JOURNAL OF APPLIED POLYMER SCIENCE VOL. 19, PP. 83-95 (1975)

Theory of Reverse Osmosis and Some Other Membrane Permeation Operations

CHENG H. LEE, *Corporate Research Department, Monsanto Company, St. Louis, Missouri 63166*

Synopsis

The general permeation equations for various transport operations using membranes were correlated according to the solution-diffusion theory. It was shown that for some important conditions, the permeation properties for reverse osmosis can be generated from those of pervaporation. The use of reverse osmosis with pressure smaller than 2000 psi is calculated to be of limited use for the purification of water with small amounts of organic compounds.

INTRODUCTION

Molecular transport process may be classified into two types: mediated or nonmediated processes.[1] The former process needs a third component, or carrier, to mediate the transport. This process in general occurs in the biologic membrane in which enzymes or other carriers mediate the transport. The specific interactions between the substrate and carrier constitute this transport process. For the nonmediated process, the permeation is due to the existing chemical potential gradient across the membrane for each component. The gradient may be the concentration gradient, pressure gradient, field gradient, etc. Thus, reverse osmosis, dialysis, pervaporation, etc., are nonmediated transport processes. Many theories, such as the solution-diffusion theory, irreversible thermodynamics, or pore model,[2] were proposed to describe this type of permeation. However, no overall theoretical correlation of the permeation equations among all the nonmediated transport processes, such as those between pervaporation and reverse osmosis, has been investigated. It is the purpose of this paper to attempt such a correlation for a mixture of components.

Paul et al.[3,4,5] have tried to correlate the permeation fluxes between the pervaporation and reverse osmosis for a single component through the swollen polymer membranes by using the solution-diffusion theory. The basic assumption in those calculations was that the membrane pressure is the same throughout the membrane. In other words, the driving force for reverse osmosis is due to the concentration gradient which is the result of decreased swelling at the downstream surface of the membrane.

We will use the solution-diffusion theory to generalize the permeation equation for all the nonmediated transport processes. Under certain conditions and assumptions, the permeation properties, i.e., the separation factor and the total permeation rates, for reverse osmosis can be generated from those of pervaporation. A simple calculation will indicate the order of magnitude pressure needed in order to purify water with small amounts of organic compounds using reverse osmosis.

SOLUTION DIFFUSION THEORY

According to the solution-diffusion theory,[2] each component of the permeation molecules dissolves in the membrane in accordance with an equilibrium distribution law and diffuses through the membrane in response to the concentration gradient. Thus, the flux J_i for the i in the absence of an electric field is given by a relationship of the type

$$J_i(X) = \frac{-D_i(X)C_i(X)}{RT} \nabla\mu_i(X) \tag{1}$$

and

$$\mu_i(X) = \mu_{i_0} + RT \ln a_i(X) + \int_{P_{\text{ref}}}^{P(X)} \bar{V}_i dP - \int_{T_{\text{ref}}}^{T(X)} S_i dT \tag{2}$$

where $J_i(X)$ = the flux rate for component i through the membrane at the position X in the membrane; $D_i(X)$ = self-diffusion coefficient for component i at the position X in the membrane; $C_i(X)$ = the concentration of component i at the position X in the membrane; $\mu_i(X)$ = the chemical potential of component i at the position X in the membrane; μ_{i_0} = the chemical potential of component i at the reference state; $a_i(X)$ = the activity of component i at the position X in the membrane; $\bar{V}_i(X)$ = the partial molar volume of component i at the position X in the membrane; $P(X)$ = the pressure at the position X in the membrane, and P_{ref}, T_{ref} = reference pressure and temperature.

The above equations apply to any position in the membrane. In the case of a flat membrane, the flux rate J_i at steady state in the case of one dimension isothermal permeation will become

$$J_i = \frac{-D_i(X)C_i(X)}{RT}\left[RT \frac{\partial}{\partial X} \ln a_i(X) + \bar{V}_i \frac{\partial}{\partial X} \mathrm{P}(X)\right]. \tag{3}$$

Thus, the permeation rate will depend on the diffusion constant, the concentration, the activity gradient, and the pressure gradient in the membrane.

CONCENTRATION GRADIENT

The concentration gradient profile in the membrane may be obtained through the solution of Fick's diffusion equation. Fick's law of diffusion for a stationary coordinate system is[6]

$$\eta_1 = w_1(\eta_1 + \eta_r) - \rho D \nabla W_1 \tag{4}$$

where 1, r refers to the penetrant and membrane; η_1 = flux in mass units for penetrant; η_r = flux in mass units for membrane; W_1 = weight fraction for penetrant; ρ_1 = density of penetrant; and D = mutual diffusion coefficient for penetrant and membrane (the relation between this D and the D_i, self-diffusion coefficient, in eq. (1) can be referred to Crank[7,8]).

If the membrane r is in a stationary state, then η_r is equal to zero. Therefore,

$$\eta_1 = \frac{\rho_1 D}{1 - W_1} \nabla W_1. \tag{5}$$

If the diffusion coefficient is independent of concentration, the concentration profile becomes[3]

$$1 - W_1(X) = [1 - W_1(l_1)] \left[\frac{1 - W_1(l_2)}{1 - W_1(l_1)}\right]^{X - l_1/l_2 - l_1} \tag{6}$$

where the coordinate of the membrane is shown in Figure 1.

If the weight fraction of the penetrant is much smaller than that of the membrane, eq. (5) can be approximated to be

$$\eta_1 = -\rho_1 D \nabla W_1. \tag{7}$$

At the steady state, η_1 is constant. If the diffusion constant is independent of concentration, the concentration profile in this case becomes linear. In other words, it is given by eq. (8):

$$C_i(X) = \frac{-1}{l}\,[C_i(l_1) - C_i(l_2)]X + \frac{1}{l}\,[C_i(l_1)l_2 - C_1(l_2)l_1] \tag{8}$$

where $C_i(X)$ is the concentration of component i at the membrane X position; and $C_i(l_1)$ and $C_i(l_2)$ are, respectively, the concentration of component

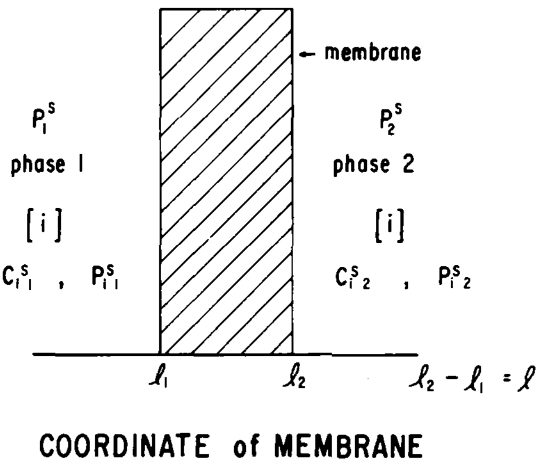

Fig. 1. The schematic of the permeation through a membrane.

i at the membrane boundary of upstream and downstream. The thickness of the membrane is l.

MEMBRANE BOUNDARY CONCENTRATION

The concentration of penetrant at the boundary of the membrane may be calculated from thermodynamic principles. Assume that the membrane was in contact with a system, either liquid or gas, the chemical potential at the boundary of the membrane, $\mu_{i_1}^{m}(\mu_{i_2}^{m})$, and that in the adjacent phase solution, $\mu_{i_1}^{s}(\mu_{i_2}^{s})$, must be equal. Therefore

$$\mu_{i_1}^{s} = \mu_{i_1}^{m} \qquad \mu_{i_2}^{s} = \mu_{i_2}^{m} \tag{9}$$

where 1 and 2 refer to the upstream and downstream, respectively.

Application of these conditions to eq. (2) gives the following relationships between the activities in the solution, $a_{i_1}^{s}(a_{i_2}^{s})$, and that at the boundary of the membrane, $a_{i_1}^{m}(a_{i_2}^{m})$ (Appendix I):

$$a_{i_1}^{m} = a_{i_1}^{s} \exp[-\bar{V}_i(P_1^{m} - P_1^{s})/RT] \tag{10}$$

$$a_{i_2}^{m} = a_{i_2}^{s} \exp[-\bar{V}_i(P_2^{m} - P_2^{s})/RT] \tag{11}$$

where $P_1^{m}(P_2^{m})$ and $P_1^{s}(P_2^{s})$ are, respectively, the pressure at membrane boundary and adjacent phase solution.

If the membrane pressure[6] was assumed to be constant and equal to that in the upstream phase solution, which is larger than that in the downstream phase solution, one may rewrite eqs. (10) and (11) to be

$$a_{i_1}^{m} = a_{i_1}^{s} \tag{12}$$

$$a_{i_2}^{m} = a_{i_2}^{s} \exp[-\bar{V}_i(P_1^{s} - P_2^{s})/RT]. \tag{13}$$

As the activities are equal to the product of the concentration and the activity coefficient, the membrane boundary concentration for any component i, $C_{i_1}^{m}(C_{i_2}^{m})$, may be correlated with the adjacent phase solution concentration, $C_{i_1}^{s}(C_{i_2}^{s})$:

$$C_{i_1}^{m} = \frac{\gamma_{i_1}^{s}}{\gamma_{i_1}^{m}} C_{i_1}^{s} \tag{14}$$

$$C_{i_2}^{m} = \frac{\gamma_{i_2}^{s}}{\gamma_{i_2}^{m}} C_{i_2}^{s} \exp[-\bar{V}_i(P_1^{s} - P_2^{s})/RT] \tag{15}$$

where $\gamma_{i_1}^{m}(\gamma_{i_2}^{m})$ and $\gamma_{i_1}^{s}(\gamma_{i_2}^{s})$ are the activity coefficients for the component i at the membrane boundary and adjacent phase solution.

If one defines the solubility constant K_{i_1} (K_{i_2}) as the ratio of activity coefficient at the membrane boundary and adjacent phase solution, then

$$C_{i_1}^{m} = K_{i_1} C_{i_1}^{s} \tag{16}$$

$$C_{i_2}^{m} = K_{i_2} C_{i_2}^{s} \exp[-\bar{V}_i(P_1^{s} - P_2^{s})/RT] \tag{17}$$

where

$$K_{i_1} = \frac{\gamma_{i_1}^{s}}{\gamma_{i_1}^{m}} \quad \text{and} \quad K_{i_2} = \frac{\gamma_{i_2}^{s}}{\gamma_{i_2}^{m}}. \tag{18}$$

PERMEATION EQUATION

Combining eqs. (3), (8), (16), and (17) and assuming the membrane pressure to be constant, one can derive the following general permeation equation for all the nonmediated transport processes:

$$J_i = \frac{D_i}{l}\left\{K_{i_1}C_{i_1}{}^s - K_{i_2}C_{i_2}{}^s \exp[-\bar{V}_i(P_1{}^s - P_2{}^s)/RT]\right\} \tag{19}$$

or

$$J_i = \frac{D_iK_{i_1}}{l}\left\{C_{i_1}{}^s - \alpha_iC_{i_2}{}^s \exp[-\bar{V}_i(P_1{}^s - P_2{}^s)/RT]\right\} \tag{20}$$

or

$$J_i = \frac{P_i}{l}\left\{C_{i_1}{}^s - \alpha_iC_{i_2}{}^s \exp[-\bar{V}_i(P_1{}^s - P_2{}^s)/RT]\right\} \tag{21}$$

where

$$\alpha_i = \frac{K_{i_2}}{K_{i_2}}, \qquad P_i = D_iK_i \tag{22}$$

where P_i is called the permeability constant for the component i in the membrane. If the activity coefficient of the penetrant in the membrane is constant, eq. (22) can be rewritten to be

$$\alpha_i = \frac{\gamma_{i_2}{}^s}{\gamma_{i_1}{}^s}. \tag{23}$$

In this case, α_i becomes independent of the membrane properties. Because it depends only on the ratio of the activity coefficient of downstream and upstream phase solution, α_i may be called the partition coefficient.

Equations (19) or (20) are only valid under the following conditions which are true in most cases: (1) Membrane pressure is constant and equal to that in upstream phase solution. (2) The diffusion constant, activity coefficient, and partial molar volume for all penetrants are independent of the concentration. (3) The concentration of each penetrant in the membrane is very small so that eq. (7) is valid. (4) The partial molar volume of penetrant, i, in the membrane is equal to that in the upstream phase solution.

Based on eqs. (19), (20), and (21), we will discuss the permeation equation for each individual permeation process, such as pervaporation, dialysis, reverse osmosis.

Pervaporation

If the upstream phase is liquid and the downstream phase is a gas or vapor, the permeation process is called pervaporation. In other words, the transport process is permeation through the membrane and evaporation from the membrane. From eq. (21), the permeation equation for pervaporation can be given by

$$J_i = \frac{P_i}{l} C_{i_1}^s \left\{1 - \frac{P_{i_2}^s}{P_{i_1}^s} \exp[-\bar{V}_i(P_1^s - P_2^s)/RT]\right\} \tag{24}$$

since

$$\gamma_{i_1}^s C_{i_1}^s = P_{i_1}^s \quad \text{and} \quad \gamma_{i_2}^s = P_{i_2}^s \tag{25}$$

where $P_{i_1}^s$ and $P_{i_2}^s$ are the partial pressure for component i at the upstream and downstream phase. Equation (25) was obtained by assuming the pressure equal to the fugacity or activity.

In most cases eq. (24) may be approximated to be

$$J_i = \frac{P_i}{l} C_{i_1}^s \left(1 - \frac{P_{i_2}^s}{P_{i_1}^s}\right). \tag{26}$$

Since

$$P_1^s \approx 1 \text{ atm}, \qquad P_2^s \approx 0, \qquad \bar{V}_i \approx 20 \text{ cm}^3\text{/mole}$$

$$(P_1^s - P_2^s)\bar{V}_i \approx 2 \times 10^7 \text{ erg}, \qquad RT \approx 25 \times 10^{10} \text{ erg}$$

so that

$$\exp\ [-(P_1^s - P_2^s)\bar{V}_i/RT] \approx 1.0.$$

Considering two components (i,J) for the penetrant system, the separation factor SF_J^i was defined as follows:

$$SF_J^i = \frac{J_i}{J_J} \times \frac{C_{J_1}^s}{C_{i_1}^s}. \tag{27}$$

Hence, the separation factor for the pervaporation may be obtained from eqs. (26) and (27):

$$SF_J^i = \frac{P_i}{P_J}\left[\frac{\left(1 - \frac{P_{i_2}^s}{P_{i_1}^s}\right)}{\left(1 - \frac{P_{J_2}^s}{P_{J_1}^s}\right)}\right] \tag{28}$$

If both $P_{i_2}^s$ and $P_{J_2}^s$ are close to zero, eqs. (26) and (28) may be simplified to

$$SF_J^i = \frac{P_i}{P_J} \quad \text{and} \quad J_i = \frac{P_i}{l} C_{i_1}^s. \tag{29}$$

Therefore, the separation factor for any two penetrants for the pervaporation through the membrane is just the ratio of the permeability constant of each penetrant in the membrane when the downstream pressure is close to zero.

Liquid/Liquid Dialysis

In the case of liquid/liquid dialysis, the pressure in both phases is almost equal. Therefore, eq. (21) becomes

$$J_i = \frac{P_i}{l}\left(C_{i_1}^s - \alpha_i C_{i_2}^s\right) \tag{30}$$

where α_i, as mentioned before, is the partition coefficient of component i between the downstream phase and the upstream phase.

Similarly, one may obtain the separation factor SF_J^i for the two-penetrant system from eqs. (27) and (30):

$$SF_J^i = \frac{P_i}{P_J}\left[\frac{\left(1 - \alpha_i \dfrac{C_{i_2}^s}{C_{i_1}^s}\right)}{\left(1 - \alpha_J \dfrac{C_{J_2}^s}{C_{J_1}^s}\right)}\right]. \tag{31}$$

Gas Permeation

Since both phases are gaseous in the case of gas/gas permeation, eqs. (18) and (19) cannot apply in this case (see Appendix I). The permeation equations, however, can be obtained similarly. If the ideal gas and constant membrane pressure are assumed, this permeation equation may be obtained from eqs. (3), (8), and (9):

$$J_i = \frac{D_i K_{im_1}}{l}\left(P_{i_1}^s - P_{i_2}^s\right) \tag{32}$$

where

$$K_{im_1} = \frac{1}{\gamma_{i_1}^m}$$

or

$$J_i = \frac{P_i}{l}\left(P_{i_1}^s - P_{i_2}^s\right) \tag{33}$$

where $P_i = D_i K_{im_1}$. It is important to realize the activity coefficient in eq. (32) should be corrected to pressure of standard state (1 atm) from the membrane pressure. Therefore, the permeation rate depends only on the difference between each penetrant partial pressure in both phases. The separation factor in this case becomes

$$SF_J^i = \frac{P_i}{P_J}\left[\frac{\left(1 - \dfrac{P_{i_2}^s}{P_{i_1}^s}\right)}{\left(1 - \dfrac{P_{J_2}^s}{P_{J_1}^s}\right)}\right]. \tag{34}$$

Reverse Osmosis

Let us consider two components subject to reverse osmosis operation. Let J be solute whose molar concentration is very small, and i be solvent whose molar concentration is approximately one. The partition coefficient for both solvent and solute, α_i and α_J, are about equal to one in this case.

Therefore, from eq. (21), the permeation flux for both solute and solvent may be given by

$$J_i = \frac{P_i}{l}\left\{C_{i_1}^s - C_{i_2}^s \exp[-\bar{V}_i\,(P_1^s - P_2^s)/RT]\right\} \tag{35}$$

$$J_J = \frac{P_J}{l}\left\{C_{J_1}^s - C_{J_2}^s \exp[-\bar{V}_J(P_1^s - P_2^s)/RT]\right\}. \tag{36}$$

Equation (35) can be arranged to be

$$J_i = \frac{P_i}{l} C_{i_1}^s \left\{1 - \exp[-\bar{V}_i(P_1^s - P_2^s - \Pi)/RT]\right\} \tag{37}$$

where Π is called osmotic pressure and is given by

$$\Pi = \frac{RT}{\bar{V}_i} \ln \frac{C_{i_2}^s}{C_{i_1}^s}. \tag{38}$$

Thus, the total permeation flux J_{total} and separation factor SF_J^i for reverse osmosis can be obtained from eqs. (36) and (37):

$$\begin{aligned} J_{\text{total}} &= J_i + J_J \approx J_i \\ &= \frac{P_i}{l} C_{i_1}^s \left\{1 - \exp[-\bar{V}_i(P_1^s - P_2^s - \Pi)/RT]\right\} \end{aligned} \tag{39}$$

and

$$SF_J^i = \frac{P_i\left\{1 - \exp[-\bar{V}_i(P_1^s - P_2^s - \Pi)/RT]\right\}}{P_J\left\{1 - \dfrac{C_{J_2}^s}{C_{J_1}^s} \exp[-\bar{V}_J(P_1^s - P_2^s)/RT]\right\}}. \tag{40}$$

At steady state for reverse osmosis, the following relationship must hold:

$$SF_J^i = \frac{J_i C_{J_1}^s}{J_J C_{i_1}^s} \approx \frac{C_{i_2}^s C_{J_1}^s}{C_{J_2}^s C_{i_1}^s} \approx \frac{C_{J_1}^s}{C_{J_2}^s}. \tag{41}$$

The above equation is valid because the molar concentration of solvent in both streams is approximately equal to one.

Combining eqs. (41) and (40), one can obtain the separation factor for reverse osmosis, and it is given by

$$\begin{aligned} SF_J^i &= \exp[-\bar{V}_J(P_1^s - P_2^s)/RT] \\ &\quad + \frac{P_i}{P_J}\left\{1 - \exp[-\bar{V}_i(P_1^s - P_2^s - \Pi)/RT]\right\}. \end{aligned} \tag{42}$$

It is important to realize that all the derivations of the permeation equations for reverse osmosis assume the membrane favoring the permeation of the solvent, which is the purpose of using reverse osmosis for separations. Equation (39) and (42) are general permeation equations for reverse osmosis.

In summary, the permeation equations for all the nonmediated transport processes are shown in Table I.

TABLE I
The Permeation Equations for Various Processes Using Membranes

Permeation Process	Phase 1	Phase 2	Permeation flux J_i	SF_{ji}
Pervaporation	liquid	gas	$\frac{P_i}{l} C_{i_1}^s \left(1 - \frac{P_{i_2}^s}{P_{i_1}^s}\right)$[a]	$\frac{P_i}{P_j} \left[\frac{1 - \frac{P_{i_2}^s}{P_{i_1}^s}}{1 - \frac{P_{j_2}^s}{P_{j_1}^s}}\right]$[a]
Liquid/liquid dialysis	liquid	liquid	$\frac{P_i}{l} (C_{i_1}^s - \alpha_i C_{i_2}^s)$	$\frac{P_i}{P_j} \left[\frac{1 - \alpha_i \frac{C_{i_2}^s}{C_{i_1}^s}}{1 - \alpha_i \frac{C_{j_2}^s}{C_{j_1}^s}}\right]$
Gas/gas permeation	gas	gas	$\frac{P_i}{l} (P_{i_1}^s - P_{i_2}^s)$[a]	$\frac{P_i}{P_j} \left[\frac{1 - \frac{P_{i_2}^s}{P_{i_1}^s}}{1 - \frac{P_{j_2}^s}{P_{j_1}^s}}\right]$[a]
Reverse osmosis	liquid	liquid	$\frac{P_i}{l} C_{i_1}^s \{1 - \exp[-\bar{V}_i(P_1^s - P_2^s - \Pi)/RT]\}$ and $\Pi = \frac{RT}{\bar{V}_i} \ln \frac{C_{i_2}^s}{C_{i_1}^s}$	$\exp[-\bar{V}_j(P_1^s - P_2^s)/RT]$ $+ \frac{P_i}{P_j} \{1 - \exp[\bar{V}_i(P_1^s - P_2^s - \Pi)RT]\}$

[a] $P_{i_1}^s$, $P_{i_2}^s$ are the partial pressure for the component i at upstream and downstream, respectively (i = solvent; j = solute).

EFFECTS OF PRESSURE ON REVERSE OSMOSIS

Equations (39) and (42) show the permeation rate and separation factor as a function of pressure. We will discuss two extreme cases.

Case 1: $(P_1^s - P_2^s - \Pi)\bar{V}_i \ll RT$ and $(P_1^s - P_2^s)\bar{V}_J \ll RT$

In this case, one can expand the exponential terms in eqs. (39) and (42). Therefore, the permeation equations become

$$J_{\text{total}} = \frac{P_i}{l} C_{i_1}^s \frac{(P_1^s - P_2^s - \Pi)\bar{V}_i}{RT} \tag{43}$$

$$SF_J^i = 1 - \frac{\bar{V}_J(P_1^s - P_2^s)}{RT} + \frac{P_i}{P_J}\left[\frac{(P_1^s - P_2^s - \Pi)\bar{V}_i}{RT}\right] \tag{44}$$

Combining eqs. (29), (43), and (44), one may rewrite eqs. (43) and (44) as follows:

$$J_{\text{total}} \text{ (reverse osmosis)} = J_{\text{total}} \text{ (pervaporation)} \frac{(P_1^s - P_2^s - \Pi)\bar{V}_i}{RT} \tag{45}$$

$$\begin{aligned} SF_J^i \text{ (reverse osmosis)} &= 1 - \frac{\bar{V}_J(P_1^s - P_2^s)}{RT} \\ &\quad + SF_J^i \text{ (pervaporation)} \times \frac{(P_1^s - P_2^s - \Pi)\bar{V}_i}{RT} \end{aligned} \tag{46}$$

where the permeation flux and separation factor for pervaporation are obtained when the downstream pressure is close to zero.

Let us consider a system of water with a small amount of organic compound, and it is desired to purify the water using reverse osmosis. In this case, we may estimate the permeation results for reverse osmosis. Thus assume

$$C_{i_1}^s = 0.995 \qquad C_{J_1}^s = 0.005 \text{ (where } i = \text{H}_2\text{O}, J = \text{organic compounds)}$$

$$\bar{V}_i = 18 \text{ cm}^3\text{/mole} \qquad \bar{V}_J \approx 25 \text{ cm}^3\text{/mole}$$

$$P_1^s = 200 \text{ psia} \qquad P_2^s = 15 \text{ psia} \qquad T = 300^\circ\text{K}$$

$$\Pi = \frac{RT}{\bar{V}_i} \ln \frac{C_{i_1}^s}{0.995} \leq \frac{RT}{\bar{V}_i} \ln \frac{1.0}{0.995} \approx 0.005 \frac{RT}{\bar{V}_i}$$

$$RT = 2.5 \times 10^{10} \text{ erg}$$

$$(P_1^s - P_2^s - \Pi)\bar{V}_1 \approx 2.5\times10^8 \text{ erg} \qquad (P_1^s - P_2^s)\bar{V}_J \approx 3.5\times10^8 \text{ erg}$$

$$J_{\text{total}} \text{ (reverse osmosis)} = J_{\text{total}} \text{ (pervaporation)} \left(\frac{1}{100}\right)$$

$$SF_J^i \text{ (reverse osmosis)} \approx 1 + SF_J^i \text{ (pervaporation)} \left(\frac{1}{100}\right).$$

From the above rough calculations, the permeation rate for reverse osmosis with 200 psia is shown to be 1% of that for pervaporation, and the separation factor decreases very much. For example, a membrane with separation factor for pervaporation SF_j^i of 100 gives a separation factor for reverse osmosis of only around 2.0.

Case 2: $(P_1^s - P_2^s = \Pi)\bar{V}_i \gg RT$ and $(P_1^s - P_2^s)V_j \gg RT$

This is the case when the upstream pressure becomes infinite. From eqs. (39) and (42), the permeation rate and separation factor can be easily shown to be

$$J_{\mathrm{total}} = \frac{P_i}{l} C_{i_1}^{\,s} + \frac{P_j}{l} C_{j_1}^{\,s} \text{ and } SF_j^{\,i} = \frac{P_i}{P_j}.$$

Therefore, the permeation equations for the reverse osmosis with infinitive pressure approach those for pervaporation.

The permeation rate and separation factor for reverse osmosis other than the two extreme cases above will depend on the pressure and increase as an exponential function as shown in eqs. (39) and (41).

SUMMARY

We have used the assumption of constant membrane pressure in deriving all the permeations of nonmediated transport processes. The permeation equation for different types of processes was correlated. It is possible to generate the permeation properties of reverse osmosis from those of pervaporation under certain important conditions. The use of reverse osmosis to purify water with small quantities of organic compounds is calculated to be of limited use with the pressure under 2000 psia. There are some experimental facts to substantiate the above conclusions. It was found[9] that the permeation rate and separation factor for the water with some organic compounds for reverse osmosis is decreased greatly by comparing with those of pervaporation as expected from the above permeation equations.

Physically, the difference between the process of pervaporation and reverse osmosis is different types of driving force. The maximum driving force at the upstream membrane boundary for pressure induced transport is that of pervaporation which is equal to RT/l, where l is thickness. As the driving force was defined as the gradient of chemical potential, the above relation can be easily shown from eq. (2) when using the assumption of linear concentration gradient profile (Appendix II).

The effects of pressure on the structure of membrane may not be neglected. Therefore, the permeation correlation pervaporation and reverse osmosis may be modified a little. However, the above conclusions are still valid.

Appendix I

The chemical potential at the boundary of membrane, $\mu_{i_1}^m$ ($\mu_{i_2}^m$), are given by

$$\mu_{i_1}^s = \mu_{i_0} + RT \ln a_{i_1}^s(x) + \int_{P_{\rm ref}}^{P_1^s} \bar{V}_{i_1}^s \, dp \tag{A1}$$

$$\mu_{i_1}^m = \mu_{i_0} + RT \ln a_{i_1}^m(x) + \int_{P_{\rm ref}}^{P_1^m} \bar{V}_i \, dp \tag{A2}$$

$$\mu_{i_2}^s = \mu_{i_0} + RT \ln a_{i_2}^s(x) + \int_{P_{\rm ref}}^{P_2^s} \bar{V}_{i_2}^s \, dp \tag{A3}$$

$$\mu_{i_2}^m = \mu_{i_0} + RT \ln a_{i_2}^m(x) + \int_{P_{\rm ref}}^{P_2^m} \bar{V}_i \, dp \tag{A4}$$

where $\bar{V}_{i_1}^s$ and $\bar{V}_{i_2}^s$ are the partial molar volume of component i in the upstream and downstream phase solution, respectively; and $\bar{V}_i$ is the partial molar volume of component i in the membrane and is assumed to be constant.

If $P_{\rm ref}$ is equal to P_2^s, the following correlation equations can be obtained from eq. (9):

$$a_{i_2}^m = a_{i_2}^s \exp[-\bar{V}_i(P_2^m - P_2^s)/RT] \tag{A5}$$

$$a_{i_1}^m = a_{i_1}^s \exp\{[Y - \bar{V}_i(P_1^m - P_1^s)]/RT\} \tag{A6}$$

where

$$Y = \int_{P_2^s}^{P_1^s} (\bar{V}_{i_1}^s - \bar{V}_i)\, dp. \tag{A7}$$

Thus, eqs. (10) and (11) are valid if the partial molar volume of penetrant i in the membrane is equal to that in the upstream phase solution. This assumption is in general true when the upstream is liquid for pervaporation, liquid/liquid dialysis, reverse osmosis, but not for gas/gas permeation.

Appendix II

If the driving force is defined as the gradient of chemical potential, the driving force $F_i(x)$ for the penetrant i at the position X in the membrane is given by

$$F_i(X) = \frac{-RT}{l}\,\frac{C_i(l_i) - C_i(l_2)}{C_i(x)} \tag{A8}$$

The above equation is obtained by assuming the linear concentration gradient of the penetrant in the membrane. Thus, the driving force at the *upstream membrane boundary* ($X = l_1$) is

$$F_i(l_1) = -\frac{RT}{l}\left[1 - \frac{C_i(l_2)}{C_i(l_1)}\right]. \tag{A9}$$

The absolute maximum driving force at the upstream membrane boundary will be equal to RT/l when the concentration of penetrant i at the downstream membrane boundary, $C_i(l_2)$, is equal to zero, which is the case of pervaporation at zero downstream pressure.

In the case of pressure induced transport, the driving force for the penetrant at the upstream membrane boundary is given by

$$F_i(l_1) = -\frac{RT}{l}\,\{1 - \exp[-(P_1^s - P_2^s)\bar{V}_i/RT]\} \tag{A10}$$

since

$$C_i(l_2) = C_i(l_1)\exp[-(P_1^s - P_2^s)\bar{V}_i/RT].$$

Therefore, the driving force at the upstream membrane boundary for the pressure-induced transport is much smaller than that for the pervaporation at zero downstream pressure.

The central point in these discussions is that the concentration for the penetrant at the membrane boundary can be obtained from equilibrium principles. Therefore, the driving force at the *membrane upstream boundary* can reflect the permeation properties.

The author's special thanks are due to Eli Perry, Corporate Research Department, Monsanto Company, St. Louis, Missouri, for his thorough review, criticism, and the experimental information about reverse osmosis and pervaporation of water with small amounts of organic compounds. Professor J. J. Hermans at the University of North Carolina is also acknowledged for his helpful comments.

References

1. A. Kotyk, *Biochim. Biophys. Acta*, **300**, 183–210 (1973).
2. E. Lacey and S. Loeb, *Industrial Processing with Membranes*, Wiley-Interscience, New York, 1972.
3. D. R. Paul and O. M. Ebra-Lima, *J. Appl. Polym. Sci.*, **14**, 2201 (1970).
4. D. F. Paul and O. M. Ebra-Lima, *J. Appl. Polym. Sci.*, **15**, 2199 (1971).
5. D. R. Paul, *J. Appl. Polym. Sci.*, **16**, 771 (1972).
6. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York, 1970.
7. J. Crank, *Mathematics of Diffusion*, Oxford University Press, London, 1956.
8. J. Crank and G. S. Park, *Diffusion in Polymers*, Academic Press, London and New York, 1968.
9. E. Perry, Corporate Research Department, Monsanto Company, St. Louis, Missouri, private communication.

Received May 14, 1974
Revised June 26, 1974