PERMEATION EQUATIONS DEVELOPED FOR PREDICTION OF MEMBRANE PERFORMANCE IN PERVAPORATION, VAPOR PERMEATION AND REVERSE OSMOSIS BASED ON THE SOLUTION-DIFFUSION MODEL

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General permeation equations based on the solution-diffusion model were proposed for pervaporation (PV), vapor permeation (VP) and reverse osmosis (RO) on two different assumptions about the pressure gradient inside a membrane: a flat gradient (case 1) and a linear gradient (case 2). With these equations the permeation properties in PV, RO and VP can be estimated once the transport parameter of a membrane is known.

The effect of upstream pressure on selectivity and flux in RO and PV was estimated by sample calculations for water- and ethanol-selective membranes in ethanol-water system. Flux and selectivity in RO is smaller and, reaching that in PV at infinite pressure. This ultimate value is different in cases 1 and 2, and in the latter the molar volume ratio of the permeants becomes important. The effect of downstream pressure in PV was also estimated and compared with the case of vacuum-enhanced membrane distillation (MD) with a porous membrane. With increasing pressure the separation factor approaches that of vapor-liquid equilibrium in both PV and MD. With decreasing pressure that in MD is governed by the ratio of diffusion coefficients inside the membrane. Since the Knudsen diffusion coefficient of water is larger than that of ethanol, the separation factor decreases in ethanol-water separation with decreasing downstream pressure. This was verified by experiment, using PTFE membranes.

Introduction

For separating aqueous organic mixtures such as ethanol-water system by membranes, there are three methods: reverse osmosis (RO), pervaporation (PV) and vapor permeation (VP). It is essential to know the relationships among these processes and to determine which of them is advantageous for separating a given mixture with a given membrane. The permeation properties of PV^{7,8)} and RO¹¹⁾ and the relation between them^{3,9,10)} have been formulated by using the solution-diffusion model, but in these analyses it was assumed that the pressure inside the membrane is constant and is equal to the upstream pressure. This last assumption has not been verified experimentally.

The permeation properties of VP have been formulated, but the relationship between VP and PV, or that between VP and RO has not yet been studied on the basis of the same equations. Lee⁶⁾ proposed general equations for PV, RO, gas permeation and dialysis, but there were some problems in his derivation, one of which was that in the definition of

the standard chemical potential, μ_0 , the same value was used for the pure liquid and pure vapor at the pressure P_2 (downstream pressure), not at its saturation vapor pressure. Also, the definitions of symbols used for PV and gas permeation were different, so that his equations are not suitable for investigating the relationships among VP, PV and RO.

In the present paper, general permeation equations are proposed for PV, VP and RO with the solution-diffusion model on two different assumptions concerning the pressure profile in the membrane. Using these equations, the following two subjects were studied.

1) The effect of upstream pressure in PV and RO was estimated theoretically and its pressure-profile dependency was examined.

2) The effect of downstream pressure in PV was estimated for non-porous and porous membranes and the result was experimentally verified for the latter membrane.

1. Permeation Equation

1.1 Assumptions

Symbols used and the schema of permeation are

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shown in Fig. 1. The amount of permeant in the membrane is expressed by the mole fraction, x , multiplied by total molar concentration, C^m , with its activity coefficient, γ^m . The pressure in the membrane, P^m , is evaluated by the following two assumptions.

Case 1: P^m is equal to the upstream pressure, P_1 .

$$P^m = P_1 \quad (1)$$

Case 2: P^m changes linearly through the membrane as

$$P^m = P_1 + \frac{z}{l}(P_2 - P_1) \quad (2)$$

The following assumptions are also made.

1) The diffusion coefficient, D , activity coefficient, γ^m , and C^m are constant.

2) The molar volume of a permeant, v , is constant, not dependent on the pressure.

3) Vapor behaves as ideal gas.

1.2 Diffusion in the membrane

The permeant flux is proportional to its chemical potential gradient as

$$J = -\frac{DC^m x^m}{RT} \frac{d\mu}{dz} = -\frac{DC^m}{RT} \left(RT \frac{dx^m}{dz} + x^m v \frac{dP^m}{dz} \right) \quad (3)$$

$$\text{Case 1: } J = -DC^m \frac{dx^m}{dz}$$

After integration between $z=0$ and $z=l$,

$$J = \frac{DC^m}{l} (x_1^m - x_2^m) \quad (4)$$

Case 2:

Differentiating Eq. (3),

$$\frac{dJ}{dz} = -\frac{DC^m}{RT} \left(RT \frac{d^2 x^m}{dz^2} + v \frac{dx^m}{dz} \frac{dP^m}{dz} + v x^m \frac{d^2 P^m}{dz^2} \right) = 0 \quad (5)$$

Differentiating Eq. (2),

$$\frac{dP^m}{dz} = \frac{P_2 - P_1}{l}, \quad \frac{d^2 P^m}{dz^2} = 0 \quad (6)$$

By substituting Eq. (6) into Eq. (5),

$$x^m = A \exp \left\{ \frac{v(P_1 - P_2)}{RTl} z \right\} + B \quad (7)$$

where

$$A = \frac{x_1^m - x_2^m}{1 - \exp \left\{ \frac{v(P_1 - P_2)}{RT} \right\}},$$

Fig. 1. Schema of permeation

$$B = \frac{x_2^m - x_1^m \exp \left\{ \frac{v(P_1 - P_2)}{RT} \right\}}{1 - \exp \left\{ \frac{v(P_1 - P_2)}{RT} \right\}}$$

Substituting Eq. (7) into Eq. (3) and integrating between $z=0$ and $z=l$,

$$J = \frac{DC^m}{l} \frac{v}{RT} \frac{P_1 - P_2}{1 - \exp \left\{ -\frac{v(P_1 - P_2)}{RT} \right\}} \times \left[x_1^m - x_2^m \exp \left\{ -\frac{v(P_1 - P_2)}{RT} \right\} \right] \quad (8)$$

1.3 Equilibrium at the surface of the membrane

Here the molar fraction of a permeant outside the membrane, x^s , is related to that inside the membrane, x^m .

1) For liquid in contact with the membrane on the feed side

Case 1:

In the solution: $\mu_1^s = \mu_0(P_1, T) + RT \ln \gamma_1^s x_1^s$

In the membrane: $\mu_1^m = \mu_0(P_1, T) + RT \ln \gamma_1^m x_1^m$

Since $\mu_1^s = \mu_1^m$,

$$x_1^m = \frac{\gamma_1^s x_1^s}{\gamma_1^m} \quad (9)$$

Case 2:

Eq. (9) is obtained in the same way as in Case 1.

2) For vapor in contact with the membrane on the feed side

$$\text{Case 1: } \mu_1^s = \mu_0(P_v, T) + RT \ln \frac{P_1 x_1^s}{P_v}$$

$$\mu_1^m = \mu_0(P_v, T) + v(P_1 - P_v) + RT \ln \gamma_1^m x_1^m$$

$$x_1^m = \frac{P_1 x_1^s}{P_v \gamma_1^m} \exp \frac{v(P_v - P_1)}{RT} \quad (10)$$

Case 2: Eq. (10) is derived in the same way as in Case 1.

3) For liquid in contact with the membrane on the permeate side

$$\begin{aligned}\text{Case 1: } \mu_2^s &= \mu_0(P_2, T) + RT \ln \gamma_2^s x_2^s \\ \mu_2^m &= \mu_0(P_2, T) + v(P_1 - P_2) + RT \ln \gamma^m x_2^m \\ x_2^m &= \frac{\gamma_2^s x_2^s}{\gamma^m} \exp \frac{v(P_2 - P_1)}{RT}\end{aligned}\quad (11)$$

$$\begin{aligned}\text{Case 2: } \mu_2^m &= \mu_0(P_2, T) + RT \ln \gamma^m x_2^m \\ x_2^m &= \frac{\gamma_2^s x_2^s}{\gamma^m}\end{aligned}\quad (12)$$

4) For vapor in contact with the membrane on the permeate side

$$\begin{aligned}\text{Case 1: } \mu_2^s &= \mu_0(P_v, T) + RT \ln \frac{P_2 x_2^s}{P_v} \\ \mu_2^m &= \mu_0(P_v, T) + v(P_1 - P_v) + RT \ln \gamma^m x_2^m \\ x_2^m &= \frac{P_2 x_2^s}{P_v \gamma^m} \exp \frac{v(P_v - P_1)}{RT}\end{aligned}\quad (13)$$

$$\begin{aligned}\text{Case 2: } \mu_2^m &= \mu_0(P_v, T) + v(P_2 - P_v) + RT \ln \gamma^m x_2^m \\ x_2^m &= \frac{P_2 x_2^s}{P_v \gamma^m} \exp \frac{v(P_v - P_2)}{RT}\end{aligned}\quad (14)$$

1.4 Permeation equations

Permeation equations are obtained by combining equations derived in 1.3 with those derived in 1.2.

Case 1:

PV

Substituting Eqs. (9) and (13) into Eq. (4),

$$J = \frac{DC^m}{l\gamma^m} \left(\gamma_1^s x_1^s - \frac{P_2 x_2^s}{P_v} \exp \left\{ \frac{v(P_v - P_1)}{RT} \right\} \right) \quad (15)$$

Under experimental conditions,

$$\begin{aligned}v &\simeq 10^{-5} (\text{m}^3 \text{mol}^{-1}), \quad P_1 \simeq 10^5 (\text{Pa}), \\ P_v &\simeq 10^4 (\text{Pa}), \quad T \simeq 10^2 (\text{K})\end{aligned}$$

Then

$$\frac{v(P_v - P_1)}{RT} \simeq 10^{-3} \simeq 0, \quad \exp \frac{v(P_v - P_1)}{RT} \simeq 1$$

Eq. (15) can be simplified as

$$J = \frac{DC^m}{l\gamma^m} \left(\gamma_1^s x_1^s - \frac{P_2 x_2^s}{P_v} \right) \quad (16)$$

RO

Substituting Eqs. (9) and (11) into Eq. (4),

$$J = \frac{DC^m}{l\gamma^m} \left(\gamma_1^s x_1^s - \gamma_2^s x_2^s \exp \left\{ \frac{v(P_2 - P_1)}{RT} \right\} \right) \quad (17)$$

VP

Substituting Eqs. (10) and (13) into Eq. (4),

$$J = \frac{DC^m}{l\gamma^m} \left(\frac{P_1 x_1^s}{P_v} - \frac{P_2 x_2^s}{P_v} \right) \exp \left\{ \frac{v(P_v - P_1)}{RT} \right\} \quad (18)$$

Simplifying this equation in the same way as in PV,

$$J = \frac{DC^m}{l\gamma^m} \left(\frac{P_1 x_1^s}{P_v} - \frac{P_2 x_2^s}{P_v} \right) \quad (19)$$

Case 2:

PV

Substituting Eqs. (9) and (14) into Eq. (8),

$$J = \frac{DC^m}{l\gamma^m} \Phi \left(\gamma_1^s x_1^s - \frac{P_2 x_2^s}{P_v} \exp \left\{ \frac{v(P_v - P_1)}{RT} \right\} \right) \quad (20)$$

where

$$\Phi = \frac{v}{RT} \frac{P_1 - P_2}{1 - \exp \frac{v(P_2 - P_1)}{RT}}$$

Under the condition of $(P_1 - P_2) \ll \frac{RT}{v}$,

$$\begin{aligned}\exp \frac{v(P_2 - P_1)}{RT} &\simeq 1 + \frac{v(P_2 - P_1)}{RT} \\ J &= \frac{DC^m}{l\gamma^m} \left(\gamma_1^s x_1^s - \frac{P_2 x_2^s}{P_v} \exp \left\{ \frac{v(P_v - P_1)}{RT} \right\} \right)\end{aligned}\quad (21)$$

This is the same equation as Eq. (15). The equations in Case 2 can be simplified to those in Case 1 under this condition, which is also true for RO and VP.

RO

Substituting Eqs. (9) and (12) into Eq. (8),

$$J = \frac{DC^m}{l\gamma^m} \Phi \left(\gamma_1^s x_1^s - \gamma_2^s x_2^s \exp \left\{ \frac{v(P_2 - P_1)}{RT} \right\} \right) \quad (22)$$

VP

Substituting Eqs. (10) and (14) into Eq. (8),

$$J = \frac{DC^m}{l\gamma^m} \Phi \left(\frac{P_1 x_1^s}{P_v} - \frac{P_2 x_2^s}{P_v} \right) \exp \left\{ \frac{v(P_v - P_1)}{RT} \right\} \quad (23)$$

2. Effect of Operating Pressure in PV and RO

In equations derived above, $DC^m/l\gamma^m$ is the only parameter determined from the combination of a membrane and a permeant. When this parameter is known for a particular system and membrane, flux of a permeant can be calculated for various methods of separation, namely PV, VP and RO, under various operating conditions. Or, once this parameter is determined by a given method of separation under a given condition, the permeation properties by a different method of separation under various conditions can be calculated.

2.1 Effect of upstream pressure

It is possible to study the effect of upstream pressure quantitatively using Eqs. (17) and (22) for RO, and Eqs. (15) and (20) for PV. First, equations will be derived that predict how the fluxes and separation factors change according to the increase of P_1 in cases 1 and 2. Examples of simulation calculations will then be shown for both water-selective and ethanol-selective membranes in the ethanol-water system.

1) Equations

Case 1:

In PV with downstream pressure P_2 of zero, Eq. (15) is simplified as follows. This shows that the flux is independent of P_1 .

$$J = \frac{DC^m}{l\gamma^m} \gamma_1^s x_1^s \quad (24)$$

For a binary system of i and j components, the separation factor is given as

$$\alpha_{ij} = \frac{\frac{DC^m}{l\gamma^m} \Big|_i \cdot \gamma_{1i}}{\frac{DC^m}{l\gamma^m} \Big|_j \cdot \gamma_{1j}} \quad (25)$$

In RO, when P_1 is increased to infinity, Eq. (17) becomes

$$J \rightarrow \frac{DC^m}{l\gamma^m} \gamma_1^s x_1^s \quad (26)$$

$$\alpha_{ij} \rightarrow \frac{\frac{DC^m}{l\gamma^m} \Big|_i \cdot \gamma_{1i}}{\frac{DC^m}{l\gamma^m} \Big|_j \cdot \gamma_{1j}} \quad (27)$$

This means that flux and selectivity in RO at infinite upstream pressure are equal to those in PV at zero downstream pressure, which is the same conclusion obtained previously by Lee⁶⁾ and Greenlaw *et al.*⁴⁾

Case 2:

In PV, as is evident from Eq. (20), the flux increases to infinity when P_1 is increased. The separation factor is given as

$$\alpha_{ij} = \frac{\frac{DC^m}{l\gamma^m} \Big|_i \cdot \gamma_{1i} \cdot \frac{v_i}{v_j} \cdot \frac{1 - \exp\left\{\frac{v_j(P_2 - P_1)}{RT}\right\}}{1 - \exp\left\{\frac{v_i(P_2 - P_1)}{RT}\right\}}}{\frac{DC^m}{l\gamma^m} \Big|_j \cdot \gamma_{1j} \cdot \frac{v_i}{v_j} \cdot \frac{1 - \exp\left\{\frac{v_j(P_2 - P_1)}{RT}\right\}}{1 - \exp\left\{\frac{v_i(P_2 - P_1)}{RT}\right\}}} \rightarrow \frac{\frac{DC^m}{l\gamma^m} \Big|_i \cdot \gamma_{1i} \cdot \frac{v_i}{v_j}}{\frac{DC^m}{l\gamma^m} \Big|_j \cdot \gamma_{1j} \cdot \frac{v_i}{v_j}} \quad (28)$$

When P_1 becomes large, α_{ij} becomes the product of the α_{ij} value in case 1 and the ratio of the molar volumes of components, that is,

$$(\alpha_{ij})_{\text{Case 2}} = (\alpha_{ij})_{\text{Case 1}} \cdot \frac{v_i}{v_j} \quad (29)$$

which shows the large contribution of the pressure term in Eq. (3).

In RO, as in PV, when P_1 is increased the flux increases infinitely and the difference between PV and RO becomes less. As for the separation factor,

$$\alpha_{ij} \rightarrow \frac{\frac{DC^m}{l\gamma^m} \Big|_i \cdot \gamma_{1i} \cdot \frac{v_i}{v_j}}{\frac{DC^m}{l\gamma^m} \Big|_j \cdot \gamma_{1j} \cdot \frac{v_i}{v_j}} \quad (30)$$

This means that the selectivity in RO approaches the same value in PV, which can be observed in Figs. 3 and 5.

2) Examples of simulation calculations

Examples of simulation calculations in ethanol-water system are shown in Figs. 2 and 3 for a water-selective membrane, and in Figs. 4 and 5 for an ethanol-selective membrane.

For a water-selective membrane, $DC^m/l\gamma^m$ values for ethanol and water are 3.0×10^{-3} and 6.0×10^{-2} ($\text{mol m}^{-2} \text{s}^{-1}$), respectively. These values are very close to those of Nafion¹⁾ and cellophane membranes¹⁴⁾. For an ethanol-selective membrane, $DC^m/l\gamma^m$ values for ethanol and water are 7.0×10^{-2} and 1.5×10^{-2} , respectively. Those values are imaginary, and are close to target values of recent R & D to obtain better ethanol-selective membranes.

The effect of upstream pressure on fluxes is the same for both kinds of membranes. The flux in RO is smaller and approaches that in PV at higher pressure. For case 1, fluxes converge to a constant value, while for case 2 they increase to infinity.

The effect of upstream pressure on selectivities is different for the two kinds of membranes. For a water-selective membrane, the separation factor in RO is smaller and approaches that in PV at high pressure. For case 1, the separation factor in PV is constant, but for case 2 it decreases.

For an ethanol-selective membrane, the separation factor in RO is smaller and increases to that in PV at higher pressure, and it becomes larger than that in PV at an interim pressure. For case 1, the separation factor in PV is constant, but for case 2, it increases at higher pressure. As seen from the discussion that led to Eq. (29), the separation factor in case 2 is the product of the separation factor in case 1 and the ratio of molar volumes. At 25°C the molar volume of ethanol, v_E is 5.85×10^{-5} and that of water, v_W , is 1.80×10^{-5} ($\text{m}^3 \cdot \text{mol}^{-1}$); then

$$(\alpha_W^E)_{\text{Case 2}} = (\alpha_W^E)_{\text{Case 1}} \times 3.26$$

$$(\alpha_E^W)_{\text{Case 2}} = (\alpha_E^W)_{\text{Case 1}} \times 0.307$$

Fig. 2. Effect of P_1 on Total Flux in RO and PV
Example of a water-permeable membrane, whose transport parameters are:

$$\frac{DC^m}{l\gamma^m} \text{ ethanol} = 3.0 \times 10^{-3} \text{ (mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}\text{)}$$

$$\frac{DC^m}{l\gamma^m} \text{ water} = 6.0 \times 10^{-2} \text{ (mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}\text{)}$$

at 40 (ethanol wt%) feed concentration and 25°C

Fig. 3. Effect of P_1 on Selectivity in RO and PV
Example of a water-selective membrane, whose transport parameters are same as those in Fig. 2

It is seen, however, that under ordinary upstream pressure, that is, less than 100 atm, the effect of upstream pressure is not so large in PV. **Figures. 6 and 7** show the effect of upstream pressure on selectivities in RO and their comparison to that in PV under ordinary pressure for both kinds of membranes.

2.2 Effect of downstream pressure

In the above discussion the downstream pressure in PV is assumed to be zero, but many results have shown that downstream pressure has a large effect on flux and selectivity. In the following this effect will be discussed using equations developed above. And in addition to the discussion of PV with non-porous membranes, equations will be developed and the effect

Fig. 4. Effect of P_1 on Total Flux in PV and RO
Example of an ethanol-selective membrane, whose transport parameters are as follows.

$$\frac{DC^m}{l\gamma^m} \text{ ethanol} = 7.0 \times 10^{-2} \text{ (mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}\text{)}$$

$$\frac{DC^m}{l\gamma^m} \text{ water} = 1.5 \times 10^{-2} \text{ (mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}\text{)}$$

at 40 (ethanol wt%) feed concentration and 25°C

Fig. 5. Effect of P_1 on Selectivity in PV and RO
Example of an ethanol-selective membrane, whose transport parameters are same as those in Fig. 4

of P_2 will also be discussed for a porous membrane, which is used for extracting ethanol from fermentation broth by vacuum membrane distillation (MD).

1) Effect of downstream pressure in PV

From Eq. (16) a flux is given as follows.

$$J = \frac{DC^m}{l\gamma^m} \left(\gamma_1^s x_1^s - \frac{P_2 x_2^s}{P_v} \right) = K \cdot P_2 x_2^s \quad (31)$$

where K expresses the conductance of a membrane substrate, a porous support plate and a tube between the plate and a trap, divided by a membrane area. By these equations P_2 is solved and substituted to give the following equation.

Fig. 6. Comparison of Selectivity between PV and RO with a Water-selective Membrane

Transport parameters and conditions are same as those in Fig. 2

—: PV; ----: RO ($P_1 = 50$ atm); —: RO ($P_1 = 100$ atm)

Fig. 7. Comparison of Selectivity between PV and RO with an Ethanol-selective Membrane

Transport parameters and conditions are same as those in Fig. 4.

—: PV; ----: RO ($P_1 = 50$ atm); —: RO ($P_1 = 100$ atm)

$$J = \frac{Kx_1^s}{\frac{l\gamma^m K}{DC^m\gamma_1^s} + \frac{1}{P_v\gamma_1^s}} \quad (32)$$

For a binary system of i and j components, the separation factor is given as

$$\frac{J_i}{J_j} = \frac{K_i \cdot x_{1i}^s \left(\frac{l\gamma_j^m K_j}{D_j C^m \gamma_{1j}^s} + \frac{1}{P_{vj}\gamma_{1j}^s} \right)}{K_j \cdot x_{1j}^s \left(\frac{l\gamma_i^m K_i}{D_i C^m \gamma_{1i}^s} + \frac{1}{P_{vi}\gamma_{1i}^s} \right)} \quad (33)$$

To increase P_2 is same as to reduce K to zero, and then,

$$J_i \rightarrow 0, \quad J_j \rightarrow 0, \quad \frac{J_i}{J_j} \rightarrow \frac{K_i}{K_j} \cdot \frac{x_{1i}^s P_{vi}\gamma_{1i}^s}{x_{1j}^s P_{vj}\gamma_{1j}^s} \quad (34)$$

Usually, $K_i/K_j = 1$, and Eq. (34) means that the

selectivity approaches that of a vapor-liquid equilibrium. Researches at the Univ. of Maine^{2,3,4,5,12,13} show that there are three cases of selectivity behavior in PV. The first case is better selectivity in PV than the vapor-liquid equilibrium; the second case is worse selectivity in PV, and the last case is a selectivity change in the opposite direction. These phenomena are ultimately explained by the simple result stated above.

Further, experimental results of Asai and Nagahama¹), who studied the effect of downstream pressure in the ethanol-water system using Nafion membranes, were utilized to show the validity of the above theoretical analysis. Using flux data taken for ethanol and water at $P_2 = 0.98$ (mmHg), $DC^m/l\gamma^m$ values were obtained by Eq. (16). Then fluxes and separation factors were calculated using the following set of equations.

$$J_i = \frac{D_i C^m \gamma_{1i}^s}{l\gamma_i^m} \left(x_{1i}^s - \frac{P_2 x_{2i}^s}{P_{vi}\gamma_{1i}^s} \right)$$

$$J_j = \frac{D_j C^m \gamma_{1j}^s}{l\gamma_j^m} \left(x_{1j}^s - \frac{P_2 x_{2j}^s}{P_{vj}\gamma_{1j}^s} \right)$$

$$J_i/J_j = x_{2i}^s/x_{2j}^s, \quad x_{2i}^s + x_{2j}^s = 1$$

Results are shown in Figs. 8 and 9, where agreement of estimation is good.

2) Effect of downstream pressure in MD

Equations for flux in this case are given as

$$J_i = \frac{D_{Ki}\varepsilon}{l} (P_{vi}\gamma_{1i}^s x_{1i}^s - P_2 x_{2i}^s) = K_i \cdot P_2 x_{2i}^s$$

$$J_j = \frac{D_{Kj}\varepsilon}{l} (P_{vj}\gamma_{1j}^s x_{1j}^s - P_2 x_{2j}^s) = K_j \cdot P_2 x_{2j}^s \quad (35)$$

where D_K is a diffusion coefficient, and ε is the porosity of a membrane.

By eliminating P_2 ,

$$J_i = \frac{K_i P_{vi}\gamma_{1i}^s x_{1i}^s}{1 + \frac{K_i l}{\varepsilon D_{Ki}}}, \quad J_j = \frac{K_j P_{vj}\gamma_{1j}^s x_{1j}^s}{1 + \frac{K_j l}{\varepsilon D_{Kj}}} \quad (36)$$

The same equation as Eq. (34) is obtained when P_2 is increased or K_i and K_j become zero. This means that the separation factor reaches that of a vapor-liquid equilibrium by increasing P_2 . But when P_2 becomes zero, the separation factor is given as

$$\frac{J_i}{J_j} = \frac{D_{Ki}}{D_{Kj}} \cdot \frac{P_{vi}\gamma_{1i}^s x_{1i}^s}{P_{vj}\gamma_{1j}^s x_{1j}^s} \quad (37)$$

This shows that the selectivity depends on the ratio of diffusion coefficients inside a pore. Under ordinary conditions the diffusion coefficient in a porous membrane can be given by the Knudsen equation. Since the Knudsen diffusion coefficient of water is larger than that of ethanol, the separation factor of

Fig. 8. Effect of Downstream Pressure on Flux in PV
Experimental data are from ref. 1

Fig. 9. Effect of Downstream Pressure on Selectivity in PV
Experimental data are from ref. 1

ethanol to water becomes smaller when P_2 becomes small. This trend is completely opposite to that in PV. To verify this the following experiments were performed.

3) Experimental

A schematic diagram of the experimental apparatus for vacuum-enhanced membrane distillation is shown in Fig. 10. Feed liquid is circulated from a constant-temperature bath. The permeate side is evacuated by a vacuum pump, and samples are taken from traps. The pressure on the downstream side is controlled by feeding nitrogen from a cylinder and is measured by Baratron. It is possible that nitrogen gas exists in the line between the membrane and the cold trap, and that there is some difference between the total pressure below the membrane and the pressure measured by Baratron as that of nitrogen gas. But solving the equations concerning the diffusive and convective flows of three components—water vapor,

Fig. 10. Schematic Diagram of Experimental Apparatus

ethanol vapor and nitrogen gas—analytically led to the conclusion that nitrogen gas exists only near the cold trap and that downstream pressure P_2 is almost equal to the pressure of nitrogen gas as measured by Baratron, which supports the validity of the way of measuring and controlling P_2 in this experiment. Tubes on the permeate side were heated by ribbon heaters to prevent condensation of vapor.

Membranes used were made of polytetrafluoroethylene (PTFE) having $0.1 \mu\text{m}$ pores, manufactured by Nitto Elec. Co. Inc. Concentration of ethanol was 5 ethanol mol%, and feed temperature was 40°C .

From data taken at $P_2 = 10$ (mmHg), (D_{KE}/l) for ethanol and water were determined as 2.09×10^{-3} and 4.29×10^{-3} ($\text{mol m}^{-2} \text{s}^{-1} \text{torr}^{-1}$) respectively. These values were used to calculate flux and separation factors at various P_2 . Knudsen diffusion coefficients at 40°C in $0.1 \mu\text{m}$ were calculated as 2.5×10^{-5} and 3.9×10^{-5} ($\text{m}^2 \text{s}^{-1}$), respectively for ethanol and water. Results are shown in Figs. 11 and 12, where their agreement with experimental data is good.

3. Effect of Operating Pressure in VP

For VP effects of upstream and downstream pressure were easily estimated from Eq. (19) and not repeated here.

Conclusions

General permeation equations based on the solution-diffusion model were proposed for PV, VP and RO on two different assumptions about the pressure gradient inside a membrane: flat-gradient and linear-gradient cases.

It was shown that permeation properties in PV, RO and VP are closely related, and that once the transport parameter is determined the transport properties for each method can be estimated by equations developed here. The effect of upstream pressure on flux and separation factor was estimated for PV and RO, and

Fig. 11. Effect of Downstream Pressure on Flux in MD

Fig. 12. Effect of Downstream Pressure on Selectivity in MD

their trends were demonstrated for examples of water-selective and ethanol-selective membranes in ethanol-water system. Both flux and separation factor are smaller in RO and increase to those in PV at infinite pressure. In case 2, the ultimate separation factor is influenced by molar volumes of permeants.

The effect of downstream pressure in PV was also estimated and compared to the case with a porous membrane (MD). When this pressure is increased, the separation factor approaches that of vapor-liquid equilibrium both in PV and MD, while in MD the separation factor is governed by the ratio of Knudsen diffusion coefficients. This was verified by experiments using a PTFE membrane.

Nomenclature

a	= activity	[—]
C^m	= total molar concentration in the membrane	[mol m ⁻³]
D	= diffusion coefficient	[m ² s ⁻¹]
D_K	= Knudsen diffusion coefficient	[mol m ⁻¹ s ⁻¹ Pa ⁻¹]
J	= permeation flux	[mol m ⁻² s ⁻¹]
K	= conductance per membrane area	[mol m ⁻² s ⁻¹ Pa ⁻¹]
l	= membrane thickness	[m]
P	= pressure	[Pa]
P_v	= saturation vapor pressure	[Pa]
P_v^0	= saturation vapor pressure of a feed liquid	[Pa]
Q	= mass permeation flux	[kg m ⁻² h ⁻¹]
R	= gas constant	[J mol ⁻¹ K ⁻¹]
T	= temperature	[K]
v	= molar volume	[m ³ mol ⁻¹]
x	= mole fraction	[—]
α	= separation factor	[—]
γ	= activity coefficient.	[—]
μ	= chemical potential	[J mol ⁻¹]
μ_0	= standard chemical potential	[J mol ⁻¹]

<Subscripts>

1	= feed side
2	= permeate side
E	= ethanol
W	= water

<Superscripts>

m	= inside the membrane
s	= outside the membrane

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