

Influence of the Pressure Profile inside a Dense Membrane on the Rate of Permeation

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Synopsis

Lee¹ showed that molecular transport in all isothermal membrane processes, based on dense layers, can be described with one single general equation, including only measurable conditions from outside of the membrane. Following arguments given by Paul² for homogeneous rubber membranes, Lee assumed the pressure everywhere inside the membrane to be equal to the feed side pressure. In this paper the question is stated whether this assumption always holds for very thin and/or nonhomogeneous membranes like asymmetric membranes made of semicrystalline polymers. A study based on less stringent assumptions of the pressure profile inside the membrane is performed. The results show that in most cases this pressure profile does not play a major role in the permeation process.

INTRODUCTION

Based on a general approach, Lee¹ shows that molecular transport in all isothermal membrane processes, based on dense layers, can be described with one single equation.

In the considered processes, the driving force is a difference in pressure and/or mole fraction (called concentration by Lee) or activity outside of the membrane. Assuming thermodynamic equilibrium at the membrane boundaries and a constant pressure inside the membrane, the driving force causes a concentration gradient within the membrane, resulting in diffusive transport through the membrane.

Taking into account the specific driving forces of the individual processes, the commonly used equations for these processes arise. Lee assumes a pressure inside the membrane to be constant and equal to the pressure of the upstream solution (feed or high pressure side). Thus the permeation of components is solely determined by the concentration gradient within the membrane. The question arises whether the assumption of constant pressure inside the membrane is always correct.

For relatively thick, highly swollen, flat rubber membranes, Paul and Ebra-Lima³ proved that only a concentration gradient within the membrane was responsible for the transport of the permeating components. For isotropic hollow fibers Paul² calculates that the pressure inside the membrane can have any predictable value, from even negative values up to a value above that of the feed pressure, depending on the fiber geometry and the side of the maximum pressure.

For composite or asymmetric membranes the active skin is present on top of a relatively open, porous layer. The membrane hanging above a pore can be compared to a part of an internally pressurized hollow fiber, so that the

pressure inside the membrane may deviate from the feed or permeate pressure. The pressure distribution inside a nonisotropic membrane is unpredictable beforehand. For a semicrystalline polymer the crystallites can be of the order of magnitude of the active skin layer, so that forces due to the pressure difference and difference in swelling are not evenly distributed. Considering the magnitude of thickness of modern permeation membranes, the question of the pressure distribution inside a membrane probably will remain a theoretical one. Yet the question remains how a pressure profile, different from the one assumed by Paul² and Lee,¹ influences the permeation through polymeric membranes.

In experiments of Paul and Ebra-Lima³ the concentration in the membrane at the feed boundary determined directly after permeation was equal to the equilibrium concentration for the polymer immersed in the liquid. This was considered as a proof for the assumption that the pressure inside the membrane equals the feed side pressure. Other authors⁴⁻⁷ found concentrations at the membrane boundary deviating upward or downward from the equilibrium concentration. The accuracy of the reported values for the concentrations is not very high, as can be seen from the scattering of the published data. For membranes having thicknesses comparable to the thickness of the skin of asymmetric or composite membranes, it must be considered impossible even to get an indication of the concentration as a function of the distance from the membrane boundary. Despite these uncertainties, the equations derived by Lee are applied with success in all mentioned membrane processes.

Based on less stringent assumptions of the pressure profile inside the membrane, a study is performed here that shows that in most cases this pressure profile does not play a major role in the permeation process. The pressure profile should be taken into consideration in case of very high feed pressures or permeating components having large molar volumes.

THE INFLUENCE OF THE PRESSURE PROFILE IN A DENSE MEMBRANE ON THE PERMEATION OF COMPONENTS

For a flat membrane, in the stationary state the permeation of a component can be described with (Lee¹)

$$J_i(z) = \frac{-D_i(z) \cdot C_i(z)}{RT} \cdot \frac{d\mu_i(z)}{dz} \quad (1)$$

This equation holds for very "dilute" membrane systems, in which the permeation of each component is independent of the permeation of the others. For very dilute solutions the concentration C_i is related to the mole fraction:

$$C_i = \frac{\rho_j}{M_j} \cdot x_i$$

where ρ_j and M_j correspond to the solvent (here the membrane) for which $x_j \sim 1$. It is assumed that no electrical field or temperature gradient is present. The chemical potential $\mu_i(z)$ of component i at position z is then

written as

$$\mu_i(z) = \mu_i^0 + RT \ln a_i(z) + \int_{P_{ref}}^{P(z)} \bar{V}_i dP \tag{2}$$

where $a_i(z) = \gamma_i(x) \cdot x_i(z)$. The activity coefficient γ_i within the membrane is assumed constant.

For any profile for the concentration and the pressure inside the membrane, eqs. (1) and (2) give

$$J_i = -D_i \cdot \frac{\rho_j}{M_j} \left[\frac{dx_i}{dz} + \frac{\bar{V}_i}{RT} \cdot x_i \cdot \frac{dP}{dz} \right] \tag{3}$$

From this equation it follows that not only a concentration gradient, but also a pressure gradient result in a diffusive flow. The resulting flow is related to both gradients with the same diffusion coefficient as given in this equation.

For the sake of readability \mathbb{D}_i is defined as

$$D_i \cdot \frac{\rho_j}{M_j} \equiv \mathbb{D}_i \tag{4}$$

For a constant pressure inside the membrane, eq. (3) simplifies to

$$\frac{dx_i}{dz} = - \frac{J_i}{\mathbb{D}_i} \tag{5}$$

Thus in this case a linear concentration profile exists for constant \mathbb{D}_i , and the flux can be calculated using the equation derived by Lee.

For a pressure not being constant inside the membrane, rearrangement of eq. (3) gives

$$\frac{dx_i}{dz} + \frac{\bar{V}_i}{RT} \cdot \frac{dP}{dz} \cdot x_i = \frac{-J_i}{\mathbb{D}_i} \tag{6}$$

Assuming the pressure P to be a function of the coordinate z only and \bar{V}_i independent of the concentration, this equation can be solved for x , yielding

$$x_i(z) = \exp\left\{ \frac{-\bar{V}_i [P(z) - P(0)]}{RT} \right\} \cdot \left(\frac{-J_i}{\mathbb{D}_i} \int_0^z \exp\left\{ \frac{\bar{V}_i [P(z) - P(0)]}{RT} \right\} dz + x_i^m \right) \tag{7}$$

for all z inside the membrane.

For $z = \delta$, the thickness of the membrane, this equation is rearranged to

$$J_i = \frac{\mathbb{D}_i (x_{i_1}^m - x_{i_2}^m \cdot \exp\{-\bar{V}_i [P(0) - P(\delta)]/RT\})}{\int_0^\delta \exp\{-\bar{V}_i [P(0) - P(z)]/RT\} \cdot dz} \quad (8)$$

Equilibrium at both membrane boundaries will be assumed, so that

$$x_{i_1}^m = K_{i_1} \cdot x_{i_1}^s \exp\{-\bar{V}_i [P(0) - P_1^s]/RT\} \quad (9a)$$

and

$$x_{i_2}^m = K_{i_2} \cdot x_{i_2}^s \exp\{-\bar{V}_i [P(\delta) - P_2^s]/RT\} \quad (9b)$$

where K_{i_1} and K_{i_2} are the solubility constants at the upstream and downstream boundaries resp.

Taking for reasons of simplicity $K_{i_1} = K_{i_2} = K_i$, i.e., the activity coefficients in either the membrane or the adjacent phase taken to be independent of the concentration, eq. (8) is rewritten as

$$J_i = \frac{\mathbb{D}_i K_i (x_{i_1}^s - x_{i_2}^s \exp[-\bar{V}_i (P_1^s - P_2^s)/RT])}{\exp(-\bar{V}_i \cdot P_1^s/RT) \cdot \int_0^\delta \exp(\bar{V}_i \cdot P(z)/RT) dz} \quad (10)$$

It is emphasized that J_i is not dependent on a pressure jump at one of the membrane boundaries. Only the pressure profile within the membrane is included in eq. (10).

Equation (10) resembles very much the equation, derived by Lee. The ratio of values of J_i calculated by the equation given by Lee and by eq. (10) is

$$\frac{J_i [\text{eq. (9)}]}{J_i (\text{Lee})} = \frac{\delta}{\exp(-\bar{V}_i P_1^s/RT) \cdot \int_0^\delta \exp(\bar{V}_i P(z)/RT) dz} \quad (11)$$

For three cases this ratio of fluxes is evaluated: first, for a constant pressure inside the membrane equal to the upstream pressure, second, for a linear pressure profile, ranging from the upstream pressure at the upstream side to the downstream pressure at the downstream side, and, third, for a constant pressure inside the membrane, equal to the downstream pressure. This third case is not an extreme case, as indicated by Paul² for an internally pressurized hollow fiber with a small wall thickness.

1. When $P(z) = P_1^s$ for all $0 \leq z \leq \delta$, the denominator reduces to δ and equation (9) becomes identical to the one derived by Lee.

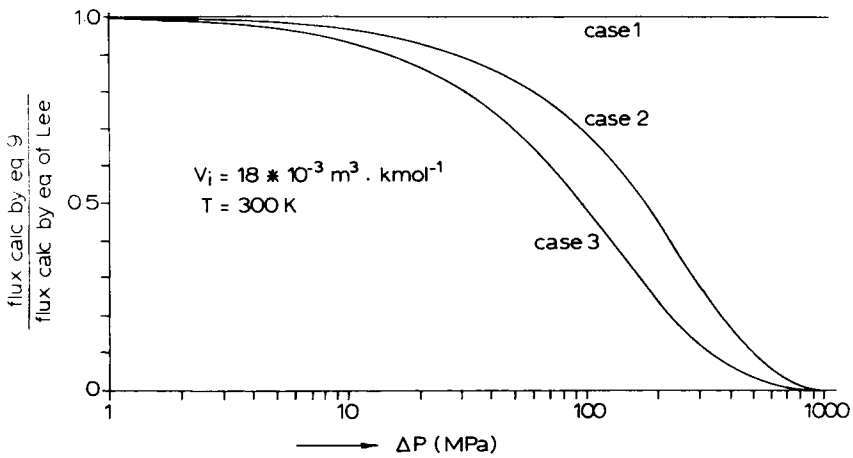


Fig. 1.

- For a linear pressure profile inside the membrane, decreasing from the upstream pressure to the downstream pressure,

$$P(z) = P_1^s - (z/\delta)(P_1^s - P_2^s) \tag{12}$$

the ratio is evaluated to

$$\frac{J_i \text{ [eq. (9)]}}{J_i \text{ (Lee)}} = \frac{1}{[RT/\bar{V}_i(P_1^s - P_2^s)] \cdot \{\exp[\bar{V}_i(P_1^s - P_2^s)/RT] - 1\}} \tag{13}$$

For low feed pressures, this ratio is almost equal to 1; however, for high pressures a significantly lower flux is calculated by eq. (10) than calculated by the equation of Lee, as illustrated in Figure 1 for the permeation of water.

- For a pressure inside the membrane equal to the downstream pressure, the ratio is evaluated to

$$\frac{J_i \text{ [eq. (9)]}}{J_i \text{ (Lee)}} = \frac{1}{\exp[\bar{V}_i(P_2^s - P_1^s)/RT]} \tag{14}$$

The ratio follows the same trend as with the former case, but a higher deviation occurs, as illustrated in Figure 1.

From Figure 1 it is clear that the deviation may be high for very high pressure difference over the membrane and low pressure levels inside the membrane. For permeating components having larger molar volumes, the curves remain the same, but are shifted to the left. From the figure it can be concluded that, for not too high feed pressure, the equation given by Lee can be used for all permeation through dense membranes, irrespective of the pressure profile inside the membrane.

DISCUSSION

Theoretically, by direct comparison of fluxes resulting from pervaporation and reverse osmosis, one can conclude whether the internal pressure inside the membrane is or is not equal to the feed side pressure. If fluxes calculated with the equation derived by Lee¹ and with eq. (10) deviate, this will only be the case when a high pressure difference is applied over the membrane. In pervaporation, use of both equations results in the same flux value, as the pressure inside the membrane, if not equal to the feed side pressure, only plays a minor role. A comparison between fluxes from both modes of operation is carried out by Paul and Ebra-Lima³ and by Paul and Paciotti,⁸ both based on experiments with flat rubber membranes. From these comparisons they concluded that the assumption of equal pressure inside the membrane and the feed side pressure is realistic. Duggal and Thompson⁹ performed pervaporation and reverse osmosis experiments with homogeneous cellulose acetate membranes. Their pervaporation experiments were combined with reverse osmosis, applying pressure to the feed and vacuum to the permeate. Surprisingly, fluxes were found in these "pressurized" pervaporation experiments that were about 30% lower than found for pervaporation with the feed only at atmospheric pressure. This, however, cannot be explained by a pressure inside the membrane being lower than the feed pressure.

From the latter result and taking into account that differences resulting from deviating pressures inside membranes become significant only at very high pressures, it may be expected that a correct conclusion about the pressure profile inside a membrane will not result from membrane filtration experiments.

APPENDIX: NOMENCLATURE

- a* activity
- C* concentration (kmol m^{-3})
- D* diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
- \mathbb{D} diffusion coefficient, defined by eq. (4) ($\text{kmol m}^{-1} \text{s}^{-1}$)
- J* flux of component through membrane (kmol m^{-2})
- K* solubility constant
- M* molecular weight (kg kmol^{-1})
- P* pressure (Pa)
- R* gas-constant (8314) ($\text{J K}^{-1} \text{kmol}^{-1}$)
- T* temperature (K)
- \bar{V} partial molar volume ($\text{m}^3 \text{kmol}^{-1}$)
- x* mole fraction
- z* coordinate (m)
- γ activity coefficient
- δ membrane thickness (m)
- ρ specific density (kg m^{-3})
- μ chemical potential (J kmol^{-1})

Subscripts

- i* component
- 1 upstream side (feed)

2 downstream side (permeate)
ref reference

Superscripts

m membrane
s solution outside membrane
0 standard

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