GEOMETRICAL ANALYSIS OF DYNAMIC PROBLEM ON THE MEMBRANE TRANSPORT USING SPECTRAL SOLUTION

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Abstract—The problem analyzed in this paper is a specific application of the composite membrane. General diffusion and convection formulation is presented for the dynamic problem. The spectral analysis considers convective transport of a single solute species across a one dimensional membrane system. The solution is obtained using operator theoretic methods. The geometrical structure of the spectrum of the operator is determined for the complete range of the various parameters including the distribution coefficient, the convective velocity and the diffusion coefficient. The structure of the spectrum allows a complete characterization of all the eigenvalues of the system in terms of all of these physical parameters. Calculation of the first eigenvalue for a number of cases shows its variation with the convective velocity for various medium porosities and allows a priori estimates of the profiles.

INTRODUCTION

Intraparticle convective transport is of current interest in a number of separation and reaction processes. In previous work several researchers [1-4] have considered the effects of convection on the selectivity of sequential chemical reactions, general catalyst performance, and on chemically induced convective currents. More recently Stephanopoulos and Tsiveriotis [5] considered the effects of intraparticle hydrodynamic convection on nutrient transport in biological pellets. Porous particles are also commonly used in a number of separation processes including size exclusion adsorption, ion exchange, and affinity chromatography. Afeyan et al. [6] have developed particles for high performance liquid chromatography that display a significant hydrodynamic convective component inside the particle. It is possible when large pressures are applied to such packed columns containing highly porous particles that convective fluid flow motion may become important. Rodrigues [7] studied the effects of intraparticle hydrodynamic convection on separation by adsorption. Recent work with gel columns under an applied electrical field also shows a convective transport component through the particle that arises from the electrical field [8]. The objective of the present chapter is to show in the geometric points of views how convective velocity, arising from fluid motion, affects separation in the membrane. A mathematical model for diffusive-convective transport is developed using one dimensional x-direction. The model formulation is developed for transient one-dimensional convective transport where the diffusion coefficient of the solute, the convective velocity, and the accessible pore volume are allowed to vary in the membrane. The operator theoretic method will utilize for constructing the solution of similar composite media problems. Specifically, the methodology will be applied to a system of three layers to study the transport at the membrane. An analysis of the relative effects of diffusive-convective transport will be performed by varying the dimen-

sionless Peclet numbers in fluid and solid phases. The three layered membrane system can approximate a membrane surrounded by two stagnant boundary layers. Operator theoretic method in this study leads to solutions to the formally non-self adjoint problem featured by the original differential model by recasting the problem in a self-adjoint form. The emphasis is on developing the underlying formal theory for a number of different physical problems, and on the evaluation of the spectra (i.e. the set of eigenvalues of the transport differential operator) for the solutions or on performing any parametric studies of the effects of the physical properties on the solute concentration profiles. Detailed consideration of the spectra will be presented to illustrate the effects of the operating on the transient solutions. The basic strategy is to extract as much information as possible without performing detailed numerical calculations. In addition, numerical computations are presented to illustrate the behavior of the system in the different parameter regions predicted by the geometrical analysis of the spectra.

THEORY

The species of interest, removing subscript "s" for convenience, and assuming one dimensional transport in rectangular coordinates is

$$\frac{\partial c_m}{\partial t} = -u_m \frac{\partial c_m}{\partial x} + D_m \frac{\partial^2 c_m}{\partial x^2} \qquad (1)$$

The Eq. (1) can be applied to composite membranes as shown in Fig. 1. This again assumes low concentration, small diffusion coefficient, and convective velocity for the solute of interest. Operator-theoretic techniques are well-suited for developing an analytical solution for this case. The solute of interest contributes to the convective velocity. Eq. (1) is the standard convection-diffusion equation. Paruleker and Ramkrishna [9] have considered single tubular flow reactor problems with infinite domain appended sections. Novy et al. [10] have considered the numerical solu-

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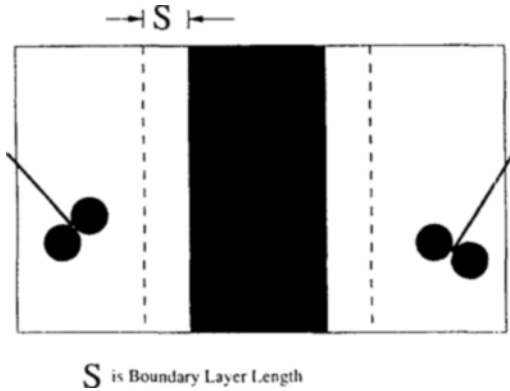
S is Boundary Layer Length

Fig. 1. Schematic picture in membrane system.

tion to convection-diffusion problems in single reactors with finite domain appended sections and various boundary conditions. In the analysis pursued in this paper the "model problem" will permit, without loss of generality, an appropriate illustration of the most important characteristics of the problem while keeping the algebraic details at a minimum. Furthermore, the three-layered membrane problem retains the most relevant aspects of the steady state and dynamic behavior of the convective transport related to more complicated problems. In the model formulation each layer is assumed to be a different phase, and therefore flux and equilibrium boundary conditions are required at the membrane interfaces. The total fluxes at the internal boundaries between each composite membrane must be equal and are given by

$$-D_{m+1}\frac{\partial C_{m+1}}{\partial x}+c_{m+1}u_{m+1}=-D_m\frac{\partial C_m}{\partial x}+c_m u_m \tag{2}$$
$$x=x_m; \quad m=1, 2$$

The convective term in the above boundary conditions is not included in former study since in that analysis, incompressible flow is assumed. The species distribution coefficients, β, gives the linear phase equilibrium

$$\beta_{m+1}c_{m+1}=\beta_m c_m \tag{3}$$
$$x=x_m; \quad m=1, 2$$

To the above set of boundary conditions must also be added boundary conditions at the external boundaries; i.e. at $x=0$ and $x=L$. For the case of large solute in porous media these distribution coefficients represent the fractional pore available to each class of solute. For the case of a fixed concentration in the outer regions these conditions are

$$\beta_1 c_1=\beta_0 c_0 \qquad \text{at } x=0 \tag{4}$$

$$\beta_2 c_2=\beta_L c_L \qquad \text{at } x=L \tag{5}$$

The conditions of constant concentration used here would physically represent a well mixed region.

The nondimensional form of the differential equations in (1) and boundary conditions (2)-(7) are given as follows. Dimensionless variables are

$$\tau\equiv\frac{tD_o}{L^2}, \quad Pe_m\equiv\frac{u_m L}{D_m}$$

$$\phi_m\equiv\frac{D_m}{D_o}, \quad s\equiv\frac{x}{L}, \quad C_m'\equiv\frac{C_m}{c_o}$$

Transformation variable is $C_m=C_m'\exp(-Pe_m s/2)$

The differential Eq. (1) can be rewritten with dimensionless terms of Eq. (6) and transformation variable as

$$\frac{\partial C_m}{\partial \tau}=\phi_m\left(\frac{\partial^2 C_m}{\partial s^2}-\frac{Pe_m^2 C_m}{4}\right) \tag{6}$$

and boundary conditions are $C_o(0)=C_o$, $C_m(1)=C_L\exp(-Pe_L/2)$ and internal boundaries at $s=s_m$ for $m=1, 2, 3$ are given by

$$\frac{r_m(s_m)\phi_m}{\beta_m}\left(-\frac{\partial C_m}{\partial s}+Pe_m\frac{C_m(s_m)}{2}\right)=\frac{r_{m+1}(s_m)\phi_{m+1}}{\beta_{m+1}}$$
$$\left(-\frac{\partial C_{m+1}}{\partial s}+Pe_{m+1}\frac{C_{m+1}(s_m)}{2}\right) \tag{7}$$

and equilibrium condition is

$$C_m(s_m)r_m(s_m)=C_{m+1}(s_m)r_{m+1}(s_m) \tag{8}$$

where $r_m(s_j)=\exp(Pe_m s_j/2)$ for arbitrary i and j. The solution methodology for the general model will be illustrated with the case of membrane surrounded by two fluid layers. A brief outline of the operator formulation and solution methodology will be presented in the next section and detailed consideration of the structure of the spectrum of the operator (i.e. the set of eigenvalues of the problem) will thereafter be made in order to illustrate the technique. Several geometrical regions in the parameter space of the spectrum will be studied and their implications to the model dynamics will be clearly identified. Illustrations of the effects of the parameters on the solution concentration profiles will also be discussed in order to describe the dynamics of the solute accumulation in the system.

Several physical parameters such as the Peclet number-the relative ratio of convective transport to diffusive transport, ϕ-the relative ratio of diffusion coefficients, and β_m of the equilibrium distribution coefficient are included in the model given by the Eqs. (1)-(3). The model can accurately describe variations from layer to layer in the system. For example, a variation in β represents the pore space avilable for a particular molecule. The variation in Pe (i.e. the ratio of convective motion to diffusive transport) would occur if the convctive velocity changes from fluid phase to solid phase. Convective veloity in the membrane arises due to both changes in pore construction.

1. Solution Methodology

The solution to the transient problem will be solved by linear operator theory. The following differential operations associated with the physical problem and arising from the Eq. (6) are

$$L_k\equiv-\phi_k\left(\frac{d^2}{ds^2}-\frac{Pe_k^2}{4}\right) \tag{9}$$

where for $k=1, 2, 3$. The composite differential operation L (i.e., the operations associated with the membrane of the physical problem) is now defined on the basis of Eq. (6) as $L\equiv[L_{jk}]\delta_{jk}$ where $L_{kk}\equiv L_k$, $k=1, 2, 3$ and $L_{jk}\equiv0$, $j\neq k$

The domain associated with this differential operation is given by

$$D(L)=\{w\in H \text{ and } Lw\in H: u_1(0)=0; u_k(s_k) r_k(s_k)$$
$$=u_{k+1}(s_k)r_{k+1}(s_k);$$
$$\frac{\beta_k\phi_{k+1}}{\beta_{k+1}\phi_k}\hat{N}_{k+1}(s_k)=\hat{N}_k(s_k); k=1, 2, 3; u_3(1)=0\} \tag{10}$$

where the following operations have been defined

$$N_i(s_i) = \left[\frac{du_i}{ds} - Pe_i \frac{u_i}{2} \right] r_i(s_i) \tag{11}$$

and $r_i(s_i) = \exp(Pe_i s_i/2)$ for any i and j. The composite differential operator defined in the Hilbert space, H, is given by $L = \{L, D(L)\}$. H is direct-sum Hilbert space defined as

$$H = \bigoplus_{i=1}^{\cdot} \sum H_i \tag{12}$$

with a k-inner product of the form

$$(u_i, u_j)_k = \int_{s_k}^{s_{k'}} u_{ik} u_{jk} \, ds \quad k = 1, 2, 3 \tag{13}$$

In the above equation u_{ij}, {u}, j = 1, 2 are vectors in each Hilbert space, H_k, $k = 1, 2, 3$. If we define an arbitrary vector $w \in H$ as

$$w^i = \{u_{i1}, u_{i2}, \cdots u_{ij}, \cdots u_{in}\}, \quad i = 1, 2 \tag{14}$$

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

$$<w_i, w_j> = \sum_{j=1}^{M} \delta_j (u_i, u_j). \tag{15}$$

with the δ's given by

$$\delta_{k+1} = \delta_k \left[\frac{r_{k-1}(s_k)}{r_k(s_k)} \right] \frac{\beta_k}{\beta_{k+1}}, \quad k = 1, 2 \tag{16}$$

with $\delta_1 = 1$ and $\delta_j > 0$ for all $j = 2, 3$.

The transport operator L given by Eq. (9) is a self-adjoint, non-negative definite operator in the direct sum Hilbert space H. From the spectral theorem [11] eigenfunctions of L that belong to different eigenvalues are orthogonal to each other. Furthermore, the set of eigenfunctions constitutes a a complete set and all non-zero eigenvalue of L are positive.

The eigenvalue problem associated with the operator L previously defined in (9), is given by $LW = \lambda W$. This equation yields the following two types of problems

$$u_k'' + q_k^2(\lambda) u_k = 0 \quad q_k^2(\lambda) = \lambda - \gamma_k \tag{17}$$

and

$$u_k'' + q'_k{}^2(\lambda) u_k = 0 \quad q'_k{}^2(\lambda) = \gamma_k - \lambda \tag{18}$$

The general solution to these two differential equations can be written as

$$u_k(\lambda, s) = A_k \eta_k(\lambda, s) + B_k \eta'_k(\lambda, s) \tag{19}$$

where A_k and B_k are constants to be properly determined by the use of the D (L). Two cases must be identified to obtain the functions $\eta(\lambda, s)$ and $\eta'(\lambda, s)$. For the first case, $\lambda > \gamma_k$, the functions $\eta(\lambda, s)$ and $\eta'(\lambda, s)$ are given by

$$\eta(\lambda, s) = \sin[q_k(\lambda) s']$$
$$\eta'(\lambda, s) = \cos[q_k(\lambda) s'] \tag{20}$$

The second case arises when $\lambda < \gamma_k$ and the functions are given by

$$\eta(\lambda, s) = \sinh[q'_k(\lambda) s']$$
$$\eta'(\lambda, s) = \cosh[q'_k(\lambda) s']$$

In Eqs. (17) and (18), $\gamma_k = (Pe_k^2/4)\delta_k$ and s' is given by $s' = s - s_k$, k = 1; k = 2, 3, $s' = 1 - s_k$, k = 3. These changes of variables allows the eigenfunction to automatically satisfy the external (Dirichlet) bound-

ary conditions at s = 0 and s = 1 with B = 0 and B = 0. The application of the boundary conditions at all the interfacial regions facilitates the construction of the characteristic equation. The co-efficient A_1 is set equal to 1 and the other coefficients of A_k and B_k are determined by applying the corresponding inner product equation to the boundary conditions of D (L). The eigenvalues are obtained from the characteristic equation yielded by the transport operator L as

$$\Omega(\lambda) = \Phi[Q(\lambda), \lambda] \tag{21}$$

where the function Φ contains all the trigonometric and hyperbolic eigenfunctions of $Q(\lambda)$, and $\Omega(\lambda)$ is directly a function of λ. There are different types of functions depending upon the relative values of Ω and λ, these functions change their form from trigonometric tangent functions to hyperbolic tangent functions. The Φ function contains a sum of the trigonometric functions, and associated with each function is a set of vertical lines where the function goes to zero, i.e. where Φ goes to infinity. These limiting lines greatly facilitate the numerical calculation of the eigenvalues since the eigenvalues can be found from the intersection of the monotonic function Ω with the function Φ. It should be noted that the degree of effort needed to construct the function Φ increases rapidly with the number of layers in the problem. As the physical properties change, i.e. the Pe_k and δ_k, the type of eigenfunctions changes. The solution methodology for developing the characteristic equation will be analyzed in composite membrane problem.

The formal solution to the transient problem can now be constructed. Applying the inner product, Eq. (19), to Eq. (6) and utilizing the proper δ_k's of Eq. (19), to give a self-adjoint eigenvalue problem gives

$$\frac{d<C, u_n>}{d\tau'} = \lambda_n <C, u_n> + <g_n, u_n> \tag{22}$$

where the function g_n can be a function through self-adjoint boundary conditions. And for the present problem $C_i(0) = 1$ and C_i is a given input condition. The formal solution can be easily written as

$$C_n = \sum_{n=1} u_{nn} \exp(-\lambda_n \tau') \{<C(\tau' = 0), u_n>$$

$$+ \int <g_n, u_n> \exp(\lambda_n t) dt\} \tag{23}$$

Eq. (23) in turn can be written as a sum of a transient term which is described by the exponential term and a steady state term as

$$C_n = C_n^\cdot + \sum_{n=1} u_{nn} \exp(-\lambda_n \tau') \left\{ <C(\tau' = 0), u_n> - \frac{<g_n, u_n>}{\lambda_n} \right\} \tag{24}$$

The steady state solution, $C_n^\cdot$, of above equation can be developed from the ordinary differential Eq. (6). The constant concentration by Dirichlet boundary conditions used in the above problem can be physically achieved only with an infinite sink at the boundaries. This may correspond to a stagnant boundary layer with very large well mixed cells. However, in order to account for the finite size of the mixing cells outside of the composite media it is necessary to perform a more detailed analysis of the physics of the boundary region.

2. Characterization of Spectrum L in the Membrane

The characteristic Eq. (21) is given for membrane problem by

Table 1. Various cases for eigenfunctions

	$Pe_f/Pe_g < 1.0$			$Pe_f/Pe_g > 1.0$		
Range	Fluid phase	Solid phase	Range	Fluid phase	Solid phase
Low region $0 < \lambda < \gamma_g$	H	T	Low region $0 < \lambda < \gamma_f$	H	T
Middle region $\gamma_f < \lambda < \gamma_g$	H	H	Middle region $\gamma_g < \lambda < \gamma_f$	T	H
High region $\lambda > \gamma_f$	T	T	High region $\lambda > \gamma_g$	T	T

*H : Eigenfunction as Hyperbolic function

**T : Eigenfunction as Trigonometric function

$$\Omega(\lambda) \equiv \beta\phi\left(\frac{Pe_1}{Pe_2}\right)\left[Q_2^2 + \frac{Pe_2^2}{4}\left(1 - \frac{1}{\beta\phi}\right)\right]^2 \qquad (25)$$

$$\Phi\{Q(\lambda), \lambda\} = \frac{Q_1}{\Pi(Q_1 s_1)}\left[\frac{Pe_2 Q_1}{Pe_1\beta\phi\Pi(Q_1 s_1)} + \frac{2Q_2}{\Pi\{Q_2(s_2 - s_1)\}}\right] \qquad (26)$$

where $Q_k = (\lambda - \gamma_k/4)^{1/2}$, $\Pi = \eta/\eta'$. The function, Ω, in Eq. (25) is a monotonic function of λ while the function Φ has the non-linear transcendental function. This nolinear function may change its geometrical shape depending upon the relative magnitudes of λ, Pe_f, Pe_g and ϕ since they change from hyperbolic co-tangents to trigometric co-tangents. This very important feature of the spectrum of L seems to have been overlooked in the previous analysis [11]. Four possible regions (as shown in Table 1) for the behavior of Ω and Φ as functions of λ arise for the specific membrane problem considered here. For example, at very low Pe_f and Pe_g, the non-linear functions are both trigometric co-tangent functions. Each co-tangent function has a group of *vertical lines* associated with it for the function going to $\pm$ infinity. These vertical lines play an important role in the calculation of eigenvalues of the operator L since they are *apriori* bounds between which the eigenvalues of the composite operator L are located. A bisection routine is a natural choice for the numerical determination of these eigenvalues because the vertical lines define the range over which to search for a root. Further evaluation of the spectra, again referring to Fig. 2, shows that only one or two roots can occur between two adjacent vertical lines.

An interesting connection between these lines and the physical problem can be made. The dynamics of the composite membrane problem can be related to the dynamic of the individual single layer problems though the position of the eigenvalues of the composite operator L with respect to the location of the vertical lines. The vertical lines represent the eigenvalues of the problem. The eigenvalues for a single isolated layer with Dirichlet boundary conditions can be given from Eq. (26). For the membrane problem the vertical lines are given as

$$\lambda = (n\pi/s_1)^2 + \gamma_f \quad \text{and} \quad \lambda = (n\pi/1 - 2\ s_1)^2\phi_1 + \gamma_g \qquad (27)$$

where the subscript "a" denotes the single isolated layer and γ is defined in Eq. (17). Division by a_1, the dimensionless size of the fluid layer, and $1 - 2\ a_1$, the dimensionless size of the membrane layer, does not affect the comparison to the isolated case since the overall length of the composite system cancels in the product of λ and $\tau (= tD_f^2/x_u^2)$.

It is clear from Table 1, that at larger values of γ_f and γ_g one or both of the non-linear functions of the characteristic equation may be hyperbolic co-tangent functions for the region for low
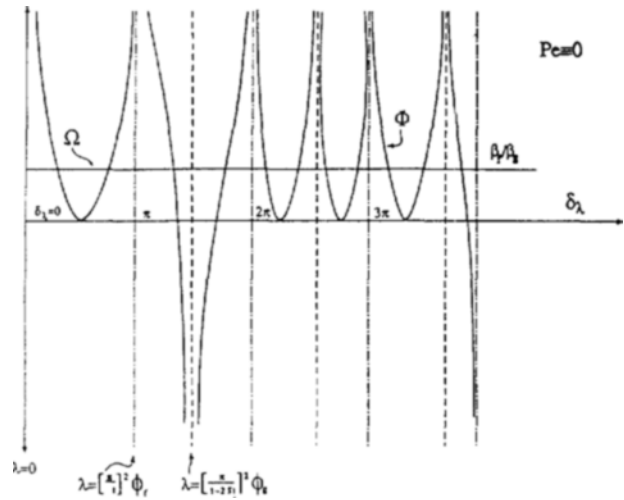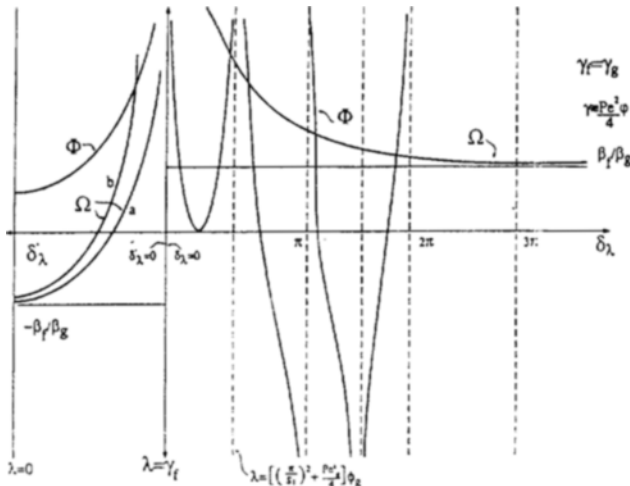

Fig. 2. Spectra for $\gamma_f = \gamma_g = 0.0$.

λ. The characteristic equation and eigenfunctions will have to be modified in this region in order to correctly calculate the eigenvalues. However, as λ increases, i.e. for larger numbers of eigenvalues, the system will revert to the high region when $\lambda > \gamma_k$ for all k. In order to study the structures of the spectra and the influence of the system parameters on the eigenvalues four general cases will be considered. The first case, where no convection occurs (i.e. $\gamma_f = \gamma_g = 0$), serves as a base case for comparison. The other three cases include $\gamma_f = \gamma_g$, $\gamma_f > \gamma_g$ and $\gamma_f < \gamma_g$. By changing the values of parameters γ_f and γ_g, the relative importance of te diffusive transport and convective transport changes in each layer.

Fig. 2 shows the spectra for the case of no convection. The two functions Φ and Ω are plotted as functions of the general axial coordinate $\delta_\lambda = Q_1(\lambda)s_1$. For this case with no convection δ_λ reduces to $(\lambda)^{1/2}$. The monotonic function, Ω is given by a constant value of $\beta_f/\beta_g (= \beta)$ in composite membrane problem and the transcendental function Φ contains two sets of vertical lines. The first eigenvalue is bounded between zero and the smaller of the two isolated layer eigenvalues i.e. $\lambda = (\pi/s_1)^2$ or $\lambda = \{\pi/(1 - 2s_1)\}^2\phi_1$. Therefore, the composite eigenvalues move toward one of the two isolated eigenvalues due to changes in both the relative sizes of each layer and the relative magnitude of the diffusion coefficients in each layer, and this has a major influence on the dynamics. For example, a large value of s_1 would give rise to control by the fluid layer by making the composite eigenvalue closer to the isolated fluid (layer) eigenvalue while a small value of a_1 and small ϕ_1 would give rise to control by the membrane as making the composite eigenvalue go to zero and the increased capacity of the membrane for solute drastically reduces the speed of the dynamics of the interacting membrane layered system.

Once convection is introduced a number of interesting features, as shown in Fig. 3, arise. In the case with equal convective transport in all layers $\gamma_f = \gamma_g = \gamma$ in order to develop the composite spectra in λ it is necessary to consider the two regions $\lambda > \gamma$ and $\lambda < \gamma$. For $\lambda > \gamma$ the most convenient axial coordinate for a geometrical representation of the spectra is δ_λ as defined above and given by

$$\delta_\lambda = \sqrt{\lambda - \frac{Pe_f^2}{4}}\ s_1 \qquad (28)$$

Fig. 3. Spectra for $\gamma_f = \gamma_g = \gamma$.

Fig. 4. Spectra for $\gamma_f > \gamma_g$.

and for $\lambda < \gamma$ the proper scale is

$$\delta'_\lambda = \sqrt{\frac{Pe_f^2}{4} - \lambda} \; s_1 \tag{29}$$

The addition of the above region of the spectra (i.e. $\lambda < \gamma$) is unique to this type of layered problem with convective transport. It is possible to show that when the additional constraint is met at

$$\frac{Pe_f}{Pe_g} = \theta_2 \tag{30}$$

the Ω function is a straight line equal to $-\beta$ for $0 < \delta'_\lambda$ and equal to β for $\delta_\lambda > 0$. $\theta_2 = 1/\beta\phi$. In this case no eigenvalues occur in the region between 0 and $\lambda = \gamma$ and the first eigenvalue is bounded by γ and the smaller of the isolated and interacting eigenvalues

$$[(\pi/s_1)^2 + \gamma] \text{ or } [\{\pi/(1-2 \; s_1)\}^2\phi_1 + \gamma] \tag{31}$$

The first eigenvalue is thus shifted to larger values than for the no convection case. Thus, convection increases the speed of the dynamics of the process, i.e. it increases the rate at which steady-state is approached. It also drastically changes the steady-state.

Fig. 3 shows two other possibilities for the behavior of the Ω function for this same case of $\gamma_f = \gamma_g$. It is possible that for certain parameter values the first eigenvalue can occur between 0 and $\lambda = \gamma$. One can show that if

$$[\Phi(\lambda = 0) - \Omega(\lambda = 0)][\Phi(\lambda = \gamma - \varepsilon) - \Omega(\lambda = \gamma - \varepsilon)] < 0 \tag{32}$$

is met, where ε is some small distance from $\lambda = \gamma$, then a single eigenvalue occurs between $\lambda = 0$ and $\lambda = \gamma$.

Fig. 4 shows the geometrical shape of Φ and Ω functions verses δ_λ and δ'_λ for the next case where $\gamma_f > \gamma_g$. A number of roots may occur in the region $\gamma_g < \lambda < \gamma_f$. This implies that the membrane phase is reducing the speed of the dynamics of the process, i.e. the eigenvalues of the isolated membrane phase, and thus the membrane phase is controlling the dynamics of the composite layered system. A very interesting spectrum occurs for the case of $\gamma_f < \gamma_g$ as shown in Fig. 5. This figure shows four specific examples of the behavior of the Ω function. When the following relationships holds
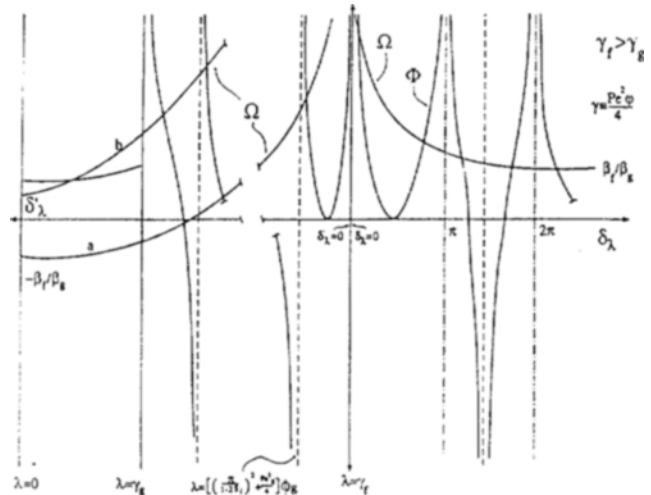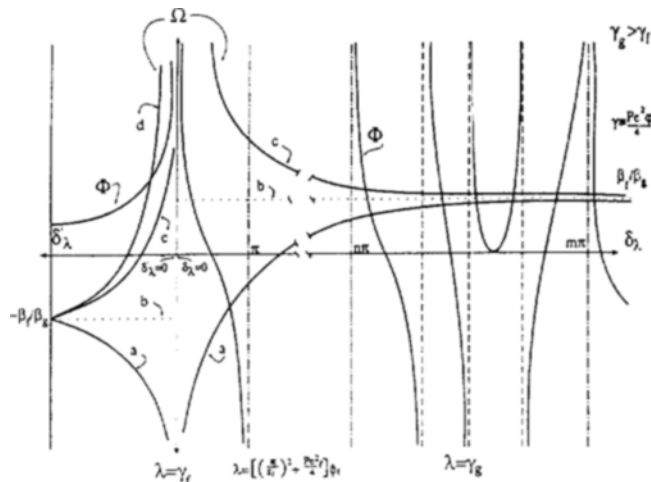
Fig. 5. Spectra for $\gamma_f < \gamma_g$.

$$\frac{Pe_f}{Pe_g} < \frac{\dfrac{2}{\theta_2}}{\left(\dfrac{1}{\theta_2^2} + \dfrac{1}{\phi_1}\right)} \tag{33}$$

example (a) in Fig. 4 results and the first eigenvalues are shifted to values greater than γ_f. Example (b) arises when

$$\frac{Pe_f}{Pe_g} = \frac{\dfrac{2}{\theta_2}}{\left(\dfrac{1}{\theta_2^2} + \dfrac{1}{\phi_1}\right)} \tag{34}$$

for no eigenvalue occurring between $\lambda = 0$ and $\lambda = \gamma_f$. A single eigenvalue will occur between $\lambda = 0$ and $\lambda = \gamma_f$ if in addition to

$$\frac{Pe_f}{Pe_g} > \frac{\dfrac{2}{\theta_2}}{\left(\dfrac{1}{\theta_2^2} + \dfrac{1}{\phi_1}\right)} \tag{35}$$

the following constant is also satisfied

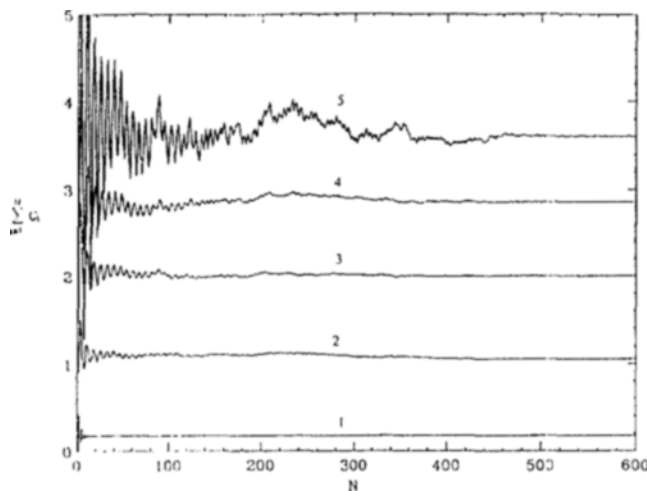Fig. 6. Spectral solution by eigenvalues when $Pe_f = Pe_g = 20.0$: (1) $Pe_f = Pe_g = 0$, $\beta = \phi = 0.5$; (2) $Pe_f = Pe_g = 1.0$; (3) $Pe_f = Pe_g = 5.0$; (4) $Pe_f = Pe_g = 10.0$; (5) $Pe_f = Pe_g = 20.0$.

$$[\Phi(\lambda = 0) - \Omega(\lambda = 0)] \ [\Phi(\lambda = \gamma - \varepsilon) - \Omega(\lambda = \gamma - \varepsilon)] < 0 \qquad (36)$$

where again ε is a small and positive number. One of the main advantages and purposes of analyzing the spectrum for this type of problem in such detail is to obtain information on the interaction between the various layers. As shown above the membrane or fluid layer can control the dynamics of the process depending upon the various parameter values. Numerical illustration will be presented in a section below showing the effects of the different parameter values on the behavior of the transient profiles whose qualitative features are predicted by the analysis of the spectral discussed in this section.

RESULTS AND DISCUSSION

1. Spectral Solution

A mathematical formulation is developed for the transient convective transport system. The solution of the model requires accurate calculation of eigenvalues. An efficient method to find appropriate eigenvalues is discussed in this section. The characteristic Eq. (26) is a nonlinear function. The solution to this equations is achieved by substituting different eigenfunctions in four different regions as shown in Table 1. The series solution oscillates significantly in the high Peclet region. They, however, converge for large Peclect numbers when the number of eigenvalues becomes large. For example, the transient solution oscillates less at eigenvalues of more than 600 when $Pe_f = Pe_g$ is equal to 20.0 as seen in Fig. 6. Fig. 6 shows the spectral results by Pe_f as the convective velocity in the fluid phase increases. Transient solution at large time becomes equal to the steady state solution. In order to reduce these difficulties, the transient solution is considered as a sum of two terms like Eq. (24), a transient term and a steady state term. The transient series rapidly converges because the exponential term, $\exp(-\lambda\tau)/\lambda$, of the transient series allows rapid damping, while the steady state term produces considerable oscillation and slowly converges with increasing λ. This steady state term given by the series expansion can be substituted with the steady state determined from the solution of the ordinary differential steady state equations. In the case of $Pe_f = Pe_x = 20.0$, the
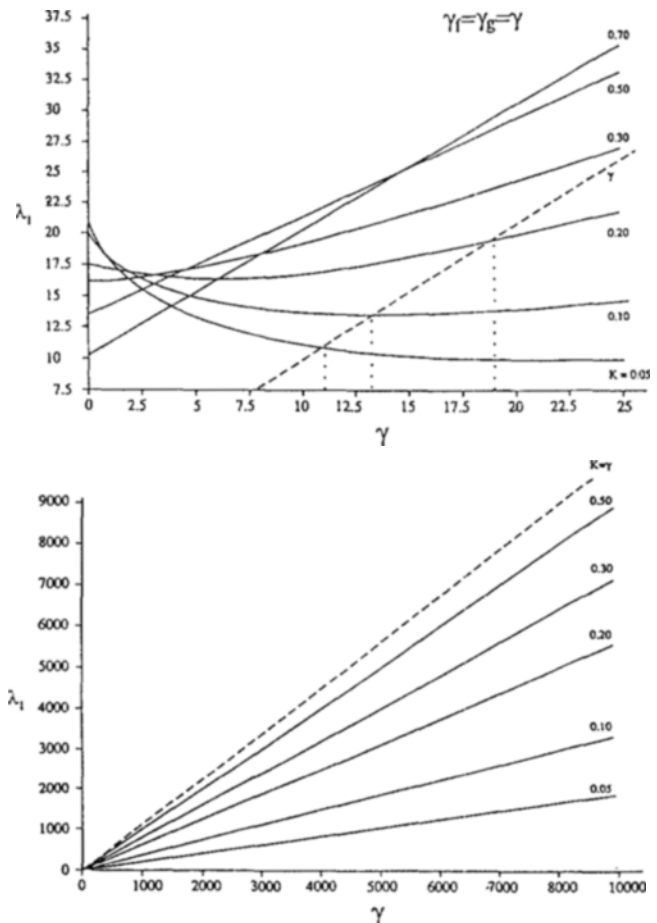

Fig. 7. First eigenvalue at different porosity.

transient series converged with 100 eigenvalues. The transient solution exactly corresponds to steady state solution at large dimensionless time.

This operator-theoretic technique gives straightforward and very elegant methodology to solve complicated nonlinear differential models without the complete numerical solution. This also leads to the analysis of the composite system for understanding and predicting the dynamic behavior of three layer composite systems. The model developed can be numerically illustrated with the application to convective transport in a membrane surrounded by two stagnant fluids. The five parameters, Pe_f, Pe_g, ϕ, β and a_1 can be reduced to four parameterts Pe_f/Pe_g, ϕ, β and a_1. The Peclet number contains the major control variable, i.e. the fluid flow rate. Here β is the membrane porosity, i.e. the accessible pore volume in the membrane phase for the solute of interest. Generally $0 < \beta < 1$ for membrane media. It is now possible to consider the three cases (1) $Pe_f = Pe_g$; (2) $Pe_f > Pe_g$; and (3) $Pe_f < Pe_g$.

The first case occurs when $u_g(V/L)_g/u_f(V/L)_f = D_g/D_f$ and will give rise to $\gamma_f = \gamma_g$. For Pe less than some critical value Pe_{crit} the first eigenvalue will be bounded by γ and $\gamma + (\pi/s_1)^2$. However, above this critical value given by the solution of Eq. (26), the upper limit of the first eigenvalue will be given by γ. The lower limit is zero. Fig. 7 shows the behavior of the first eigenvalue as a function of γ for various values of porosity, β. The eigenvalues are calculated by the solution of the characteristic equation. Increasing β increases λ for large values of γ, and thereby this
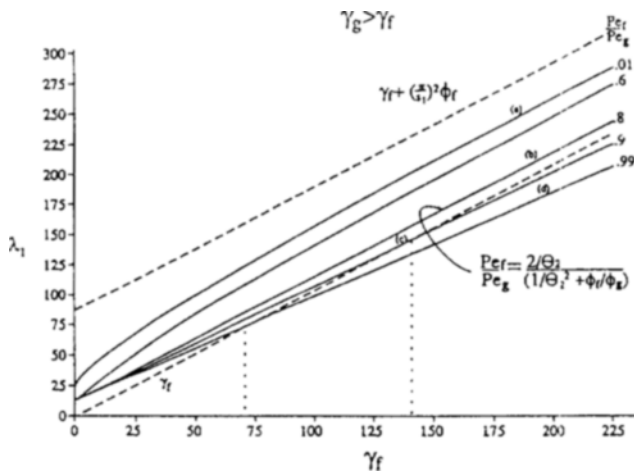
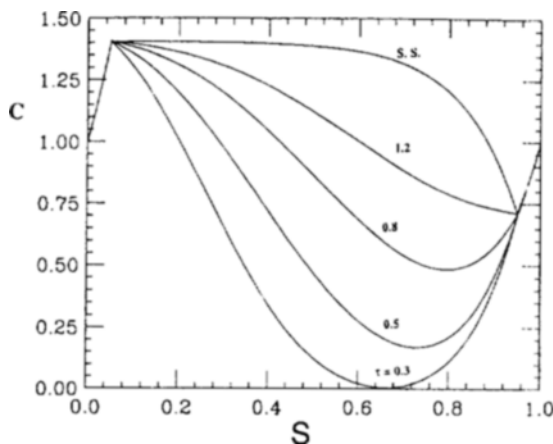Fig. 8. First eigenvalue as a function of $\gamma_f < \gamma_g$.

Fig. 10. Concentration profiles for $\gamma_f > \gamma_g$, $Pe_f = 3.0$, $Pe_g = 1.0$, $\beta = \phi = 0.5$.

Fig. 9. Concentration profiles for $\gamma_f < \gamma_g$, $Pe_f = 1.0$, $Pe_g = 3.0$, $\beta = \phi = 0.5$.

motion. Fig. 10 shows transient concentration profiles for the case with $\gamma_f > \gamma_g$. As the convection increases in both regions, the concentration in the membrane increases greatly. This implies a very fast dynamic since the eigenvalues are all shifted to larger values.

CONCLUSION

An operator theoretic method has been used to solve a transient and convective-diffusive problem in a composite membrane. A complete analysis of the spectrum associated with the convective transport operator of a membrane system has allowed for a full description of the effects of system parameters including diffusion coefficients, convective velocity, and membrane distribution coefficient, on the dynamics of the problem. The analysis has shown the power of the spectral analysis for understanding and predicting the dynamic behavior of a fairly complicated composite systems. The methodology is reliable, straight-forward and elegant. It allows an almost complete a priori characterization of the solution with minimal computation. Furthermore, the investigation has also illustrated the power of operator-theoretic methods over other numerical approaches to solve a vast class of problems of transport in fairly complicated domains. The only numerical work required in the solution of these problems is the solution of a non-linear algebraic equation (i.e. the characteristic equation) which can be easily accomplished by inexpensive computational routines. Furthermore, these calculations can be greatly guided by analyzing the characteristic equation. The study reported in the paper is useful to guide the analysis and the design of devices on laboratory and other scales required for a variety of membrane separations. Since the results of the study are highly analytical, they will also be of great importance to guide the design of experiments to obtain transport parameters in these applications.

increases the speed of the dynamics of the composite layered system. However, for the case of small values of γ the trend reverses. It is also interesting to note that in the region of small γ the first eigenvalue decreases with increasing γ for small values of β.

The case of $Pe_f < Pe_g$ gives rise to the only realistic possibility where $\gamma_f < \gamma_g$. The value of β plays a smaller role than in the last case, although it will certainly affect the actual value of λ_1 it has no affect on the bounds for λ_1. Regions (a), (b), (c) and (d) given in Fig. 8 correspond to those given in the spectra of Fig. 3. In regions (a) and (b) the upper bound is always given by $\gamma_f + (\pi/s_1)^2$ and the lower bound in γ_f. Case (b) represents a transition below which two different behavior occur. For γ_f below a critical value case (c) gives γ_f as the lower limit on the first eigenvalue, however above this critical value of γ_f the upper limit for the first eigenvalue becomes γ_f. Fig. 9 shows the transient concentration profiles of the membrane for $\gamma_g > \gamma_f$. The fluid region, as shown in this figure, reaches the steady-state sooner than the membrane phase. This clearly indicates the control of the dynamics of the composite system by the membrane.

The last case occurs when $Pe_f > Pe_g$. This occurs when $u_g(V/L)_g / u_f(V/L)_f > D_g/D_f$ i.e. when the ratio of the convective motion in the membrane to that in the fluid exceeds the ratio of diffusive
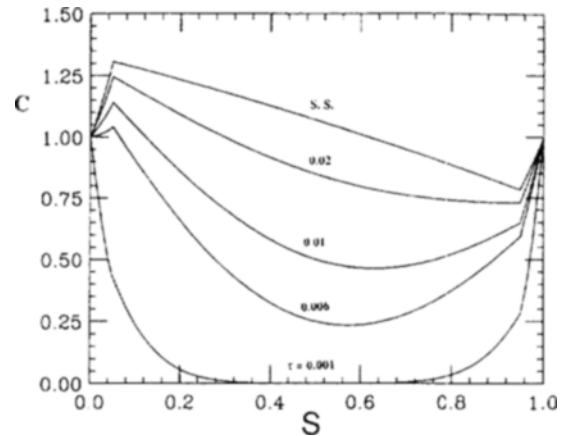
NOMENCLATURE

a   : cross sectional area
a_1 : thickness of the single isolated layer in Eq. (27)
c_i : solute concentration
C_i : dimensionless concentration of solute
D_k : diffusion coefficient of species
$D(L)$: domain of the differential operation L
f   : feed to external boundary region

F : volumetric flow rate into external boundary regions
H : direct-sum Hilbert space
k : layer of the composite membrane
L : total length of composite membrane
L* : differential operation defined in Eq. (17)
Pe : Peclet number
Pe_g : Peclet number in composite gel
Pe_f : Peclet number in buffer solution
q_k : functions defined after Eq. (17)
q_k' : functions defined after Eq. (18)
s_j : dimensionless term (x'/L) in membrane layer
t : time variable
u : convective velocity
w : element of the Hilbert space H
x : dimensional spacial coordinate
x_o : length of membrane

Greek Letters

ϕ : diffusivity ratio
β : porosity of the membrane
β_{eff} : effective distribution coefficient of solute
Φ : monotonic function of λ
Ω : transcendental function of λ
η : fundamental solutions to differential equation
τ' : dimensionless time in three layer problem
θ : non-dimensional parameter
λ : eigenvalue
κ : normalization factor of the eigenvector

Subscripts

f : feed to external boundary region
o : first layer of the composite media
<,> : composite inner product

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