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Two-Dimensional Permeate Transport with Facilitated Transport Membranes

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Abstract

An analytical model has been developed for steady-state permeate transport with facilitated transport membranes. The model contains no adjustable parameters. The model accounts for both axial permeate transport parallel to the membrane and facilitated permeate transport through the membrane. The model predicts the fraction of permeate separated through the membrane as a function of physical properties and operating conditions. The model was derived for a cylindrical geometry but can be applied to a planar geometry. Also, the model could be used for the simple diffusion case when no facilitation is present. Reasonable agreement with experimental data is presented.

INTRODUCTION

Facilitated transport is a separation process by which an active chemical carrier will selectively bind with a permeate, transport the permeate across a liquid film, and release the permeate at the other boundary. It has high potential for obtaining high selectivity while achieving high enough flux rates to be commercially feasible. There are several review articles which describe this process in detail (*1–9*).

The most common mechanism postulated is

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} AB \tag{1}$$

where A = component being transported across the membrane
B = active chemical carrier

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AB = active carrier complex

An arrow next to A indicates that it is the component being transported.

There have been various models developed to describe the steady-state one-dimensional flux of a permeate. Olander (*10*) described simultaneous mass transfer combined with an equilibrium chemical reaction. He showed the effect of reaction on the total mass transfer rate. Four different cases were analyzed. Friedlander and Keller (*11*) used a linearized form of the reaction rate expression to describe the flux of permeate with reversible chemical reaction to the simple diffusional flux. Their assumptions were based on the reacting system being near reaction equilibrium. Ward (*12*) derived analytical solutions for the steady-state transport of NO through ferrous chloride solution under two limiting conditions, reaction-limited ("frozen" condition) and diffusion-limited (reaction equilibrium). He found that this system was not operating at a limiting condition but somewhere in between. He used a numerical method to solve for the flux. Kreuzer and Hoofd (*13*) used the concept of a reaction boundary layer to explain the physical problems by assuming instantaneous reaction equilibrium at the membrane boundary. Their results showed that an equilibrium core existed through the main portion of the membrane with reaction boundary layers at each boundary. Goddard et al. (*14*) and Smith et al. (*15*) also demonstrated this result.

Yung and Probstein (*16*) used a similar transform method to develop a single equation which described the concentration profiles for all components. The equation describes steady-state conditions in flat plate geometry. The equation could be evaluated by numerical methods to obtain the facilitated flux over the entire range of operating conditions. The solution is iterative and could cause some convergence problems. They also present some simplifications under limiting conditions.

Donaldson and Quinn (*17*) developed an analytical expression for facilitation factor in planar geometry under steady-state conditions. They derived their expression for tracer diffusion through a reactive membrane solution equilibrated with a constant partial pressure of untagged gas. This expression is an exact solution for the facilitated tracer flux in the limiting vanishingly small tracer concentration. Smith and Quinn (*18*) showed that the expression has the proper limiting form for both large and small Damkohler numbers.

Hoofd and Kreuzer (*19*) developed an analytical solution to steady-state facilitated transport. They approximated the permeate concentration as having two components. One component is based on the assumption of chemical reaction equilibrium and is a function of carrier concentration. The second term accounts for departures from chemical equilibrium and is a function of position only. By solving for these two components, one obtains an analytical solution. Their result is consistent with Smith and Quinn's for this case.

There has been some previous work done on one-dimensional facilitated transport in cylindrical geometry. Stroeve and Eagle (*20*) developed equations for the facilitation factor in reactive slabs, cylinders, and spheres. They studied dispersed phase shapes in a continuous phase and provided a graph which shows the effect of geometry when subjected to a uni-directional flux of the diffusing species. Hoofd and Kreuzer (*21*) solved the problem of oxygen uptake in a cylindrical muscle. They used the same mathematical approach as they had earlier used in planar geometry (*19*). Their calculations compared very well with previous calculations. Folkner and Noble (*22*) developed plots for the transient facilitation factor in cylindrical geometry. Noble (*23*) developed analytical expressions for shape factors under both limiting conditions of being either diffusion-limited or reaction-limited. These expressions allowed one to determine facilitated flux for cylindrical or spherical geometries if one knows the flux for a flat-plate geometry. He found that a flat-plate geometry yielded the highest flux under identical operating conditions.

The objectives of this study are as follows. The main objective is to develop a steady-state mathematical model with no adjustable parameters which accounts for axial permeate transport parallel to the membrane and facilitated transport of the permeate through the membrane. An analytical solution is developed. The result describes the fraction of permeate separated as a function of physical properties and operating conditions. The importance of accounting for axial permeate concentration gradients is shown.

THEORY

The hollow fiber is shown in Fig. 1. The mixture containing the permeate is transported axially through the tube and the permeate is transported radially through the tube walls by facilitated transport. It can be assumed that there is no axial transport in the tube walls due to the pore structure.

A steady-state macroscopic mass balance on the permeate in the tube (see the control volume in Fig. 1) yields

$$\langle v_x \rangle \frac{dC_A}{dx} = -\frac{A}{V} N_{A_T} \tag{2}$$

where $\langle v_x \rangle$ = average velocity in axial direction (assume constant)
C_A = bulk (cup-mixing) concentration of permeate in the interior

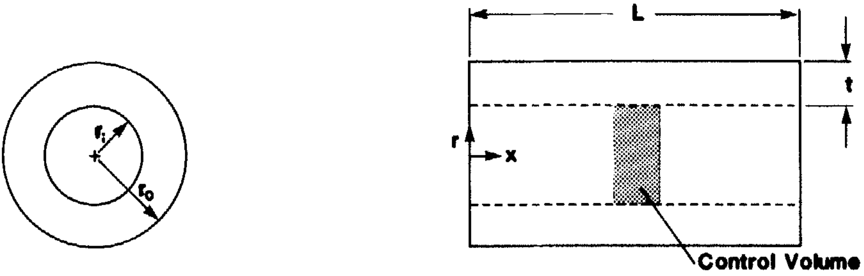

FIG. 1. Hollow fiber tube.

(hollow) region of tube
A/V = effective surface area to volume ratio
N_{A_T} = flux of permeate into tube wall

Equation (2) neglects radial diffusion in the hollow portion of the hollow fiber tube.

The permeate flux through the tube walls can be written as

$$N_{A_T} = \left(\frac{2\pi r_0 L}{2\pi r_i L}\right)(S)(F)\frac{D_A}{t}(C'_A - C'_{A_0}) \tag{3}$$

if Eq. (1) describes the reversible reaction taking place in the pores of the tube wall (liquid film), D_A = permeate diffusion coefficient in liquid film, C'_A = permeate concentration in liquid film at $r = r_i$, C'_{A_0} = permeate concentration in liquid film at $r = r_0$, and S is the shape factor defined by Noble (*23*). It relates the facilitated flux in a cylindrical geometry to the facilitated flux in a planar geometry. S is based on the outside surface area. That is why the surface area ratio is included in Eq. (3). For a planar geometry, S equals 1. F is the facilitation factor in a planar geometry. This is the ratio of the total facilitated flux in planar geometry to the simple diffusion flux in planar geometry. F equals 1 corresponds to the case of simple molecular diffusion with no facilitation. Analytical expressions are available for both S and F:

$$S = \frac{t/r_0}{\ln\left[\dfrac{1}{\left(1 - \dfrac{t}{r_0}\right)}\right]} \tag{4}$$

Equation (4) is the equation described by Noble (*23*) for the case where the system is diffusion-limited (reaction equilibrium). This equation will hold for a wide range of conditions. Equation (4) is equivalent to the log-mean area for cylindrical geometry.

$$F = \frac{1 + A}{1 + \dfrac{A}{\phi} \tanh \phi} \tag{5}$$

$$\text{where } A = \frac{D_{AB} K_{eq} C_B}{D_A} \tag{6}$$

$$\phi = \frac{1}{2} \sqrt{\frac{k_1 C_B t^2}{D_A} \left(\frac{1 + A}{A} \right)} \tag{7}$$

D_{AB} = diffusion coefficient of carrier–permeate complex in liquid film

$K_{eq} = k_1 / k_2$

C_B = carrier concentration in liquid film (assumed constant)

Equation (5) was derived by Hoofd and Kreuzer (*19*) by approximating the permeate concentration as having two components. One component is based on the assumption of chemical reaction equilibrium and is a function of carrier concentration. The second term accounts for departures from reaction equilibrium and is a function of position only. By solving for these two components, one obtains an analytical solution. Donaldson and Quinn (*17*) derived the same result for tracer diffusion in a reactive membrane.

Substituting Eq. (3) into Eq. (2), one obtains

$$dC_A / dx = -\Lambda (C_A - C_{A_0}) \tag{8}$$

$$\text{where } \Lambda = \frac{2}{r_i} \left(\frac{r_0}{r_i} \right) \frac{(S)(F) D_A}{\langle v_x \rangle t H} \tag{9}$$

$H = C_A / C_A'$ = partition coefficient

Note that Λ is a constant and independent of permeate concentration. Equation (8) can be made dimensionless by defining the following dimensionless variables:

$$C_A^* = C_A / C_{A_i} \tag{10}$$

where C_{A_i} = inlet permeate concentration

$$\mathrm{X} = X/L \tag{11}$$

Equation (8) then becomes

$$dC_A^*/d\mathrm{X} = -\Lambda L(C_A^* - C_{A_0}^*) \tag{12}$$

Equation (12) can be solved with the following boundary conditions:

$$\mathrm{X} = 0; \qquad C_A^* = 1 \tag{13}$$

The solution is

$$\frac{C_A^* - C_{A_0}^*}{1 - C_{A_0}^*} = e^{-\Lambda L \mathrm{X}} \tag{14}$$

Equation (14) can be substituted into Eq. (3) to obtain the permeate flux at any position X:

$$N_{A_T} = \left(\frac{r_0}{r_i}\right)(S)(F)\frac{D_A C_{A_i}}{Ht}(1 - C_{A_0}^*)e^{-\Lambda L \mathrm{X}} \tag{15}$$

Equation (15) can be integrated along the axial length of the tube to obtain total permeate flux through the tube walls:

$$\int_0^1 N_{A_T}\,d\mathrm{X} = \eta = \left(\frac{r_0}{r_i}\right)\frac{D_A C_{A_i}}{Ht}\,\frac{(S)(F)}{\Lambda L}(1 - C_{A_0}^*)[1 - e^{-\Lambda L}] \tag{16}$$

Equation (16) can be rearranged to yield the ratio of the permeate flow rate through the membrane to the inlet permeate flow rate:

$$\Omega = \frac{\eta}{\langle v_x \rangle C_{A_i}}\left(\frac{2L}{r_i}\right) = (1 - C_{A_0}^*)[1 - e^{-\Lambda L}] \tag{17}$$

The same ratio can be calculated if one neglects the effect of the change in axial permeate concentration:

$$\Omega = \frac{2\pi r_0 L(S)(F)\dfrac{D_A}{t}(C_A - C'_{A_0})}{\pi r_i^2 \langle v_x \rangle C_{A_i}} = \Lambda L(1 - C^*_{A_0}) \qquad (18)$$

One method for determining the importance of an axial permeate concentration gradient is to look at the limit of Eqs. (17) and (18) as L becomes very large. Assuming $C^*_{A_0}$ equals zero, Eq. (17) approaches 1 as L becomes large. Equation (18) is linearly proportional to L and can become much greater than 1 for large axial length. Therefore, neglecting axial concentration gradients can lead to large errors in calculating Ω.

Examination of Eq. (17) shows the proper functional relationship between the variables and Ω. As C_{A_0} increases, the gradient across the tube wall decreases and Ω decreases. As L increases, Ω increases since more surface area becomes available for radial transport. As Λ increases, Ω increases. An examination of the factors contained in Λ indicates that this makes sense physically.

To check the validity of Eq. (17), model predictions were compared to experimental data presented by Hughes, Mahoney, and Steigelman (*24*). Their data for ethylene permeation through hollow fiber walls is shown in Table 1. The value of Ω calculated from their experimental data as well as predictions based on Eqs. (17) and (18) are shown in Table 2. As can be seen from Table 2, the agreement between the experiments and model predictions (Eq. 17) is very reasonable based on the assumptions used. The values of Ω calculated from Eq. (18) are also shown for comparison. The fact that Eq. (18) gives reasonable agreement in this case is due to the very short effective axial length (see Table 1). As discussed above, as L increases, Eq. (18) would increase in error.

CONCLUSIONS

An analytical model of two-dimensional permeate transport with facilitated transport membranes has been developed. The model is steady state and has no adjustable parameters. The model was developed for cylindrical geometry but can be used with planar geometry. The model was also developed for facilitated transport membranes but could also be for simple diffusion cases. The model gives reasonable agreement with experimental data. It has been shown that axial permeate concentration gradients are important and should not be neglected.

TABLE 1

Experimental Data of Hughes, Mahoney, and Steigelman (*24*) for Ethylene Permeation through Hollow Fiber Tubes

$r_i = 1.07 \times 10^{-2}$ cm $r_0 = 1.15 \times 10^{-2}$ cm	effective dimensions for radial transport
$A = 4.15 \times 10^{-4}$ cm^2;	cross-sectional area available for flow
$L = 1.78$ cm;	effective axial length based on effective surface area
$D_A = 1.85 \times 10^{-5}$ cm^2/s	
$H = 0.879 \dfrac{(\text{g-mol/cm}^3)_{\text{gas}}}{(\text{g-mol/cm}^3)_{\text{liquid}}}$	
$F = 34.3$;	average value calculated from data in their Table IV for 6.0 *M* AgNO$_3$ assuming the same path length for Teflon film and hollow fibers
$F = 27.8$;	average value calculated from their Table IV for 2.0 *M* AgNO$_3$ assuming the same path length for Teflon film and hollow fibers
$\langle v_x \rangle = 5.95 \times 10^2$ cm/s;	calculated from permeation rate data in their Table VII for a carrier concentration of 6.0 *M* AgNO$_3$
$C_{A_i} = 2.00 \times 10^{-4}$ g-mol/cm^3 $C_{A_0} = 5.91 \times 10^{-5}$ g-mol/cm^3	calculated from data in their Table VII for a carrier concentration of 6.0 *M* AgNO$_3$
$\langle v_x \rangle = 4.60 \times 10^2$ cm/s;	calculated from permeation rate data in their Table V for a carrier concentration of 2.0 *M* AgNO$_3$
$C_{A_i} = 1.68 \times 10^{-4}$ g-mol/cm^3 $C_{A_0} = 2.68 \times 10^{-5}$ g-mol/cm^3	calculated from data in their Table V

TABLE 2

Comparison of Model Results with Experimental Data. System: Olefin Separation with AgNO$_3$ as Carrier in Water

Carrier concentration (*M*)	Ω_{exp}	Ω (Eq. 17)	Ω (Eq. 18)
6.0	0.34	0.28	0.36
2.0	0.26	0.38	0.46

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