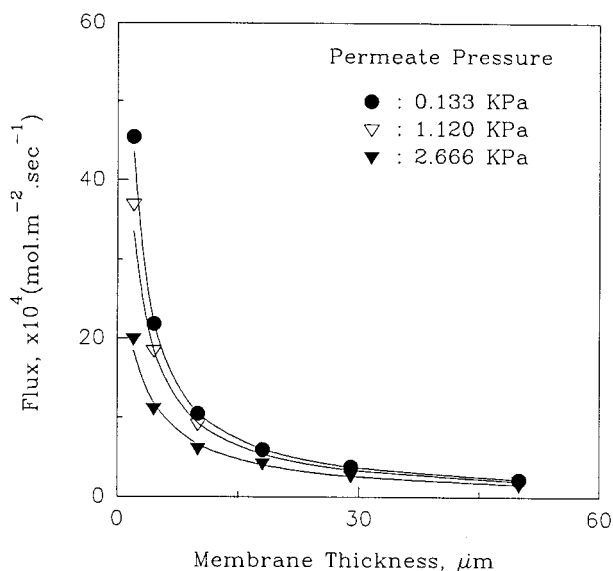


Figure 7 Comparison of calculated fluxes from model with experimental fluxes: (lines) simulated fluxes, (points) experimental fluxes.

mental fluxes, as shown in Figure 7. Excellent agreement between the calculated fluxes and the experimental data was found within an error of $\pm 5\%$, reflecting that the determined coefficients would be reliable.

As discussed above, the desorption mass transfer coefficient, which is a function of permeate pressure, is constant with membrane thickness, whereas the diffusion mass transfer coefficient in the membrane, defined as L_μ/t , is inversely proportional to membrane thickness. It is important to see how the membrane thickness affects the overall process. The membrane thickness can change the relative importance of the desorption resistance against the diffusion resistance by changing the diffusion resistance. In this study, the ratio of diffusion to desorption mass transfer coefficients (or the ratio of desorption to diffusion resistances) was used as a measure of the relative importance of the desorption resistance. Figure 8 presents the plots of the ratio of desorption to diffusion resistances with membrane thickness at various permeate pressures. The ratio of the resistances is observed to decrease with membrane thickness because the desorption resistance is kept constant while the membrane resistance decreases with decreasing membrane thickness at a given permeate pressure and temperature. The desorption resistance becomes more important when membrane thickness is smaller. When membrane thickness was larger than $20 \mu\text{m}$, the ratio was very small,

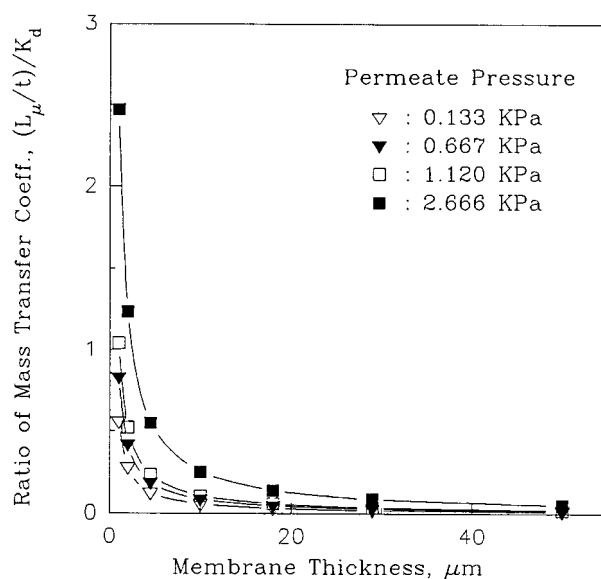


Figure 8 Ratio of diffusion to desorption mass transfer coefficients (Coeff.) against membrane thickness at different permeate pressures for water permeation.

indicating that the desorption resistance is not important and that the diffusion step is rate determining. When the membrane thickness was below $2 \mu\text{m}$, the ratio of the coefficients is so high that the desorption resistance could be significantly comparable to the diffusion resistance. On the other hand, at lower permeate pressure, the ratio of the coefficients was smaller, mainly because of the higher value of the mass transfer coefficient in desorption. As a result, it can be summarized that the value of desorption resistance is affected by permeate pressure, while the relative importance of the resistance against the membrane resistance can be dependent on membrane thickness as well as the value of the desorption resistance.

Usually, the driving force across a membrane is expressed in terms of a difference in the concentrations or activities of the permeant at both surfaces of the membrane. Figures 9 and 10 show how the desorption resistance can influence the characteristics of the membrane surface on the permeate side. By the use of eq. (13) or (15), the chemical activities of water at the downstream side interface of the membrane were calculated and illustrated in Figure 9. The results of calculations from these two equations were consistent with each other within a difference of $\pm 2\%$. If the desorption resistance is negligible, the activity of water on the membrane surface on the permeate side should be zero at a permeate pressure well below the saturated vapor pressure of

water. When the permeate pressure was low enough, especially 0.133 KPa, the activity was very small, less than 0.01, regardless of membrane thickness. However, as the permeate pressure increased further, the activity increased as the result of an increase in the desorption resistance. This observation could support the fact that the magnitude of desorption resistance is determined mainly by permeate pressure. In the range of large membrane thickness, the activity was almost constant with membrane thickness at a given permeate pressure, while in the small-thickness region, the increase of activity with decreasing membrane thickness was more remarkable at higher permeate pressure. The concentrations of the permeant on the membrane surface on the permeate side were calculated from eqs. (16) and (17) and are presented in Figure 10. The equilibrium sorption data should be needed to calculate the concentrations. The equilibrium sorption of water in the PEI membrane at 70°C was measured as 3.092 vol %. The permeant concentration changed with membrane thickness at a given permeate pressure in the same way as the permeant activity did. From these observations, it can be thought that the desorption resistance makes the activity of a permeant on the permeate side surface of membrane increase, and at the same time, the concentration of the permeant increased correspondingly; finally, the difference of the activity or concen-

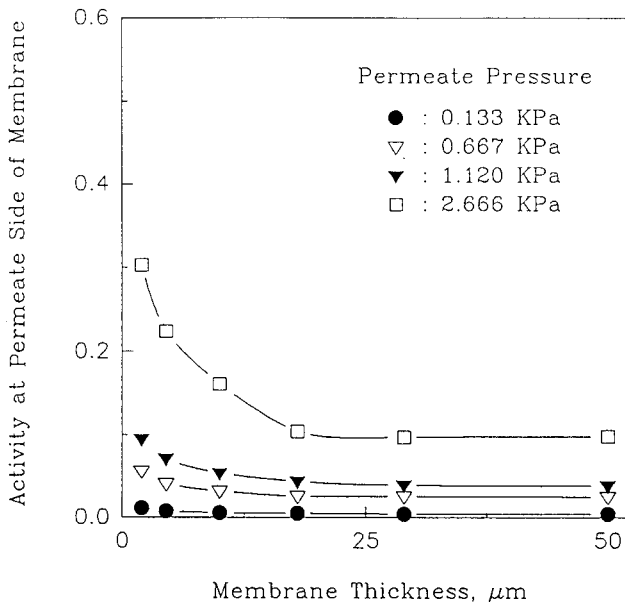


Figure 9 Water chemical activities at the permeate side interface of the membrane with membrane thickness.

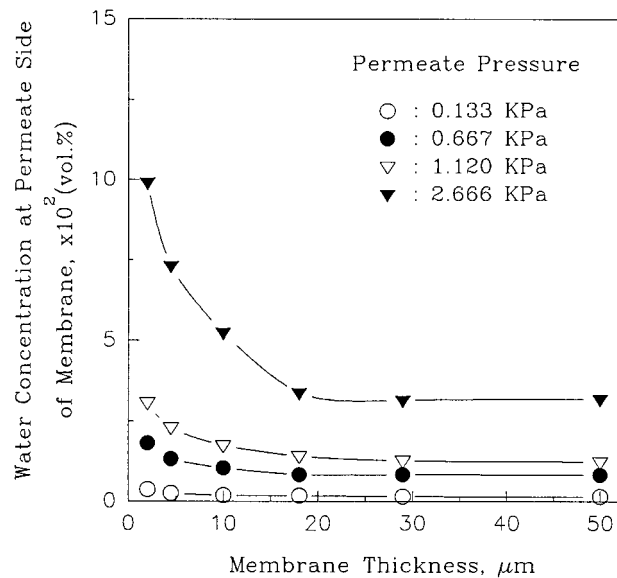


Figure 10 Water concentration at the permeate side interface of the membrane with membrane thickness.

tration of the permeant between both sides of the membrane must be reduced, that is, reduced driving force could be applied across the membrane so that the reduced flux came out. That is why the flux was more depressed at high permeate pressure and/or small membrane thickness, as shown in Figure 4.

From the analysis on the water permeation data with help of the model, it is found that the desorption resistance at the downstream interface of the membrane should not be negligible but must be taken into account for the permeation through a thin membrane and/or at high permeate pressure. In practical applications, now, thin composite membranes are used to enhance flux and somewhat high permeate pressure is used because of economical considerations. From this point of view, the importance of desorption resistance could be more pronounced in determining membrane performance than expected. Even though this study was carried out on the permeation of pure water through dense PEI, the principle proposed in this study can be extended to the pervaporation separations of liquid mixtures through other polymeric membranes and could contribute to the understanding of the property changes taking place on the permeate side surface of the membranes.

CONCLUSIONS

In this study, we investigated the important role the desorption step plays in pervaporation perfor-

mance under practical conditions which can be used in real applications. A theoretical approach incorporating the resistance-in-series model was adopted to derive the governing equation to demonstrate the importance of the desorption resistance in the permeation of a single component. In order to exclude concentration polarization in feed just adjacent to the membrane surface and to determine quantitatively the desorption resistance from the model equations, the permeation of pure water through a scarcely swollen dense PEI membrane was taken as a system.

The mass transfer coefficients in each step were determined from the model by the use of experimental pervaporation flux data. The coefficient L_μ had a slight increase with increasing permeate pressure while the coefficient K_d in desorption decreased. Also, the chemical activity and concentration of water at the permeate side surface of the membrane could be determined from the model. It is found that the magnitude of the desorption resistance is determined by permeate pressure and that the importance of the desorption resistance relative to the membrane resistance (diffusion resistance) can be estimated depending on membrane thickness as well as the magnitude of the desorption resistance. At high permeate pressure, the desorption resistance was more significant for the overall process because membrane thickness decreased, and at low permeate pressure, the desorption resistance was not very important, regardless of membrane thickness. The desorption resistance makes the activity and concentration of water increased at the permeate side surface of the membrane, which caused flux to be reduced. In the design of a membrane module or process, the desorption resistance for permeation through a thin membrane and/or at high permeate pressure should be taken into account.

NOMENCLATURE

a	chemical activity
C	permeant concentration ($\text{mol}\cdot\text{m}^{-3}$)
D	diffusion coefficient ($\text{m}^2\cdot\text{sec}^{-1}$)
J	flux ($\text{mol}\cdot\text{m}^{-2}\cdot\text{sec}^{-1}$)
K	mass transfer coefficient ($\text{m}^2\cdot\text{N}^{-1}\cdot\text{m}^{-3}\cdot\text{sec}^{-1}$)

L_μ	phenomenological coefficient ($\text{m}^2\cdot\text{N}^{-1}\cdot\text{m}^{-2}\cdot\text{sec}^{-1}$)
P	pressure ($\text{N}\cdot\text{m}^{-2}$ or Pa)
P^*	saturated vapour pressure ($\text{N}\cdot\text{m}^{-2}$ or Pa)
R	gas constant
t	membrane thickness (m)
T	operating temperature (K)
v	volume fraction of permeant in membrane
V	molar volume ($\text{m}^3\cdot\text{mol}^{-1}$)
V_{pp}	molar volume of membrane ($\text{m}^3\cdot\text{mol}^{-1}$)
x	distance along which diffusion takes place (m)
χ_p	interaction parameter between permeant and membrane
μ	chemical potential ($\text{N}\cdot\text{m}\cdot\text{mol}^{-1}$)

subscript

d	desorption
F	feed phase
$m1$	upstream side interface of membrane
$m2$	downstream side interface of membrane
P	permeate vapour phase
t	overall process

REFERENCES

1. P. Côté and C. Lipski, Proceedings of the Third International Conference on Pervaporation Processes in the Chemical Industry, Nancy, France, September 19–22, 449 (1988).
2. P. Côté and C. Lipski, Proceedings of the Fourth International Conference on Pervaporation Processes in the Chemical Industry, Ft. Lauderdale, Florida, December 3–7, 304 (1989).
3. H. H. Nijhuis, M. H. V. Mulder, and C. A. Smolders, *J. Membr. Sci.*, **61**, 99 (1991).

4. B. Raghunath and S.-T. Hwang, *J. Membr. Sci.*, **65**, 147 (1992).
5. H. H. Nijhuis, M. H. V. Mulder, and C. A. Smolders, *J. Appl. Polym. Sci.*, **47**, 2227 (1993).
6. E. Bode, Proceedings of the Fourth International Conference on Pervaporation Processes in the Chemical Industry, Ft. Lauderdale, Florida, December 3–7, 103 (1989).
7. E. Bode, M. Busse, and K. Ruthenberg, *J. Membr. Sci.*, **77**, 69 (1993).
8. K. W. Böddeker, G. Bengtson, and H. Pingel, *J. Membr. Sci.*, **54**, 1 (1990).
9. K. W. Böddeker and G. Bengtson, *J. Membr. Sci.*, **53**, 143 (1990).
10. T. Q. Nguyen and Ken Nobe, *J. Membr. Sci.*, **30**, 11 (1987).
11. C. K. Yeom and R. Y. M. Huang, *J. Membr. Sci.*, **67**, 39 (1992).
12. M. Thomas, M. Escoubes, P. Esnault, and M. Pineri, *J. Membr. Sci.*, **49**, 57 (1989).
13. B. Raghunath and S.-T. Hwang, *J. Membr. Sci.*, **65**, 147 (1992).

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