Effect of Upstream Pressure on the Flux of Single Permeant in Pervaporation

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ABSTRACT: The effect of the upstream pressure on the pervaporation flux of water was studied both theoretically and experimentally. The increase in the pervaporation flux with an increase in the upstream pressure was predicted using newly developed transport equations that allow the pressure change across the membrane and include both liquid and vapor phase transport. The conventional solution-diffusion model, on the other hand, fails to predict the effect of the upstream pressure, particularly when an assumption is made that the pressure of the permeant inside the membrane is constant across the membrane and is equal to the upstream pressure. The pervaporation flux of water through a polydimethylsiloxane membrane and an aromatic polyamide membrane was found, experimentally, to increase with an increase in the upstream pressure.

KEY WORDS Pervaporation / Membrane / Aromatic Polyamide / Polydimethylsiloxane / Membrane Transport /

Pervaporation has been recognized recently as one of the most versatile membrane separation processes. Fundamental research on pervaporation has been carried out intensively parallel to the growth of the number of industrial applications. At present the majority of studies on pervaporation transport is based on the solution-diffusion model¹⁻⁵ with few exceptions that are based on the pore model.⁶⁻⁸ Although the transport equations derived from both models explain the effect of the downstream pressure on pervaporation flux equally well, they come to different conclusions regarding the effect of the upstream pressure; *i.e.*, the solution-diffusion model predicts little effect of the upstream pressure, when the downstream pressure is nearly equal to zero, while the pore model predicts that the pervaporation flux should change linearly with an increase in the upstream pressure. There are

also two different kinds of experimental data. Whereas Greenlaw *et al.* and Paul and Ebrahima concluded that the pervaporation flux remained constant with an increase of the upstream pressure for the system hexane/polyethylene and cyclohexane/highly swollen cross-linked rubbery membrane,^{5,9} respectively, Okada and Matsuura showed that the flux increased linearly for the system ethyl alcohol/heptane mixture in cellulose membranes of different pore sizes.⁶

It has to be noted that the solution-diffusion mechanism does not necessarily predict no upstream pressure effect. The above prediction can only be made under an assumption that the pressure of the permeant remains the same as the upstream pressure across the membrane. When the above assumption is removed, the change of the pervaporation flux is predicted with a change in the upstream pressure. It is

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obvious, therefore, from above discussions that no conclusive evidence has been obtained so far either theoretically or experimentally about the effect of upstream pressure on pervaporation flux.

It is the objective of this work to study the effect of the upstream pressure on the pervaporation flux in detail, both theoretically and experimentally. In particular, pervaporation experiments are conducted for the permeation of water through polydimethylsiloxane and aromatic polyamide membranes. While the former membrane represents rubbery hydrophobic membranes, the latter represents glassy hydrophilic membranes.

EXPERIMENTAL

Membranes

A casting solution was prepared by mixing 10.3 wt% aromatic polyamide (poly-*m*-phenylene-iso(70)-*co*-terephthalamide, abbreviated as APA), 3.8 wt% LiCl, and 85.9 wt% dimethyl acetamide. The filtered and air bubble free casting solution was cast onto a glass plate by a casting knife to the thickness of 5.08×10^{-5} m at room temperature and kept in an oven at 95°C for two hours. The membrane looked completely dry and transparent after a long evaporation period and is considered to be dense and symmetric. Then, the membrane was immersed in ice cold water to be removed from the glass plate. A commercial polydimethylsiloxane (PDMS) membrane of thickness 5.08×10^{-5} m was supplied by General Electric Co.

Pervaporation Experiments

The pervaporation system consists of a static permeation cell made of stainless steel and with an effective membrane area of 9.6×10^{-4} m², permeate collection traps and a vacuum pump. About 100 g of feed liquid was loaded in the cell at room temperature (23°C) and nitrogen pressure was applied to the feed liquid from a nitrogen cylinder. This pressure is called

hereafter upstream pressure. Then vacuum was applied on the permeate side by turning on the vacuum pump. The pressure of the permeate side was adjusted to a predetermined value by introducing dry air stream into the vacuum line. This pressure is called hereafter downstream pressure. The downstream pressure can also be adjusted to a predetermined value by controlling a pressure control valve installed between the permeate collection trap and the vacuum pump. It was confirmed experimentally that the pervaporation flux at a given downstream pressure did not depend on whether it was achieved by introducing dry air stream or by adjusting the control valve. The ranges of the upstream and downstream pressures were 1.01×10^5 – 1.14×10^6 Pa (0–150 psig) and 400–4000 Pa (3–30 mmHg), respectively. The feed liquid was water in most cases except few experiments with an aqueous acetic acid solution of 0.08 mol fraction. The permeate product was condensed in the permeate collection trap cooled by liquid nitrogen. Stable permeation rates were reached usually within 120 minutes after permeate collection was started. The permeation rate was determined by weighing the cold trap filled with the permeate. The composition of the permeate sample was analyzed using gas chromatograph when the feed was an aqueous acetic acid solution.

Reverse Osmosis

Reverse osmosis experiments were conducted also by using a static permeation cell. About 150 g of feed aqueous sodium chloride solution (1700 ppm) was loaded in the cell at room temperature and nitrogen pressure was applied to the feed liquid to adjust the feed pressure to 1825008 Pa (250 psig). The permeate side was maintained at an atmospheric pressure. The first five ml of the permeate was discarded before the permeate sample collection was started. The permeation rate was determined by weighing the permeate sample collected during a predetermined period. The

sodium chloride concentration of the feed and the product sample was analyzed by conductivity measurement. The solute separation, f , was defined as,

$$f = \frac{\text{feed}_{\text{NaCl ppm}} - \text{permeate}_{\text{NaCl ppm}}}{\text{feed}_{\text{NaCl ppm}}} \quad (1)$$

Scanning Electron Microscope

Selected samples of the membranes were prepared for the scanning electron microscope (SEM) observations. Cross sections of the membranes were prepared by quenching in liquid nitrogen, then breaking without damaging the membrane. The sample was then attached to the carbon holder and shadowed with a thin gold layer to prevent any charging by the electron beam. The membrane section was subjected to a narrow beam of electrons with kinetic energies of 1–25 kV causing the liberation of low energy electrons from the atoms in the surface which create the image on the micrograph.

THEORETICAL

Some transport equations are developed for a pervaporation system where the transport of a single component is involved.

The pervaporation flux through a membrane segment of thickness dx is related to the chemical potential gradient by

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

where c_m and f_m are the permeant concentration in the membrane (mol m^{-3}) and the friction ($J \text{ s m}^{-2} \text{ mol}^{-1}$) to the movement of the permeant in the membrane, respectively.¹⁰

Liquid Phase Transport

At the upstream face of the membrane the permeant in the membrane is in equilibrium with the feed liquid under the upstream pressure, p_2 . Therefore, the chemical potential of

Figure 1. Schematic illustration of the imaginary liquid and vapor phase that are in thermodynamic equilibrium with the permeant in the membrane.

the permeant in the membrane is equal to that of the feed liquid which can be written as,

$$\mu = \mu^* + v(p_2 - p_*) \quad (3)$$

where μ^* is the chemical potential of liquid at the saturation vapor pressure, p_* , and v is the molar volume of the feed liquid.

At a distance x from the upstream interface, a membrane segment whose thickness is dx is considered (see Figure 1). (It would be possible to assume the presence of an imaginary pure liquid phase which is in equilibrium with the permeant in the membrane segment when the distance x is not large.) An attempt is made in the following to calculate the chemical potential change $d\mu$ in the above imaginary pure liquid phase.

The pressure of the pure liquid phase changes from p to $p + dp$ as the distance increases from x to $x + dx$, dp having a negative sign. Since the molar volume of the permeant is constant, the change in the chemical potential of the permeant from distance x to $x + dx$ should be,

$$d\mu = v dp \quad (4)$$

Although the above equation was developed for the imaginary pure liquid phase, it should also be applicable to the membrane phase. The pressure of the imaginary pure liquid phase continues to decrease as the distance x increases, and at a distance δ_a , the pressure becomes the saturation vapor pressure. Since the concentration of the permeant in the membrane, c_m , can be assumed to be constant from $x=0$ to $x=\delta_a$ (Lonsdale made the same assumption when he developed his reverse osmosis transport equations¹¹), eq 2 can be integrated into,

$$J \int_0^{\delta_a} dx = \frac{-c_m}{f_m} v \int_{p_2}^{p_*} dp \quad (5)$$

Therefore,

$$J = \frac{c_m}{f_m} v \frac{(p_2 - p_*)}{\delta_a} \quad (6)$$

An assumption was made in the above integration that f_m is also unchanged throughout the integration. As for c_m , the following relationship was established by Greenlaw *et al.* between c_m and the activity,⁵

$$c_m = \sigma a + \tau a^m \quad (7)$$

The activity used in the above equation is considered to be that of imaginary pure liquid phase, hence $a=1$. Then,

$$c_m = \sigma + \tau \quad (8)$$

As for f_m , it is related to the diffusion coefficient D_m by,

$$f_m = \frac{RT}{D_m} \quad (9)$$

Furthermore, Greenlaw *et al.* has given the relation between D_m and c_m as,⁵

$$D_m = D_{m0}(1 + \alpha c_m^n) \quad (10)$$

Combining eq 6, 8, 9, and 10,

$$J = \frac{(D_{m0}/RT)(\sigma + \tau)(1 + \alpha(\sigma + \tau)^n)v}{\delta_a} (p_2 - p_*) \quad (11)$$

Vapor Phase Transport

From the distance $x=\delta_a$ to $x=\delta$ the equilibrium phase is considered to be in the vapor phase (see Figure 1) and the pressure changes from p_* to p_3 . The change in the chemical potential in a small segment dx can be written as,

$$d\mu = \frac{RT}{p} dp \quad (12)$$

assuming ideal gas law. Thus, the chemical potential gradient is established by eq 4 and 12, respectively, in the liquid transport and vapor transport region. Then, eq 2 is written as,

$$J = -\frac{c_m}{f_m} \frac{d\mu}{dx} \quad (13)$$

$$= -\frac{c_m}{f_m} \frac{RT}{p} \frac{dp}{dx} \quad (14)$$

Rearranging,

$$J dx = -\frac{c_m RT}{f_m} \frac{dp}{p} \quad (15)$$

Since the activity of the vapor in the equilibrium phase can be written as,

$$a = p/p_* \quad (16)$$

Combination of eq 7, 9, 10, 15, and 16 yields,

$$J dx = \frac{-(\sigma(p/p_*) + \tau(p/p_*)^m)RT}{[RT/D_{m0}(1 + \alpha(\sigma(p/p_*) + \tau(p/p_*)^m)^n]} \frac{d(p/p_*)}{(p/p_*)} \quad (17)$$

Rearranging,

$$Jdx = -\frac{D_{m0}(\sigma(p/p_*) + \tau(p/p_*)^m)(1 + \alpha(\sigma(p/p_*) + \tau(p/p_*)^m)^n)}{(p/p_*)} d(p/p_*) \quad (18)$$

Setting $\zeta = p/p_*$,

$$Jdx = -\frac{D_{m0}(\sigma\zeta + \tau\zeta^m)(1 + \alpha(\sigma\zeta + \tau\zeta^m)^n)}{\zeta} d\zeta \quad (19)$$

Integrating from $x = \delta_a$ to $x = \delta$,

$$J \int_{\delta_a}^{\delta} dx = - \int_{p_*/p_*}^{\zeta_3} \frac{D_{m0}(\sigma\zeta + \tau\zeta^m)(1 + \alpha(\sigma\zeta + \tau\zeta^m)^n)}{\zeta} d\zeta \quad (20)$$

and,

$$J = \frac{\int_{\zeta_3}^1 \frac{D_{m0}(\sigma\zeta + \tau\zeta^m)(1 + \alpha(\sigma\zeta + \tau\zeta^m)^n)}{\zeta} d\zeta}{\delta_b} \quad (21)$$

where $\zeta_3 = p_3/p_*$ and $\delta_b = \delta - \delta_a$.

Combination of Liquid Phase and Vapor Phase Transport.

From eq 11,

$$\delta_a = \frac{(D_{m0}/RT)(\sigma + \tau)(1 + \alpha(\sigma + \tau)^n)v}{J} (p_2 - p_*) \quad (22)$$

and from eq 21,

$$\delta_b = \frac{\int_{\zeta_3}^1 \frac{D_{m0}(\sigma\zeta + \tau\zeta^m)(1 + \alpha(\sigma\zeta + \tau\zeta^m)^n)}{\zeta} d\zeta}{J} \quad (23)$$

Since $\delta = \delta_a + \delta_b$

$$\delta = \frac{(D_{m0}/RT)(\sigma + \tau)(1 + \alpha(\sigma + \tau)^n)v}{J} (p_2 - p_*) + \frac{\int_{\zeta_3}^1 \frac{D_{m0}(\sigma\zeta + \tau\zeta^m)(1 + \alpha(\sigma\zeta + \tau\zeta^m)^n)}{\zeta} d\zeta}{J} \quad (24)$$

Therefore,

$$J = \frac{(D_{m0}/RT)(\sigma + \tau)(1 + \alpha(\sigma + \tau)^n)v}{\delta} (p_2 - p_*) + \frac{\int_{\zeta_3}^1 \frac{D_{m0}(\sigma\zeta + \tau\zeta^m)(1 + \alpha(\sigma\zeta + \tau\zeta^m)^n)}{\zeta} d\zeta}{\delta} \quad (25)$$

The above equation is valid when $p_2 \leq p_*$. When $p_3 > p_*$ the imaginary equilibrium phase is liquid across the membrane, and the flux should be written as,

$$J = \frac{(D_{m0}/RT)(\sigma + \tau)(1 + \alpha(\sigma + \tau)^n)v}{\delta} (p_2 - p_3) \quad (26)$$

Equations 25 and 26 give explicitly the effect of the upstream pressure and the downstream pressure on the pervaporation rate. (Note that this approach is closely related to Lonsdale's approach for reverse osmosis transport and allows the change in the permeant pressure across the membrane.) The main features of the transport equations are:

1. The transport mechanism includes the pressure change across the membrane.
2. The transport mechanism includes both liquid transport and vapor transport.

Greenlaw *et al.*⁵ and Lee¹² discussed the pervaporation transport using the solution-diffusion model with an assumption that the pressure of the permeant inside the membrane is constant and equal to the upstream pressure across the membrane. In particular, Greenlaw *et al.* have shown explicitly the effect of the upstream and the downstream pressure on the pervaporation flux and calculated the flux numerically under different conditions using the parameters listed in Table I. The results are summarized in Figure 2. The same numerical parameters were used in eq 25 and 26 and results illustrated in Figure 3. While Greenlaw *et al.* predict no upstream pressure effect on pervaporation flux at $p_3=0$, the flux increases linearly with an increase in the upstream pressure, p_2 , according to the newly developed transport equations. The linear relationship was also predicted by the transport equations based on the pore flow model.⁶

Table I. Greenlaw parameters for calculating the pervaporation flux at different upstream and downstream pressures

Parameter	Value	Units
D_{m0}	$= 24.2 \times 10^{-13}$	$\text{m}^2 \text{s}^{-1}$
α	$= 0.001788$	
n	$= 1.33$	
m	$= 3.4$	
τ	$= 545.3$	mol m^{-3}
σ	$= 137.9$	mol m^{-3}
p_*	$= 24918$	Pa
v	$= 130.58 \times 10^{-6}$	$\text{m}^3 \text{mol}^{-1}$

Kataoka *et al.*¹³ discussed the effect of the upstream pressure on the pervaporation (at downstream pressure = 0 Pa) and the reverse osmosis flux (at downstream pressure =

Figure 2. Effects of upstream and downstream pressure on the pervaporation flux by the transport equations of Greenlaw *et al.*⁵

Figure 3. Effects of upstream and downstream pressure on the pervaporation flux by the newly developed transport model.

Figure 4. Effects of upstream and downstream pressure on the pervaporation flux by Kitaoka *et al.*¹²

101,325 Pa) for the following two cases.

1) The pressure of the permeant inside the membrane is constant and equal to the upstream pressure across the membrane.

2) The pressure of the permeant inside the membrane changes across the membrane from the upstream pressure to the downstream pressure linearly.

Although their assumption of permeant concentration and diffusion coefficient being constant across the membrane seems unrealistic, their conclusions, summarized below, seems to be valid.

1) In case 1), the upstream pressure has no effect on the pervaporation flux. The reverse osmosis flux approaches the pervaporation flux as the upstream pressure approaches infinity.

2) In case 2), the pervaporation flux increases and approaches infinity as the upstream pressure approaches infinity. The reverse osmosis flux also increases and becomes nearly equal to the pervaporation flux as the upstream pressure approaches infinity. One of their results is reproduced in Figure 4.

RESULTS AND DISCUSSION

Electron micrographic observation of APA membranes revealed neither finger-like nor sponge-like structures that are usually prominent in the asymmetric membranes.

In order to examine whether the membranes used in the present work were free from pinholes, pervaporation separation of an aqueous acetic acid solution and reverse osmosis separation of an aqueous sodium chloride solution were conducted for the PDMS membrane and the APA membrane, respectively. Pervaporation and reverse osmosis experiments were considered best to examine the absence of pinholes, particularly when one side of the membrane was in contact with the feed liquid and in a considerably swollen state. Using the PDMS membrane, acetic acid mole fraction increased from 0.079 in the feed to 0.126 in the product, which is in agreement with our previous result.¹⁴ Reverse osmosis separation of sodium chloride solute by the APA membrane, on the other hand, was 44%, which value seems considerably lower than the separation obtained for an asymmetric reverse osmosis membrane of the same material. There is a considerable amount of information, however, that the sodium chloride separation of the dense homogeneous membrane is lower than that of the asymmetric membrane with respect to cellulose acetate material,¹¹ probably due to difference in the alignment of the polymer segment in the dense active layer of the asymmetric membrane from that of the thick homogeneous membrane. Therefore, the above sodium chloride separation was considered acceptable for the dense homogeneous membrane of APA material. Figure 5 illustrates the results of pervaporation experiments for the system water-PDMS membrane. Three series of experiments were conducted; *i.e.*, the upstream pressure was maintained at 101.325 kPa (0 psig, or atmospheric pressure), 446 kPa (50 psig), and 791 kPa (100 psig), respectively, while the downstream pressure was changed

Figure 5. Experimental pervaporation data with respect to PDMS membranes.

in the range 0.133–4 kPa (1–30 mmHg). It should be noted that a high initial permeation rate was observed when a higher than atmospheric pressure was applied on the upstream side of the membrane, while the downstream side was maintained at an atmospheric pressure. The permeation rate, however, started to decrease when vacuum was applied on the downstream side until a steady state was reached. Figure 5 presents the permeation rate data obtained after the steady state was achieved. These experimental results can be summarized as follows.

1) When the upstream pressure was an atmospheric pressure, practically no permeation flux was observed at downstream pressures above the saturation vapor pressure of water (2.8 kPa or 21 mmHg at 23°C). Pervaporation flux increased parabolically with a decrease of the downstream pressure when the latter pressure was below the saturation vapor pressure of water, confirming the tendency that has been observed previously by different authors.^{5,6} Inflection points are given in Figure

5 at 2.6 to 2.9 kPa, depending on the upstream pressure. It is difficult to say if there was a shift of the inflection point from the saturation vapor pressure. Such a shift was attributed to permeant-membrane interaction.^{14,15}

2) When the upstream pressure was 446 kPa, the permeation flux was nearly equal to that of an atmospheric pressure in the entire range of the downstream pressure.

3) When the upstream pressure was 791 kPa, very low but above zero permeation fluxes were observed at downstream pressures higher than the saturation vapor pressure. When the downstream pressure was lower than the saturation vapor pressure, the pervaporation fluxes were much greater than the ones observed at lower upstream pressures.

Figure 6 presents the data on permeation of water through an APA membrane. Four series of experiments were conducted; *i.e.*, the upstream pressure was maintained at 101, 446, 791, and 1136 kPa, respectively, while the downstream pressure was changed in the range 0.4–5.1 kPa (3–38 mmHg). The main features of the experiments can be summarized as follows.

1) When the upstream pressure was maintained at an atmospheric pressure, the permeation flux was low at downstream pressures higher than the saturation vapor pressure of water (2.8 kPa or 21 mmHg at 23°C). With a further decrease of the downstream pressure pervaporation flux increased parabolically. Inflection point appeared at 2.4 kPa, which is less than the saturation vapor pressure.

2) When the upstream pressure was increased from 101 kPa (atmospheric pressure) to 446 kPa, a significant increase in the permeation flux from that of the lower upstream pressure was observed at downstream pressures higher than the saturation vapor pressure. With a further decrease of the downstream pressure the pervaporation flux increased parabolically but only moderately. As a result the pervaporation flux at the lowest

Figure 6. Experimental pervaporation data with respect to APA membranes.

downstream pressure was almost equal for upstream pressures of 101 kPa and 446 kPa. The inflection point appeared at 1.7 kPa. Contrary to the previous work,^{14,15} the inflection points are at the pressures lower than the saturation vapor pressure. Neither permeant-membrane interaction nor the transport model can explain this phenomena.

3) When the upstream pressure was 791 kPa, a further increase in permeation flux (from the permeation flux corresponding to the upstream pressure of 446 kPa) was observed at the downstream pressures higher than the saturation vapor pressure. The pervaporation flux was almost constant in the entire range of downstream pressure.

4) The tendency observed at the upstream pressure of 1136 kPa was the same as that for 791 kPa.

Some of the data in Figures 5 and 6 were replotted in Figure 7 as the permeation flux versus the upstream pressure. In Figure 7 the pervaporation line represents the data obtained at downstream pressures ranging from 333 to

Figure 7. Flux versus upstream pressure for PDMS and APA membranes.

613 Pa (2.5 to 4.6 mmHg), while the reverse osmosis line represents data obtained at downstream pressures above 2.8 kPa.

Comparing the shape of the curves experimentally obtained (Figures 5 and 6) with those predicted by transport theories (Figures 2 and 3), it is obvious that neither of the transport theories represents experimental data well. In particular, the assumption of the constant permeant pressure across the membrane predicts that a change in the upstream pressure has no effect on the pervaporation flux at zero downstream pressure, which contradicts the experimental results for both PDMS and APA membranes. Apparently, the experimental data for APA shown in Figure 7 have closest resemblance to the case (2) of Kataoka *et al.* However, the upstream pressure at which pervaporation flux meets with the reverse osmosis flux in Figure 7 is much lower than the prediction by Kataoka *et al.*¹³

CONCLUSIONS

The following conclusions can be drawn

from the present investigations.

1) The transport equations newly developed for pervaporation allow the permeant pressure change across the membrane and include liquid as well as vapor transport. These equations predict that the pervaporation flux (at the downstream pressure close to zero Pa) increases linearly with an increase in the upstream pressure. The effect of upstream pressure on pervaporation rate was also predicted by the pore model.

2) The solution-diffusion model predicts no upstream pressure effect on the permeation flux (at the downstream pressure close to zero Pa) when the permeant pressure across the membrane is assumed to be constant and equal to the upstream pressure. The upstream pressure may have an effect on the pervaporation flux when there is a pressure change across the membrane.

3) Experimental data on water permeation through PDMS and APA membranes showed an increase in the pervaporation flux with an increase in the upstream pressure. However, the tendency observed in the experimental data agrees neither of transport models.

Nomenclature

- a = activity [—]
 c_m = permeant concentration in the membrane [mol m⁻³]
 D_m = diffusion coefficient [m² s⁻¹]
 $D_{m0} = D_m$ at $c_m = 0$
 f_m = friction [J s m⁻² mol⁻¹]
 J = pervaporation flux [mol s⁻¹ m⁻²]
 m = constant defined by eq 7
 n = constant defined by eq 10
 p = pressure [Pa]
 R = gas constant
 T = absolute temperature [K]
 v = molar volume [m³ mol⁻¹]
 x = distance from the upstream interface [m]

Greek letters

- δ = effective membrane thickness [m]

δ_a = thickness of the layer where liquid transport prevails [m]

δ_b = thickness of the layer where vapor transport prevails [m]

$\zeta = p/p_*$

μ = chemical potential [J mol⁻¹]

σ = constant defined by eq 7

τ = constant defined by eq 7

Subscript

2 = properties of feed

3 = properties of permeate

* = properties of saturated vapor

REFERENCES

1. J. Hauser, A. Heintz, G. A. Reinhardt, B. Schmittecker, M. Wesslein, and R. N. Richtenthaler, "Sorption, Diffusion, and Pervaporation of Water/Alcohol Mixtures in Poly(vinyl alcohol) (PVA)-Membranes. Experimental Results and Theoretical Treatment," in "Proceedings of Second International Conference on Pervaporation Processes in the Chemical Industry," R. Bakish, Ed., Bakish Materials Corp., Englewood, NJ, 1987, pp 15—33.
2. Y. M. Lee, D. Bourgeois, and G. Belfort, "Selection of Polymer Membrane Materials for Pervaporation," in "Proceedings of Second International Conference on Pervaporation Processes in the Chemical Industry," R. Bakish, Ed., Bakish Materials Corp., Englewood, NJ, 1987, pp 249—265.
3. J. Neel, "Fundamentals and General Chemical Engineering Aspects of Pervaporation," in "Proceedings of First International Conference on Pervaporation Processes in the Chemical Industry," R. Bakish, Ed., Bakish Materials Corp., Englewood, NJ, 1986, pp 10—40.
4. J. W. F. Spitzen, E. Elsinghorst, M. H. V. Mulder, and C. A. Smolders, "Solution-Diffusion Aspects in the Separation of Ethanol/Water Mixtures with PVA Membranes," in "Proceedings of Second International Conference on Pervaporation Processes in the Chemical Industry," R. Bakish, Ed., Bakish Materials Corp., Englewood, NJ, 1987, pp 209—224.
5. F. W. Greenlaw, W. D. Prince, R. A. Shelden, and T. V. Thompson, "Dependence of Diffusive Permeation Rates on Upstream and Downstream Pressures. I. Single Component Permeant," *J. Membrane Sci.*, **2**, 141 (1977).
6. T. Okada and T. Matsuura, "A New Transport Model for Pervaporation," *J. Membrane Sci.*, **59**, 133 (1991).
7. T. Okada, M. Yoshikawa, and T. Matsuura, "A

- Study on the Pervaporation of Ethanol/Water Mixtures on the Basis of Pore Flow Model, *J. Membrane Sci.*, **59**, 151 (1991).
8. T. Okada and T. Matsuura, "Predictability of Transport Equations for Pervaporation on the Basis of Pore Flow Mechanism," *J. Membrane Sci.*, **70**, 163 (1992).
9. D. R. Paul and O. M. Ebra-lima, "The Mechanism of Liquid Transport through Swollen Polymer Membranes," *J. Appl. Polym. Sci.*, **15**, 2199 (1971).
10. U. Merten, "Transport Properties of Osmotic Membranes," in "Desalination by Reverse Osmosis," U. Meten, Ed., The M.I.T. Press, Cambridge, Massachusetts, 1966, pp 15—54.
11. H. K. Lonsdale, "Properties of Cellulose Acetate Membranes," in "Desalination by Reverse Osmosis," U. Merten, Ed., The M. I. T. Press, Cambridge, Massachusetts, 1966, pp 93—160.
12. C. H. Lee, "Theory of Reverse Osmosis and Other Membrane Permeation Operations," *J. Appl. Polym. Sci.*, **19**, 83 (1975).
13. T. Kataoka, T. Tsuru, S. Nakao, and S. Kimura, "Membrane Transport Properties of Pervaporation and Vapor Permeation in Ethanol–Water System Using Polyacrylonitrile and Cellulose Acetate Membranes," *J. Chem. Eng. Jpn.*, **24**, 334 (1991).
14. M. Yoshikawa, T. Matsuura, and D. Cooney, "Studies on the State of Permeant in the Membrane and Its Effect on Pervaporation Phenomena," *J. Appl. Polym. Sci.*, **42**, 1417 (1991).
15. M. Yoshikawa and T. Matsuura, "Studies on the State of Methanol in a Polydimethylsiloxane Membrane by Differential Scanning Calorimetry and Pervaporation Technique," *Polym. J.*, **23**, 1025 (1991).