

STUDY OF DYNAMIC EFFECTS BY CONVECTIVE VELOCITY IN THE MEMBRANE PROCESS: OPERATOR THEORETIC APPROACH

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Abstract – This paper studies the dynamic mass transfer effects of solute through fluid-solid interactions in a heterogeneous system. It is found that the convective velocity in internal pores of the membrane can be used to accelerate the speed of the solute by convective velocity at the fluid phase. The theoretical model for the membrane transport is studied in this paper by using the operator theoretic method. A typical example of this dynamic interaction problem is applied in a multi-layered composite membrane. Danckwerts Boundary conditions are analyzed in the inner and outer regions of membrane process. A spectral evaluation of the transport operator is performed by the operator properties in the system. The findings of this paper are useful in guiding the design of membrane separation devices as well as in proving useful to the synthetic performance of composite membrane.

Key words : Composite Membrane, Multi-Layered Membrane, Fluid-Solid Interaction, Operator Theory

INTRODUCTION

Many of the theoretical and numerical modelling efforts for membrane transport have traditionally been restricted to linearized models (for example, linear irreversible thermodynamics for transport and dissipation, and neglecting convection as a source of nonlinearity). Many membrane separations involve solid-fluid contacting in the membrane system which exhibits an asymmetric structure consisting of a thin microporous layer (skin layer) supported by a macroporous support. The selective layers of a membrane providing information about pore size and shape in the membrane layer have been shown by microscope [Bessieres et al., 1996]; and they are therefore of importance for separating solutes in a system with average pore size from a few nanometers up to a few microns.

A wide range of naturally occurring or synthetically constructed chemical phenomena can be studied within this framework of mass transport. The operator-theoretic technique [Ramkrishna and Amundson, 1985] allows a full characterization of the dynamic behavior of systems without complete numerical calculation of the governing differential models. This also allows for a coupling of different levels of information in a given system and leads to the analysis of the membrane composite system. The motivation of this paper is to show how the external force of a domain influences the transport processes that occur inside sub-domains, as well as those occurring between the domains through the environmental media. In this paper, convective-diffusive transport deals with a variety of applications of current interest in chemical engineering. The overall objective is to investigate the chemical function that arises from the diffusion and convection of molecular species. The emphasis is on applying operator-theoretic

techniques to analyze the dynamics of transport problems with multi-components and in a multi-dimensional domain of hierarchical structure.

The dynamic problem by fluid-solid interaction results from the diffusive or convective coupling through adjoining boundaries between macromolecules, organic chemicals and organelles. The general model of the multi-layered composite membrane will be developed as the model for direct interaction via fluid and solid phases. A dynamic interaction problem mediated by a fluid medium has been displayed in the packed column, which was studied earlier by Park [Park, 1995, Park et al., 1995]. An operator theoretic approach in indirect interactions has been used to solve the intraparticle mass transport problem in the previous paper. And this method leads to the formally non-self adjoint form. Within the framework of the interactions in the multi-layered membrane, we seek to analyze the dynamic behavior of heterogeneous phases. A spectral evaluation of the transport differential operator can be performed for a parametric study of physical properties on the solute concentration profiles. The equation for transport in the membrane reactor or the plug flow reactor is developed by a species mass balance equation.

In this hierarchical approach, a domain in the multi-layered membrane is considered in terms of sub-domains of each layered membrane and the mathematical description accounts for the transport that occurs inside each of these layered domains, as well as for those occurring between the domains of fluid and membrane throughout the environmental media.

MATHEMATICAL MODEL

1. Membrane Transport in a Multi-layered Composite Membrane

1-1. Mathematical Model

The convective-diffusive transport is mathematically modell-

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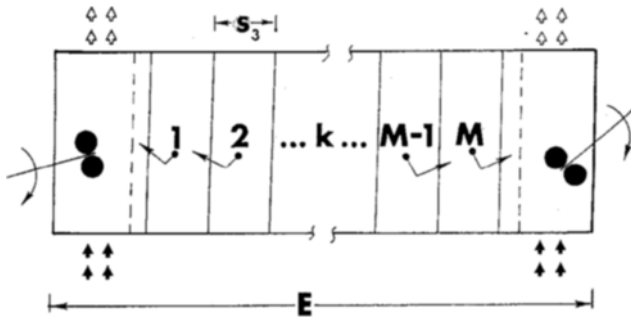


Fig. 1. Schematic picture in multi-layered membrane.

E: Total thickness of M-layered composite membrane

ed as coupling through adjoining boundaries between composite layers. Fig. 1 shows a schematic picture for M-composite layers.

The molar species conservation equations in the M-composite layers are defined as

$$\frac{\partial C'_n}{\partial t} = -U_n \frac{\partial C'_n}{\partial x} + D_n \frac{\partial^2 C'_n}{\partial x^2} \quad (1)$$

The flux boundary conditions at the internal boundaries between each composite layer are

$$-D_{n+1} \frac{\partial C'_{n+1}}{\partial x} + U_{n+1} C'_{n+1} = -D_n \frac{\partial C'_n}{\partial x} + U_n C'_n \quad (2)$$

at $x=x_n$; $n=1, 2, 3, \dots, M-1$

The species distribution coefficient by the linear phase equilibrium in each layer is given as

$$\beta_{n+1} C'_{n+1} = \beta_n C'_n \quad \text{at } x=x_n; n=1, 2, 3, \dots, M-1 \quad (3)$$

Boundary conditions at the external boundaries, i.e. at $x=0$ and $x=L$ for the case of a fixed concentration in the outer regions, are

$$\beta_1 C'_1 = \beta_0 C'_0$$

$$\beta_M C'_M = \beta_L C'_L$$

where the species molar concentration, convective velocity, and diffusion coefficient in the composite layers are given, respectively, by C'_n , U_n and D_n , and β_n -the equilibrium distribution coefficient represents the fractional pore available to each solute in a porous composite layer where the pore space available for a particular molecule varies from layer to layer.

The differential equations in Eq. (1) and boundary conditions (2)-(3) can be cast into non-dimensional form using the following change of variables,

$$\psi_n = \frac{D_n}{D_o}, \quad s = \frac{x}{L}, \quad \tau = t \frac{D_n}{L^2}, \quad Pe_n = U_n \frac{L}{D_n}$$

and the transformation variable $C_n = C'_n \exp(-Pe_n s_n / 2)$ is applied to Eq. (1). Several physical parameters such as the Peclet number (Pe_n)-the relative ratio of convective transport to diffusive transport, ψ -the relative ratio of diffusion coefficients, and a variation in Pe_n occurs if the convective velocity changes from layer to layer. The differential Eq. (1) can be written as

$$\frac{\partial C_n}{\partial \tau} = \psi_n \left(\frac{\partial^2 C_n}{\partial s^2} - \frac{Pe_n^2}{4} C_n \right) \quad (4)$$

1-2. General Boundary Conditions in the External Regions

Since we are not concerned with a chemical reaction in the external regions, the solute can only be delivered by diffusive or bulk fluid motion. The most efficient form to deliver solute to the system is by fluid flow, and we shall restrict our analysis to the case where the external phase is well-mixed fluids. Fig. 1 shows a schematic diagram of the overall process in the external regions. Two general possibilities might arise in this problem. For controlled external concentrations the above boundary conditions (3) would be sufficient; however, for a controlled rate of delivery it would be necessary to develop material balances over the external regions as discussed below. In addition, the first and last layers could be the same or different phases than the external environments at $x < 0$ and $x > L$, respectively. If the external environments are of the same phase as the first and last layers the physical problem would correspond to the case of finite stagnant boundary layers in contact on one side with a well-mixed fluid region (the external environment) and on the other side with a solid phase (the second or M-1 layer).

A more general and realistic approach that more closely represents the physical problems considered in the present analysis would require the addition of a material balance over the well-mixed external regions. This would give

$$V_o \frac{dC'_o}{dt} = C'_{of} F_o - C'_o F_o + A [D_1 \frac{\partial C'_1}{\partial x} - U_1 C'_1] \quad \text{at } x=0_+ \quad (5)$$

$$V_L \frac{dC'_L}{dt} = C'_{Lf} F_L - C'_L F_L + A [D_M \frac{\partial C'_M}{\partial x} - U_M C'_M] \quad \text{at } x=L_- \quad (6)$$

where V is the volume, C' the molar concentration, F volumetric flow into the mixed reactor, and "A" is the cross-sectional area of the membrane surface. The subscripts 0 and L represent the two well-mixed external regions, and f represents the feed stream into the two external regions. These boundary conditions must be coupled with Eq. (3), where the equilibrium coefficients at the external boundaries allow the above conditions to be applicable to the case where the end regions are of different phases from the first and last layers.

SOLUTION METHODOLOGY

1. Membrane Transport with Dirichlet Boundary Conditions

1-1. Definition of Differential Operations and Operator

The formal solution to the transient problem of M-composite layers can be constructed from Eq. (4) and the initial-boundary value problem reduces to

$$\frac{\partial C}{\partial \tau} = -LC + B(\lambda_n)I \quad (7)$$

where L is represented as an $M \times M$ diagonal matrix having M differential diagonal operations, L_k . U is an $M \times 1$ matrix representing the eigenfunctions, U_k , and I is the unit matrix. B can be calculated by a non-self adjoint form to satisfy the self-adjoint boundary conditions. Differential operation, L_k , in each composite layer is given by

$$L_k = -\psi_k \left(\frac{d^2}{ds^2} - \frac{Pe_k^2}{4} \right) \quad (8)$$

Let the interval of the dimensionless axial coordinate for the physical problem, $0 < s < 1$, be partitioned into M internal regions such that $0 < s_1 < s_2 < \dots < s_k < \dots < s_{M-1} < 1$. Now consider the following functional spaces for subinterval of the preceding partition, i.e.

$$L_2(s_{k-1}, s_k), U_k = \int_{s_{k-1}}^{s_k} u_k^2(s) ds < \infty \tag{9}$$

with $s_0=0$ and $s_M=1$. The following Hilbert spaces, H_k , can be defined :

$$H_k = [L_2(s_{k-1}, s_k)], k = 1, 2, 3, \dots, M \tag{10}$$

with a k -inner product of the form

$$(U_1, U_2)_k = \int_{s_{k-1}}^{s_k} U_{1k} U_{2k} ds, k = 1, 2, \dots, M \tag{11}$$

In the above equation $U_k = \{U_j\}_k, j = 1, 2$ are vectors in each Hilbert space, $H_k, k=1, 2, \dots, M$. In order to proceed with the solution of the mathematical model, it is convenient to define the direct-sum Hilbert space, H [Ramkrishna and Amundson, 1985], as

$$H = \bigoplus_{k=1}^M H_k \tag{12}$$

If we define an arbitrary vector $w_i \in H$ as

$$w_i^T = [U_{1i}, U_{2i}, \dots, U_{ji}, \dots, U_{Mi}], i = 1, 2 \tag{13}$$

then it is possible to write the following inner product for H :

$$\langle w_1, w_2 \rangle = \sum_{j=1}^M \delta_j (U_1, U_2)_j \tag{14}$$

where $\delta_1=1$ and the remaining $\delta_j(j=2, 3, \dots, M)$ will be properly defined in a subsequent section.

The following M differential operations associated with the physical problem and arising from Eq. (8) are

$$L_k = -\psi_k \left(\frac{d^2}{ds^2} - \frac{Pe_k^2}{4} \right) \text{ for } k = 1, 2, 3, \dots, M \tag{15}$$

The composite differential operation L (i.e. the operation associated with M layers of the physical problem) is now defined on the basis of Eq. (15) as [Ramkrishna and Amundson, 1985]

$$L = [L_{jk}] \delta_{jk} \tag{16}$$

$$L_{kk} = L_k, k = 1, 2, 3, \dots, M$$

$$L_{jk} = 0 \text{ when } j \text{ is not equal to } k.$$

The domain associated with this differential operation is given by

$$\begin{aligned} D(L) \equiv \{ & w \in \text{and } Lw \in H: u_i(0) = 0; \\ & u_k(s_k) r_k(s_k) = u_{k+1}(s_{k+1}) r_{k+1}(s_{k+1}); \\ & \beta_{k+1} \psi_{k+1} C_{k+1}(s_{k+1}) = \beta_k \psi_k C_k(s_k); \\ & k = 1, 2, 3, \dots, M-1; u_M(1) = 0 \} \end{aligned}$$

where the following operations have been defined :

$$N_i(s_j) = - \left(\frac{dU_i}{ds} - Pe_i \frac{U_i}{2} \right) r_i(s_j) \tag{17}$$

and $r_i(s_j) = e^{(Pe_i s_j/2)}$ for any arbitrary i and j . Finally, the composite differential operator is given by $L = \{L, D(L)\}$.

1-2. Eigenvalue problem

The eigenvalue problem associated with the operator L defined previously is given by $Lw = \lambda w$. This equation yields two types of problem :

$$\nabla U_k^2 + q_k^2(\lambda) U_k = 0, \quad q_k^2 = \frac{\lambda}{\psi_k} - \frac{Pe_k^2}{4} \tag{18}$$

$$\nabla^2 U_k + p_k^2(\lambda) U_k = 0, \quad p_k^2 = \frac{Pe_k^2}{4} - \frac{\lambda}{\psi_k} \tag{19}$$

where $k=1, 2, \dots, M$. The general solution to these two differential equations for the k th component can be written as

$$U_k(\lambda, s) = A_k \xi_k(\lambda, s) + B_k \zeta_k(\lambda, s) \tag{20}$$

where A_k and B_k are constants to be properly determined by the use of the domain $D(L)$. The functions $\xi_k(\lambda, s)$ and $\zeta_k(\lambda, s)$ are given by

$$\begin{aligned} \xi_k(\lambda, s) &= \sin[q_k(\lambda)s] \\ \zeta_k(\lambda, s) &= \cos[q_k(\lambda)s], \lambda > \gamma_k \end{aligned} \tag{21}$$

$$\begin{aligned} \xi_k(\lambda, s) &= \sinh[q'_k(\lambda)s] \\ \zeta_k(\lambda, s) &= \cosh[q'_k(\lambda)s], \lambda < \gamma_k \end{aligned} \tag{22}$$

where $\gamma_k = (Pe_k^2/4) \psi_k$ and s is given by $s=s_1$ for $k=1, s=s_k - s_{k-1}$ for $k=2, 3, \dots, M-1$, and $s=1 - s_{k-1}$ for $k=M$. These changes of variables allow the eigenfunction to automatically satisfy the external boundary conditions at $s=0$ and $s=1$ with $B_1=0$ and $B_M=0$. The application of the boundary conditions at all the interfacial regions gives

$$\begin{aligned} \frac{B_2}{A_2} &= \frac{[\{w_2(\lambda, s_2 - s_1)\theta_2 + Y_2\} - w_1(\lambda, s - 1)]Q_2(\lambda)}{[\{w_2(\lambda, s_2 - s_1)\} \{Y_2 - w_1(\lambda, Y_1)\} - \chi_2 Q_2^2(\lambda)]} \\ \frac{B_{k+1}}{A_{k+1}} &= \frac{\left[(w_{k+1}(\lambda, s_{k+1} - s_k)\theta_{k+1} + Y_{k+1}) \frac{B_k}{A_k} + Q_k(\lambda) \right]}{+ Q_{k+1}(\lambda)} \\ \frac{B_{k+1}}{A_{k+1}} &= \frac{\{w_{k+1}(\lambda, s_{k+1} - s_k)Y_{k+1} - \chi_{k+1} Q_{k+1}^2(\lambda)\} \frac{B_k}{A_k}}{\{w_{k+1}(\lambda, s_{k+1} - s_k)\} + Q_{k+1}(\lambda)} \\ \frac{B_{M-1}}{A_{M-1}} &= \frac{Q_{M-1}(\lambda)}{w_M(\lambda, 1 - s_{M-1})\theta_M + Y_M} \end{aligned}$$

with the parameters given in Table 1. Starting with B_{M-1} and working backwards by substituting for the B_{k+1}/A_{k+1} it is possible to develop the characteristic equation for the eigenvalues in the form

$$\Xi(\lambda, p_k, \theta_k, \mu_k) = \Omega(\lambda, p_k, \theta_k, \mu_k) \tag{23}$$

where the function contains all the trigonometric and hyperbolic eigenfunctions and Ω is monotonic function of λ . Since the physical system is composed of M layers, there are M different functions of the type $\omega_k(\lambda)$. Depending upon the relative values of γ_k and λ , these functions change their form from the trigonometric cotangent functions to hyperbolic cotangent functions, and each function is a set of vertical lines where the function goes to zero, i.e. where Ω goes to (positive or neg-

Table 1. Unknown parameter values of Eq. (20)

$Y_{k+1} = \frac{Pe_k}{2} - \frac{Pe_{k+1}}{2} \psi_k$
$\chi_{k+1} = \psi_{k+1} \alpha_{k+1} Q_{k+1}$
$\omega_{k+1}(\lambda) = \frac{\zeta_{k+1}(\lambda, s_{k+1})}{\zeta_{k+1}(\lambda, s_{k+1})}$
$\alpha_{k+1} = \begin{pmatrix} 1; \lambda > \gamma_k \\ -1; \lambda < \gamma_k \end{pmatrix}$
$Q_{k+1} = \begin{pmatrix} q_k; \lambda > \gamma_k \\ q_k'; \lambda < \gamma_k \end{pmatrix}$

ative) infinity or $1/\omega_k(\lambda)=0$. These vertical lines occur at

$$\delta(\lambda_{kn}) = \left[\left\{ \frac{n\pi}{s_k - s_{k-1}} \right\}^2 + \frac{Pe_k^2}{4} \right] \psi_k \tag{24}$$

where $\delta(\lambda)$ is equal to $q_k(\lambda)$ for $\lambda > \gamma_k$.

1-3. Transient Solution

The formal solution to the transient problem can now be constructed. Applying the inner product, Eq. (7), to give a self-adjoint eigenvalue problem yields

$$\frac{d\langle C, U_n \rangle}{d\tau} = -\lambda_n \langle C, U_n \rangle + B(\lambda_n) I \tag{25}$$

where U_n is used to indicate $U(\lambda_n, s)$ and the function $B(\lambda_n)$ is given by

$$B(\lambda_n) = \delta_1 \psi_1 C_1(0) u_1'(0, \lambda_n) - \delta_M \psi_M C_L e^{\left(\frac{-Pe_n}{2}\right)} U_n'(1, \lambda_n) \tag{26}$$

u' is the differentiation of u and for the present problem $C_1(0) = 1$ and C_L is a specific function. The notation n indicates the n th eigenvalue of the operator L . The formal solution can easily be written for the n th layer as

$$C_n(s, \tau) = \sum_{n=1}^{\infty} U_n(s, \lambda_n) e^{-\lambda_n \tau} [\langle C(\tau=0), U_n \rangle + \int_0^\tau B(\lambda_n) e^{\lambda_n \tau} d\tau] \tag{27}$$

2. Membrane Transport Problem with Generalized Boundary Conditions

2-1. Definition of Differential Operations and Operator

These generalized boundary conditions represent the addition of well-mixed vessels at both ends of the composite media. The operator formulation for this case can be developed on the basis of the previous problem. First, two new Hilbert spaces are defined in order to accommodate the time variables associated with the generalized boundary conditions, i.e.

$$H_o = \Gamma, H_{M+1} = \Gamma$$

where Γ is the space of real numbers. Second, the following inner products for the spaces defined above are given. If $u \in H_k$, with $k=0$ and $k=M+1$, then

$$\langle U_1, U_2 \rangle_k = c_k U_1 U_2$$

where c_k is a weighting function for the Hilbert space H_k .

The direct sum Hilbert space is now defined as

$$H = H_o \oplus \sum_{k=1}^M H_k \oplus H_{M+1} \tag{28}$$

where the H_k , $k=1, 2, \dots, M$ are the Hilbert spaces already in Eq. (10). A vector $w \in H$ may be written as

$$w = \begin{pmatrix} U_o(0) \\ U_1(x) \\ \vdots \\ U_{M+1}(x) \end{pmatrix} \tag{29}$$

where $U(x)$ is a vector in the direct-sum Hilbert space, H , of the previous problem. With $w_j \in H$ the inner product $\langle w_1, w_2 \rangle$ identified previously in Eq. (29) is formally applied to H . However, a reinterpretation of the δ_j , $j=0, 1, \dots, M+1$, is necessary and will be given in a subsequent section.

The following two differential operations must be defined from boundary conditions (4) and (5)

$$L_o = \lim_{s \rightarrow 0} \left(\xi_2 + \xi_3 \frac{\partial}{\partial s} \right) \tag{30}$$

$$L_{M+1} = \lim_{s \rightarrow 1} \left(\xi_{M-1} + \xi_M \frac{\partial}{\partial s} \right)$$

$$\xi_2 = -\xi_o - \frac{\psi_1 \beta_o \theta_o}{\beta_1} \frac{Pe_1}{2}, \quad \xi_3 = \frac{\psi_1 \beta_o \theta_o}{\beta_1}$$

$$\xi_{M-1} = -\xi_L + \frac{\psi_M \beta_L \theta_L}{\beta_M} \frac{Pe_M}{2}, \quad \xi_M = -\frac{\psi_M \beta_L \theta_L}{\beta_M}$$

In addition, the L_k ($k=1, 2, \dots, M$) operations defined in Eq. (30) are required to complete the set of operations to identify the composite operation, L , of the problem. Eq. (16) can be extended to include the operators L_o and L_{M+1} as

$$L = [L_{jk}] \delta_{jk} \quad (L_{kk} = L_k) \quad k = 0, 1, 2, \dots, M, M+1$$

The domain $D(L)$ associated with the operation L defined above is clearly the same as the domain $D(L)$ already identified in Eq. (25). The composite differential operator is now given by $L = \{L, D(L)\}$, where L is the operation defined in Eq. (17). The problem recast in an operator form is given by

$$\frac{dC}{d\tau} = -LC + g(\tau) \tag{31}$$

where the vector $g^T(t) = [\xi_o(t), 0, 0, \dots, 0, \xi_1(t)]$ and C is the vector of concentrations whose form is given by Eq. (15), and

$$\psi_1(\tau) = C_L \xi_L(\tau) e^{\left(\frac{-Pe_n}{2}\right)} \tag{32}$$

where we may, in general, consider 0 and L to be specified functions of time. The initial conditions for this problem are given by $C(\tau=0, s) = C_o(s)$.

2-2. Eigenvalue Problem

The eigenvalue problem for the present case is analogous to the previous cases except that the homogeneous Robin boundary conditions

$$\xi_2 U_1 + \xi_3 \frac{\partial U_1}{\partial s} = 0 \quad \text{at } s=0, \quad \xi_{M-1} U_M + \xi_M \frac{\partial U_M}{\partial s} = 0 \quad \text{at } s=1$$

must be used to obtain the characteristic equation. The development is similar to that given for the Dirichlet condition, and it will not be considered further in this part.

2-3. Transient Solution

The formal solution to Eq. (31) is analogous to the previous case and can be written as

$$C_n(\tau, s) = \sum_{n=1}^{\infty} U(s, \lambda_n) e^{-\lambda_n \tau} [< C(\tau=0), U_n > + \int_0^{\tau} < g(\tau), U_n > e^{\lambda_n \tau} d\tau] \quad (33)$$

where $g(\tau)$ is, in general, a specified function of τ through the feed condition to the mixed cells at the boundary. Again, if $g(\tau)$ is not a function of time, the spectral expansion of the steady-state solution can be replaced with the steady-state solution given in order to facilitate numerical computation of the transient solution.

RESULTS AND DISCUSSION

1. Analysis of Well-mixed Boundary Conditions in the Membrane Process

Several attempts made in the past to assess the validity of the Danckwerts boundary conditions have considered appending a semi-infinite fore section at the inlet to the membrane and semi-infinite after section at the outlet to the membrane shown in Fig. 2(1). If the appended sections are considered to be of infinite length as shown in Fig. 2(5), one faces the rather difficult task of specification of proper boundary conditions at the upstream end of the fore section and at the downstream end of the after section. It will be seen later that when the appended sections are considered to be infinite in length, the boundary conditions to be specified at the extremities of the membrane are natural.

The membrane is either preceded or succeeded by a continuous stirred reactor of constant volume serving as an intermediary open system. Boundary conditions for these situations have been proposed by Ramkrishna and Amundson. There is a need for ascribing a definite length of the appended sections; the Danckwerts boundary conditions in this case can be used. The formulation of the appropriate boundary conditions is thus governed by the configurational details of the membrane assembly.

The axial coordinate x is chosen such that the reactor properly stretches from $x=0$ to $x=L$.

$$\lim_{x \rightarrow 0^-} C' = \lim_{x \rightarrow 0^+} C', \quad \lim_{x \rightarrow 0^-} D_- \frac{\partial C'}{\partial x} = \lim_{x \rightarrow 0^+} D \frac{\partial C'}{\partial x} \quad (34)$$

$$\lim_{x \rightarrow L^-} C' = \lim_{x \rightarrow L^+} C', \quad \lim_{x \rightarrow L^-} D \frac{\partial C'}{\partial x} = \lim_{x \rightarrow L^+} D_+ \frac{\partial C'}{\partial x} \quad (35)$$

where the diffusion coefficient in the fore section, the membrane section and the after section are denoted as D_- , D and D_+ respectively. The diffusion coefficient in each section is assumed to be constant there. Let C' denote the membrane concentration and t the time. The concentration field $C'(x, t)$ then must satisfy the continuity conditions.

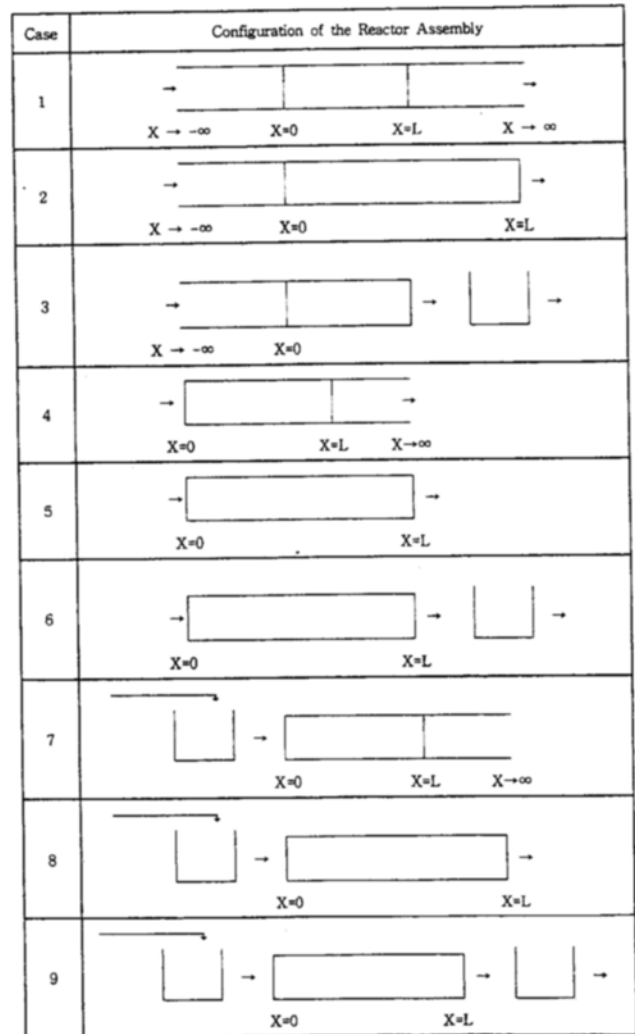


Fig. 2. Various possible configurations in membrane reactor systems.

Eq. (34) holds when the fore section is infinitely long with a finite, non-zero diffusion coefficient as shown in Fig. 2(2). Eq. (35) holds when the after section is infinitely long with a finite as shown in Fig. 2(4), non-zero diffusion coefficient. Boundary conditions for the case where a well-stirred tank of constant volume V_+ precedes the membrane can be written as

$$\lim_{x \rightarrow 0} C' = C'_f, \quad \lim_{x \rightarrow 0^+} \left[D \frac{\partial C'}{\partial x} - uC' \right] + UC'_f = \frac{V_-}{A} \frac{dC'_f}{dt} \quad (36)$$

where C'_f is the concentration in the feed, C_- is the concentration in the continuously stirred tank, and U is the uniform velocity of the fluid and A is the uniform cross section area of reactor. The boundary conditions (36) are obtained by considering mass balance in this stirred reactor. Similarly, when a well-stirred reactor of constant volume V_+ succeeds the membrane, a mass balance in the stirred tank yields the boundary condition at the reactor proper outlet as shown in Fig. 2(3).

$$\lim_{x \rightarrow L} C' = C'_+, \quad \lim_{x \rightarrow L^-} \left[-D \frac{\partial C'}{\partial x} \right] = \frac{V_+}{A} \frac{dC'_+}{dt} \quad (37)$$

C_+ is the concentration of the reactor in the well-mixed after section. It is interesting to note that the Danckwerts boundary condition may be obtained at either of the membrane ends by allowing either volume V_+ or V_- to vanish. The solution in the reactor section is independent of the degree of mixing in semi-infinite entrance and exit sections in the Fig. 2(3) and (7). Eq. (34) can also be used to establish the Danckwerts boundary condition at the membrane inlet in the limit of vanishing D_- . Similarly, the Danckwerts zero gradient condition can be derived from Eq. (35) in the limit of vanishing D_+ . When the fore section is infinitely long with a finite, non-zero diffusion coefficient, in addition to Eq. (34), one must have

$$\lim_{x \rightarrow -\infty} C' = C'_f \quad (38)$$

when an infinitely long after section is used, the concentration at $x=\infty$ must be bounded. Thus

$$\lim_{x \rightarrow \infty} C' < \infty \quad (39)$$

Pearson [1959] has shown that the boundary conditions used by Danckwerts for these cases are the proper ones by solving the problem with a diffusion coefficient that varies continuously throughout the entrance, membrane, and exit sections. This diffusion coefficient can be chosen such that in the limit it approaches the discontinuous one used by Danckwerts. Pearson then showed that the continuous solution approached the solution of Danckwerts in the limit, thereby justifying Danckwerts' boundary conditions. Eqs. (34)-(39) form a complete set of boundary conditions for various configurations of the reactor assembly. The various possibilities that may arise in dispersed systems of interest here are listed in Table 2.

The case of Fig. 2(5) represents the situation for which the Danckwerts conditions are applicable at both ends. Brenner [1962] has presented solutions for pure convective dispersion problems arising in the foregoing case. Solutions for the situation where a linear rate process occurs in a tube of finite length can be obtained in a similar manner. The solution in the membrane section is identical to that of Danckwerts. Its key conclusion is that the distribution of reactant in a reactor is entirely independent of the degree of axial mixing in entrance and exit sections.

In cases of Fig. 2(5), (6), (8) and (9), the conservation equations need be solved over a region of finite length. The boundary value problems in these cases are therefore of 'finite

domain' nature. A general approach would require the addition of a material balance over well-mixed external regions in analogy with the approach of Ramkrishna and Amundson. The Eqs. (5)-(6) can be redescribed as follows

$$V_- \frac{dC'}{dt} = C'_{-f}F_- - C'_-F_- + A[D_- \frac{\partial C'}{\partial x} - u_-C'_-] \quad (40)$$

$$V_+ \frac{dC'}{dt} = C'_{+f}F_+ - C'_+F_+ + A[D_+ \frac{\partial C'}{\partial x} - u_+C'_+] \quad (41)$$

where V is the volume, C' the molar concentration, F the volumetric flow into the mixed reactor and A the cross sectional area of the membrane. The subscript f represents the feed stream into the two external regions.

2. Transient Analysis of Membrane Transport

A complete analysis of the three layered membrane in the transient state and a full description of the effects of system parameters including diffusion coefficient, convective velocity, and porosity, on the dynamic problem are presented in this section. The detailed solution for the transient analysis has been studied in the previous paper of Park [1996]. In our transport model, diffusion and convection are assumed to govern the membrane transport. Hydrodynamic convection is neglected in order to give a representation of what would be occurring in the stagnant boundary of membrane in the fluid phase.

Concentration profiles in the membrane and in the boundary layer around the membrane can be calculated from the solution to the model solution of Eq. (27). In the model equations, the dimensionless Peclet number is a major control variable of the convection and diffusion. The convective-diffusive transport in the membrane can be analyzed through two different Peclet numbers in the fluid phase and solid phase of membrane. Transient concentration profiles in the membrane and in the boundary layer surrounding membrane are associated with the convective fluid velocity. Fig. 3 shows several of these concentration profiles at different Peclet numbers.

The membrane transport of Fig. 3(a) is governed primarily by diffusive transport due to small value of Pe_f (the relative ratio of convective velocity and diffusion coefficient in the membrane); thus the transient concentrations of solute on the two boundary regions of the membrane become nearly equal. Dynamic speed in the membrane is faster in greater Pe_f as shown in Fig. 3(c). The transient rate to approach at steady state in the membrane is significantly reduced as the con-

Table 2. Various possibilities in axially dispersed membrane systems

Case	D_-	D_+	Volume of fore section	Volume of after section	Boundary condition section	Boundary condition at outlet
1	$(0, \infty)$	$(0, \infty)$	infinite	infinite	Eq. (34)	Eq. (35)
2	$(0, \infty)$	0	infinite	-	Eq. (34)	Eq. (B)
3	$(0, \infty)$	∞	infinite	finite	Eq. (34)	Eq. (37)
4	0	$(0, \infty)$	-	infinite	Eq. (A)	Eq. (35)
5	0	0	-	-	Eq. (A)	Eq. (B)
6	0	∞	-	finite	Eq. (A)	Eq. (37)
7	∞	$(0, \infty)$	finite	infinite	Eq. (34)	Eq. (35)
8	∞	0	finite	-	Eq. (34)	Eq. (B)
9	∞	∞	finite	finite	Eq. (34)	Eq. (37)

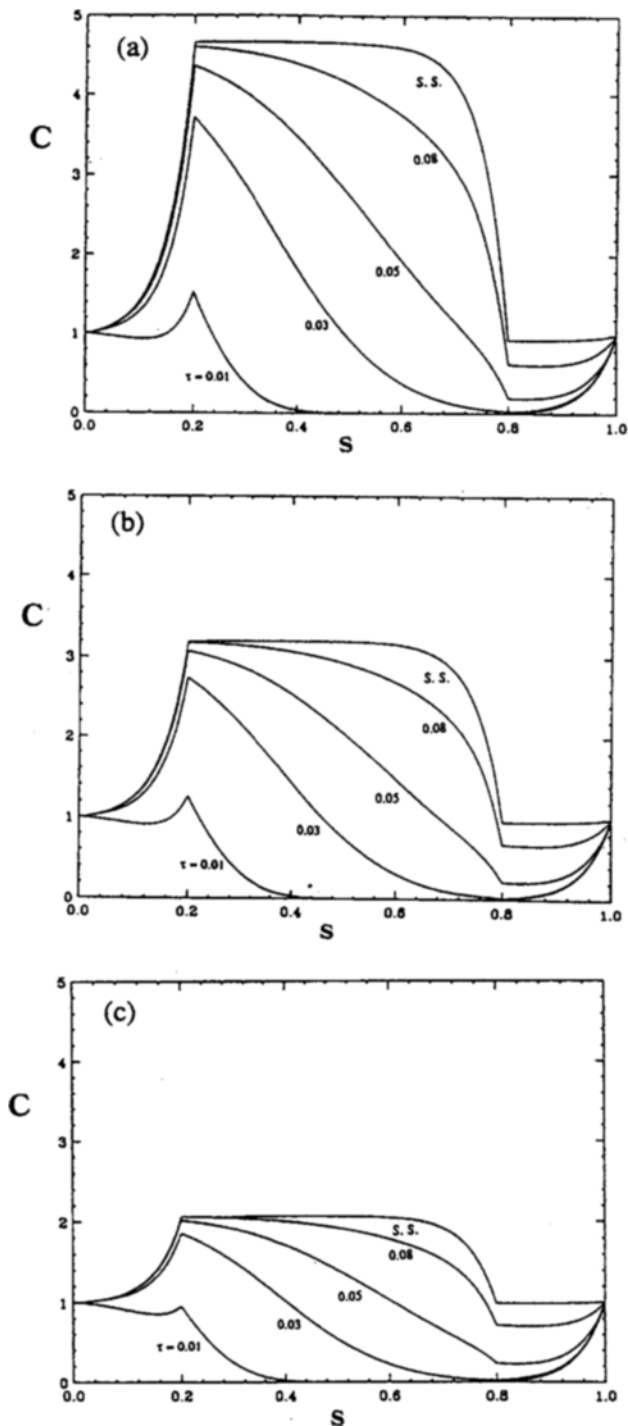


Fig. 3. Transient concentration profiles in three-layered composite membrane (The concentrations at each layer are plotted as dividing by porosity (β) of each layer).

(a) $\beta=0.5$, $\psi=0.5$, $Pe_f=Pe_g=Pe_k=10.0$

(b) $\beta=0.5$, $\psi=0.5$, $Pe_f=Pe_g=Pe_k=20.0$

(c) $\beta=0.5$, $\psi=0.5$, $Pe_f=Pe_g=Pe_k=40.0$

convective fluid velocity becomes greater when the solute penetrates farther through the membrane than $s=s_1$. It is because the dynamic speed of solute in the membrane becomes faster to approach to the steady state in the lower interphase region of membrane. It is theoretically shown in Fig. 3(b) that

the concentration gradually builds up with Peclet number as solute penetrates farther from $s=s_1$. The dependence of the concentration increase in the membrane arises because the convective velocity in the membrane depends on the dynamic behavior by the direct interaction between fluid velocity and membrane. This observation is obtained because the flux of solute that is transported to the pores of the membrane from the bulk fluid phase equals the flux transported through the membrane.

3. Membrane Transport in Multi-layered Membranes

The dynamics in the membrane process can be related to the dynamics of the individual layer problem of a multilayered membrane. The convection effect in a multilayered membrane may be enhanced due to the interactions between membrane layers. As the porosity of each membrane layer increases gradually in the multilayer membrane, the convective velocity becomes accelerated as solute passes across each membrane layer. Solute transports more quickly through the membrane with higher porosity than lower porosity. Concentrations gradually increase due to fast movement of solute as shown in Fig. 4(a). But in the reverse case, concentrations in each layer significantly decrease with lower porosity in comparison with constant porosity in each membrane layer. Also solute moves faster in more porous membrane as convective velocity is increased.

As Pe_g of each membrane layer gradually increases to the x-direction, the concentrations are linearly increased by the stacked effects of the multi-layered membranes as membrane transports are performed layer by layer as shown in Fig. 4(b). This indicates that the solute in the interface of each membrane layer can be accumulated. The accumulation of concentrations can be enhanced by the appropriate selection of physical parameters such as membrane porosity and the ratio of membrane transport in each membrane layer. It is shown in Fig. 4(b) that the concentration profile at the fifth layer of a six-layer membrane can be significantly increased with the fluid convective velocity when the porosity in each membrane layer increases layer by layer.

This result occurs because the flux of solute transport to the pores of the membrane layer equals the flux transported through next membrane. The gradients of concentrations are found to be steeper at the interfaces between each membrane layer. Even though the porosity in each membrane layer is irregularly changed, concentration profiles have maximum profiles as seen in Fig. 4(b). The porosity in each composite membrane layer affects the accumulation of concentrations. The convection effects in the multilayered membranes are determined by several physical properties of membranes. They must play an important role to design multi-layered composite membrane.

If the number of membrane layers is increased, the accumulation of solute in each membrane layer may be further enhanced. Fig. 4(c) shows that as the number of membrane layers increases from $M=3$ to $M=9$, the concentrations of membrane layer significantly increase with the number of membrane layers as the porosity gradually increases from layer to layer. Concentration in the $(M-1)$ th layer membrane is significantly increased. This kind of structural composite mem-

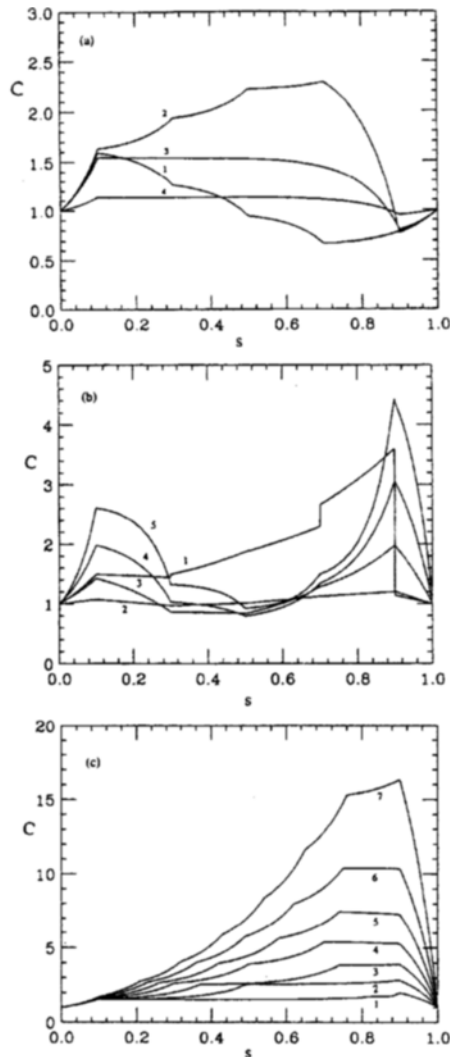


Fig. 4. Concentration profiles in multilayered membrane ($k=6$) (The concentrations at each layer are plotted as dividing by porosity (β) of each layer).

(a) Porosity effects:

- 1) $\beta_1=1, \beta_2=0.5, \beta_3=0.4, \beta_4=0.3, \beta_5=0.2, \beta_6=1.0$ and $\psi_k=0.5, Pe_k=10$
- 2) $\beta_1=1, \beta_2=0.5, \beta_3=0.6, \beta_4=0.7, \beta_5=0.8, \beta_6=1.0$ and $\psi_k=0.5, Pe_k=10$
- 3) $\beta_1=1, \beta_2=0.9, \beta_3=0.9, \beta_4=0.9, \beta_5=0.9, \beta_6=1.0$ and $\psi_k=0.5, Pe_k=10$
- 4) $\beta_1=1, \beta_2=0.5, \beta_3=0.5, \beta_4=0.5, \beta_5=0.5, \beta_6=1.0$ and $\psi_k=0.5, Pe_k=10$

(b) Convection effect:

- 1) $Pe_1=5, Pe_2=6, Pe_3=7, Pe_4=8, Pe_5=9, Pe_{10}=5$ at $\beta_1=1, \beta_2=0.1, \beta_3=0.3, \beta_4=0.5, \beta_5=0.7, \beta_6=1.0$ and $\psi_k=0.5$
- 2) $Pe_k=1$ at $\beta_1=1, \beta_2=0.5, \beta_3=0.4, \beta_4=0.3, \beta_5=0.2, \beta_6=1.0$ and $\psi_k=0.5$
- 3) $Pe_k=5$ at $\beta_1=1, \beta_2=0.1, \beta_3=0.3, \beta_4=0.2, \beta_5=0.1, \beta_6=1.0$ and $\psi_k=0.5$
- 4) $Pe_k=10$ at $\beta_1=1, \beta_2=0.1, \beta_3=0.3, \beta_4=0.2, \beta_5=0.1, \beta_6=1.0$ and $\psi_k=0.5$
- 5) $Pe_k=15$ at $\beta_1=1, \beta_2=0.1, \beta_3=0.3, \beta_4=0.2, \beta_5=0.1, \beta_6=1.0$ and $\psi_k=0.5$

(c) Effects of number of membrane layer: 1) $M=3$, 2) $M=4$, 3) $M=5$, 4) $M=6$, 5) $M=7$, 6) $M=8$, 7) $M=9$ at $\psi_k=0.5, Pe_k=10$

brane can be sufficiently designed by varying the porosity of each membrane layer. The separation of solute can be enhanced as controlling physical parameters as well as number of membrane layers.

CONCLUSION

A complete analysis of an M -layered membrane in a transient state, and a full description of the system parameters including diffusion coefficient, convective velocity, and porosity, on the dynamic problem have been presented. The methodology is a complete *a priori* characterization of the solution with minimal computations. Furthermore, these calculations can be a guide for the dynamic effect of membrane transport by direct interaction. The advantage of direct membrane convection is to make the acceleration of the speed in the membrane process possible. The speed in the membrane can be controlled by the convective fluid velocity in the external space of the system. Transport in an M -layered membrane can be significantly varied by continuously varying properties of each layer.

This study suggests a useful guide for the design of laboratory devices as well as larger scales required for a variety of membrane separations.

NOMENCLATURE

- A : cross sectional area of system
- A_k, B_k : integral constant
- c : species molar concentration
- C, C' : non-dimensional concentration
- D : species diffusivity
- $D(L)$: domain of the differential operation L
- f : kinetic function of species concentration
- F : volumetric flow rate into external boundary regions
- L : total length of composite media
- L_k : differential operation
- N : molar flux
- Pe : Peclet number
- p_k, q_k : functions defined in Eq. (18), (19)
- s : non-dimensional spatial coordinate
- t : time variable
- U : convective velocity
- V : volume of external regions
- w : element of the Hilbert space H
- x : dimensional spatial coordinate

Greek Letters

- β : equilibrium coefficient
- γ : parameter defined in Eq. (21)
- δ : constant in the inner product of H
- λ : eigenvalue
- ξ : constants defined in Eq. (21)
- ζ : constants defined in Eq. (21)
- ψ : diffusivity ratio
- Ξ : monotonic function of λ in Eq. (23)
- Ω : transcendental function of λ in Eq. (23)
- Γ : the space of real number

Subscripts

- f : feed to external boundary region
k : layer of the composite membrane layer
o : first layer of the composite membrane layer
M : total number of layers in the composite membrane layer

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