Dynamic Motion of Polyelectrolyte in a Composite Membrane : I. Macroscopic Study

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막에서 전하고분자의 동적 현상
I : 거시적 연구

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Abstract: This papr studies the dynamic effects of polyelectrolyte in the multilayered membrane. It is found that electrophoretic convection in the fluid phase can be used to accelerate the speed of the polyelectrolyte. The model in the membrane separation is studied via interactions between fluid and solid phases. The spectra evaluation using the operator theoretic method is performed for the parametric studies of the physical properties in the membrane process. The findings of this paper shoould be useful in guiding the design of separation devices. This paper shows one example for macroscopic study the theoretical review paper of membrane transport.

요 약 : 이 논문은 막을 통한 전기적 여과시 동적이동현상을 연구하는데 있다. 액상에서의 전기적 대류는 막 내에서의 전하고분자 물질의 속도를 증진시키는데, 이 문제의 해법은 액상과 교상의 직접적인 접촉을 통해 연구 되었다. 연산자이론이 이 문제를 풀기 위해 적용되었고, 막에서의 물리적 변수들을 분석하는데 이용되었다. 이 논문의 이론적 고찰은 분리 조작 설계하는데 이용된다.

1. Introduction

The electrophoretic transport of polyelectrolyte in multiphase–layer system such as membrane has an important application in a wide range of separation and purification processes. Current interest has focused on the purification of polyelectorlytes such as proteins and polymer colloids. A mumber of theoretical, empirical approaches have been made to model the electrophoretic filtration and separation through

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membranes[1, 2]. Most of these separation processes have considered the transport of polyelectorlyte across the polymeric membrane. Although a number of studies have been devoted to the fundamental problems of membrane process, there have been few detailed predictions of intraconvective transport under an electric field. Intraconvective transport is of current interest in separation process. Opong and Zydney[3] have considered hydrodynamic model to determine the hindrance factors in ultrafiltration membrane. Lu and Rodrigues [4] have studied the effects of intraconvection on separation through mass balance of an inert tracer inside the membrane. Electrodialysis [5] employs fixed-charge membranes to extract pure water from a salt solution. The membranes are positioned at the top according to the ionic charge they allow to pass. The result is to separate pure water and salt solution by an electric field across a set of membranes. Most of theses membrane processes have considered the transport of solute across membrane or through continuous membranes of unvarying properties. Many mathematical models have not predicted the dynamic behaviour of polyelectrolyte inside the membrane. This paper is macroscopically to study the convective-diffusive transport in multilayered membranes in the presence of electric field. Physical properties including porosity, electrophoretic convection, and diffusion coefficient may vary simultaneously from layer to layer in the composite membrane. The purpose of this paper is to show how intraconvective transport of polyelectrolytes influences the filtration of membrane via interactions between bulk fluid of fluid phase and membrane of solid phase. The general model for electrophoretic filtration will be developed for a M-layered membrane process. The M-layered membranes may present an approximation of a matrix with continously varying properties or a system of stacked membranes. 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 munimum.

Furthermore, the three-laye problem retains the most relevant aspects of the steady state and dynamic behavior of the electrophoretic transport related to more complicated transient problems.

An operator theoretic approach is used to solve the molar species continuity equation [6]. the spectra evaluation using the transport differential operator will be performed to show the parametric studies of the physical properties on the concentration profiles of polyelectrolyte.

2. Theory

2. 1. General Formulation for M-layered Membrane

The general species continuity equation for species "i" in a homogeneous medium "m" subject only to an electrical force and molecular diffusion can be given [7] by

$$\frac{\partial c_{i,m}}{\partial t} = \nabla \cdot (D_{i,m} \nabla c_{i,m}) - \nabla \cdot (c_{i,m} \mathbf{F} u_{i,m} z_{i,m} \nabla \Psi_m)$$

$$(1)$$

The species molar concentration, electrophoretic mobility, and diffusion coefficient in the membrane layer are given respectively by $c_{i,m}$, $u_{i,m}$, and $D_{i,m}$. $\mathbf{F}$ is the Faraday constant. Ψ is the electrostatic potential and z is the valence of polyelectrolyte. A schematic of the M-layered membrane system is shown in figure 1. The subscript m indicates the mth region of the composite membrane layer. The electric field in general is given by the solution of the Poisson's equation. Electrolyte concentration of bulk fluid is assumed to be diluted in order to neglect molecular adsorption effect. If electroneutrality in each membrane layer is assumed and if it is assumed that the diffusion coefficients are independent of concentration, multiplication of equation (1) by $\mathbf{F} z_i$ and summing over all species [8] at steady state leads to

$$\mathbf{F} \nabla^2 (\sum_{j=1}^{N} D_{i,m} c_{i,m} z_{i,m}) = + \nabla (\sum_{j=1}^{N} c_{i,m} \mathbf{F}^2 u_{i,m} z_{i,m}^2 \nabla \Psi_m)$$

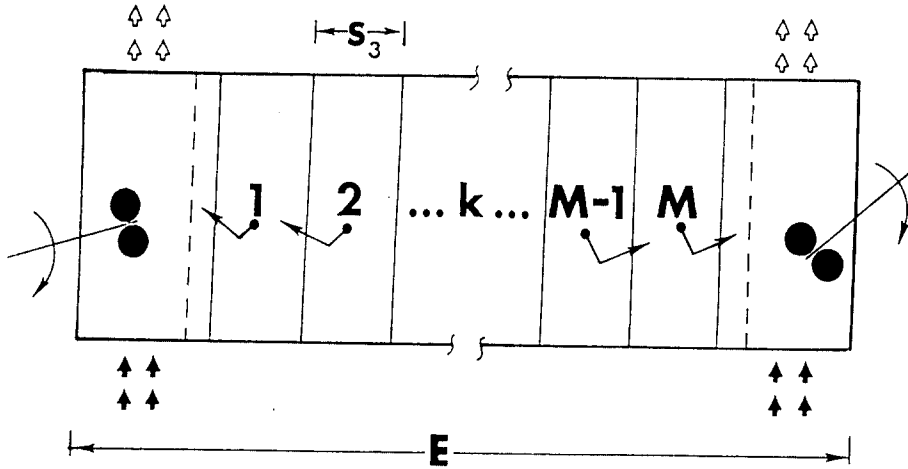$$(2)$$

If a single species, denoted by subscript s of a

Fig. 1. Schematic picture in a M-layered membrane.

polyelectrolyte with a small diffusion coefficient, the left hand side of equation (2) becomes zero by electroneutrality as

$$D_l[\sum_{j=1}^{N} c_{l,m}z_{l,m} + \frac{D_{s,m}}{D_l}c_{s,m}z_{s,m}] \cong D_l\sum_{j=1,s}^{N} c_{l,m}z_{l,m} \cong 0. \quad (3)$$

Thus, integration of equation (2) leads to the Ohm's law[7]

$$\nabla\Psi = \frac{I}{\sum_{l=1}^{N} c_l u_l z_l^2 \mathbf{F}^2} = \frac{I}{\Omega} = (\frac{V}{d}) \quad (4)$$

where I is the current, Ω is the electrical resistance, V is the electrical field and d is the length of each membrane layer. Note that this equation implies that although the field gradient is constant within specific layer, it may differ from layer to layer. The species equation, after removing subscript "s" for convenience, and assuming one-dimensional transport in membrane process, is

$$\frac{\partial c_m}{\partial t} = -u_m(\frac{V}{L})_m\frac{\partial c_m}{\partial x} + D_m\frac{\partial^2 c_m}{\partial x^2} \quad (5)$$

In the model formulation each layer is assumed to be a different phase, and therefore flux and equilibuium boundary conditions are required at the M-1 interfaces. The total fluxes at the internal bound-

aries between each composite membrane must be equal and are given by

$$-D_{m+1}\frac{\partial c_{m+1}}{\partial x'} + c_{m+1}u_{m+1}(\frac{V}{L})_{m+1} = -D_m\frac{\partial c_m}{\partial x'} + c_m u_m(\frac{V}{L})_m$$
$$\quad (6)$$

at $x'=x'_m$; $m=1,2,3,\cdots,M-1$

The distribution coefficent of species, β, gives the linear phase equilibrium

$$\beta_{m+1}C_{m+1} = \beta_m c_m \quad (7)$$
$$\text{at } x'=x'_m \text{ ; } m=1,2,3,\cdots,M-1$$

Boundary conditions at the external boundaries, i. e. at $x'=L$ must also be supplemented to the above set of internal boundary conditions. For the case of a fixed concentration in the outer regions these conditions are

$$\beta_1 c_1 = \beta_0 c_0 \qquad \text{at } x'=0 \quad (8)$$

$$\beta_M c_M = \beta_L c_L \qquad \text{at } x'=L \quad (9)$$

For polyelectrolytes in porous media these distribution coefficients represent the fractional pore available to polyelectrolyte.

Equation (5) is commonly used when the polyelectrolyte of interest does not contribute to the electrical current. This again assumes low concentration, small diffusion coefficient, and low electrophoretic mobility for the polyelectrolyte of interest.

As the concentration increases the polyelectrolyte of interest will begin to contribute to the electrical current and the dilute solution assumption will no longer hold. Under these circumstances it would be necessary to solve the Poisson equation simultaneously with equation(1) for all the electrolyte species concentrations. This is a highly non-linear problem. One important consideration of the M-layered model considered as shown in Figure 1 is the possibility that the field per unit length$(V/L)_m$ can vary from region to region in an arbitrary fashion. Thus a non-linear field variation can be imposed without altering the solution methodology.

Equation(5) is analogous to the standard convective-diffusion equation with the convective term given by the electrophoretic mobility multiplied by the electrical field per unit length. The nondimensional form of the differential equations in (5) and boundary conditions (6), (7), (8) and (9) are given below. The dimensionless variables are

$$\tau \equiv \frac{tD_o}{x_o^2}, \ Pe_m \equiv \frac{u_m(\frac{V}{L})_m x_o}{D_m}$$

$$\phi_m \equiv \frac{D_m}{D_o}, \ s \equiv \frac{x'}{L}, \ C'_m \equiv \frac{\beta_m c_m}{\beta_o c_c} \qquad (10)$$

and the transformation variable is $C_m = C'_m \exp(-Pe_m s/2)$

The differential equation (5) and boundary conditions can be written as

$$\frac{\partial C_m}{\partial \tau} = \phi_m \left[\frac{\partial^2 C_m}{\partial s^2} - \frac{Pe^2_m C_m}{4} \right] \qquad (11)$$

and $C_o(0) = C_o$ at $s=0$, $C_m(1) = C_L \exp(-Pe_M/2)$ at $s=1$

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

$$\left[-\frac{\partial C_{m+1}}{\partial s} + Pe_{m+1} \frac{C_{m+1}(s_m)}{2} \right]$$

$C_m(s_m)r_m(s_m) = C_{m+1}(s_m) \ r_{m+1}(s_m)$ at $s=s_m$; $m=1, 2, 3, \cdots, M-1$

where $r_m(s_m) = \exp(Pe_m s_m/2)$. Illustrations of the effects of the parameters on the solution concentration profiles will be discussed in order to descibe the

dynamics of the polyelectrolyte accumulation in the system.

Several physical parameters such as the Peclet number-the relative ratio of convective electrophoretic transport to diffusive transport, ϕ-the relative ratio of diffusion coefficients, and β_m-the equilibrium distribution coefficients are included in the model given by equation(7). The model can accurately describe variations from layer to layer in the system. For example, a variation in β represents a pore gradient type transport where the pore space available for a particular molecule varies from layer to layer ; and a variation in Pe(i. e. the ratio of electrophoretic convective motion to diffusive transport) will occur if the mobility changes from layer to layer.

2. 2. Solution Methodology

When M-layered membrane has a uniform stagnant boundary layer, the membrane is bounded by two stagnant boundary layer regions of the fluid phase. The formal solution to the transient problem can be constructed from equation (5) and the initial-boundary value problem reduces to

$$-\frac{\partial U}{\partial \tau} = L U + R_k I \ ; \ k=1, 2, \cdots, M \qquad (12)$$

where

$$\mathbf{L} = \begin{bmatrix} L & & & 0 \\ & \cdot & & \\ & & L_k & \\ & & & \cdot \\ 0 & & & L_M \end{bmatrix}, \ \mathbf{U} = \begin{bmatrix} u_1 \\ \cdot \\ u_k \\ \cdot \\ u_M \end{bmatrix},$$

$$L_k \equiv -\phi_k \left(\frac{d^2}{ds^2} - \frac{Pe_k^2}{4} \right) \ ; \ k=2, 3, \cdots, M-1$$

$\mathbf{I}$ is a unit matrix. L_k are M differential operations in each membrane layer and R_k can be obtained from self-adjoint boundary conditions. The solution to the transient problem is solved using operator theoretic method [6]. The solution associated with this differential operation is explained in appendix I. In the transient analysis for three-layered membrane, we assume to have the same thickness of boundary

layers in the upper and lower regions, i. e., $s_1 = 1 - s_2$. Transient solution is written as

$$C_k(x, \tau) = \sum_{i=1}^{\infty} u(s, \lambda_i) \exp(-\lambda_i \tau)$$

$$[<C(\tau=0), u_i> + \int_0^\tau R_{ki} \exp(\lambda_i \tau) d\tau] \qquad (13)$$

The inner product $<, >$ in equation (13) is given in Appendix I. Equation (13) can be separated by the exponential term and the steady state term as

$$C_k(x, t) = C_k^{ss}(x) + C_k^{tr}(x, t) \ ; \ k = 1, 2, 3 \qquad (14)$$

where

$$C_k^{tr}(x, \tau) = \sum_{i=1}^{\infty} u_i(x, \lambda_i) \exp(-\lambda_i \tau)$$

$$[-\int_0^\tau R_{ki} \exp(\lambda_i \tau) d\tau] \qquad (15)$$

The steady solution is analytically calculated from ordinary differential equation of equations (11) instead of using the spectral steady state solution.

3. Result and Discussion

A complete analysis of the multi-layered membrane in the transient state, and a full description of the effects of system parameters including diffusion coefficient, electrophoretic convective velocity, and porosity, on the dynamic problem is discussed in this section. Diffusion and electrophoretic convection are assumed to govern the transport in both fluid and solid phases. Hydrodynamic convection is neglected in order to give a representation of what would be occuring in the stagnant boundary layer of membrane in the fluid phase. The electrical field is assumed to be the same in the membrane as in the fluid phase of boundary regions because the current carrying ions can readily penetrate the membrane. Concentration profiles in the membrane and in the boundary layer around the membrane can be calculated from the solution of the model equations (11). In the model equations, the dimensionless Peclet number is the major control variable of the electrophoretic convection and diffusion in each membrane layer. Electrophoretic convective-diffu-

sive transport in the membrane can be analyzed through two different Peclet numbers in the fluid phase(Pe_f ; $Pe_1 = Pe_M$) of bulk fluid and solid phase (Pe_g ; $Pe_2 =, \cdots, = Pe_{M-1}$) of membrane. Transient concentration profiles in the membrane and in the boundary layer surrounding membrane are associated with the electrophoretic convective fluid velocity. Figure 3 shows several of these concentration profiles at different Peclet numbers when M is equal to three. At small peclet number in the fluid phase(Pe_f), the transport of poly-electrolyte is governed primarily by diffusive transport, thus the concentrations of polyelectrolyte on the two boundary regions of the membrane become nearly equal as seen in Figure 2(a).

If Pe_f is greater than Peclet number in the membrane (Pe_g), the ratio of the convective transport in the membrane to that in the boundary layer exceeds the ratio of diffusive transport. The electrophoretic convective transport may be influenced in porous membrane than the diffusive transport driven by concentration gradient. When an electric field is applied, polyelectrolyte will transport from the bulk fluid into and through the membrane. The flux of polyelectrolyte that is transported to the pores of the membrane from the fluid phase must equal the flux transported through the membrane. Figures 2 (b)-(d) show that the concentration gradients are seen to get steeper as the electric field is increased. It is necessary for the concentration profiles in the interphase region of membrane to increase in order to maintain equal fluxes in the membrane and fluid phases. The transient rate to approach at steady state in the membrane is significantly reduced as polyelectrolyte penetrates farther than $x = s_1$. This concentration increase may depend on both the magnitude of Pe_f induced by the electric field and on the size of the polyelectrolyte. The increase of concentrations in the interphase region between solid and fluid phases is related to a very fast dynamic speed to approach to the steady state. The dynamics in the membrane process can be related to the dynamics of the individual layer problems of
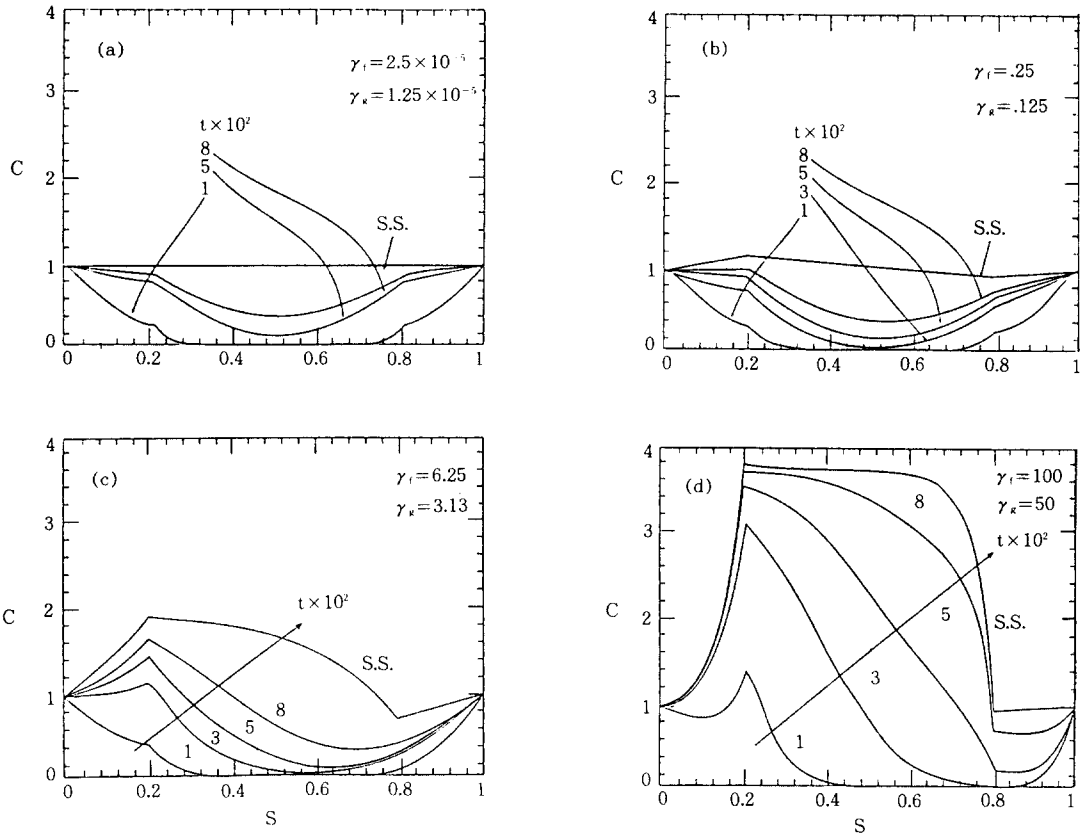
Fig. 2. Transient concentration profiles when $\gamma_i \geq \gamma_R$.

M-layered membrane. The convection effects for dynamic behavior of polyelectrolytes need to be considered from the structures of the spectra of characteristic equation (19). It can be mathematically recognized through the position of the eigenvalues by the asymptotic vertical lines of characteristic equation. Convection effects in three-layered membrane can be strongly varied by the physical parameters of each layer. This can be applied to study mass transport of M-layered composite membrane in steady state.

Convection effect in M-layered membrane is enhanced due to interations between layers. As Peclet number of each membrane layer gradually increases to the x-direction of electric field, concentrations of each layer increase linearly due to faster electrophoretic convection of each layer as seen in Figure

3(a). When Peclet number of every layer equally increase, concentrations can be significantly increased by stacked effects of multilayer as polyelectrolyte penetrates from layer to layer. This indicaties that electrophoretic convection in each layer can be accelerated by different physical properties such as membrane porosity and diffusion ratio in each layer. Figure 3 shows that concentration profile at fifth layer of six-layer membrane is significantly increased with electric field. Electrophoretic acceleration of polyelectrolyte in each layer is also related to number of layer. Figure 3(b) shows that as the number of membrane layer increases step by step from M=3 to M=10, concentrations significantly increases in multier membrane layer as membrane porosity β gradually increase from layer to layer. Concentration(M-1)th layer membrane can
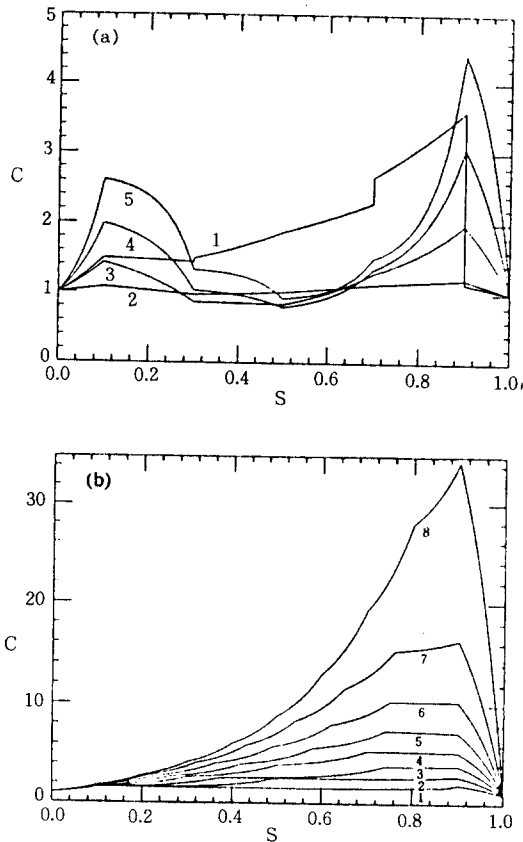
Fig. 3. Concentration profiles in M-layered membrane(M=6).

(a) 1 : $Pe_1=5.$, $Pe_2=6.$, $Pe_3=7.$, $Pe_4=8.$, $Pe_5=9.$, $Pe_6=5.$ at $\beta_1=1.$, $\beta_2=0.1$, $\beta_3=0.2$, $\beta_4=0.3$, $\beta_5=0.1$, $\beta_6=1$. and $\phi_k=0.5$; 2 : $Pe_k=1.$; 3 : $Pe_k=5.$; 4 : $Pe_k=10.$; 5 : $Pe_k=15$, where k=1, 2, ⋯6.

(b) 1 : M = 3 ; 2 : M = 4 ; 3 : M = 5 ; M : = 6 ; 5 : M=7 ; 6 : M=8 ; 7 : M=9 ; 8 : M=10

be unexpectedly increased with electric field by controlling membrane porosity β and diffusion coefficient's ratio ϕ of each layer. This Kind of structual composite membrane can be sufficiently designed, the separation of polyelectrolye can be enhanced by the controls of physical properties as well as number of membrane layer affecting intramembrane transport.

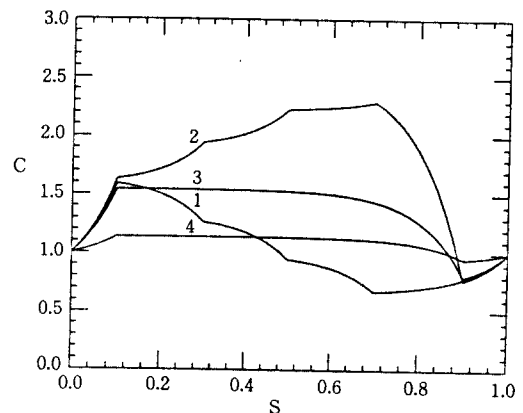In case of $Pe_R/Pe_f \gg 1$, small value of Pe_f does

Fig. 4. Transient concentration profiles when $\gamma_f < \gamma_R$, $\gamma_f=0.25$ and $\gamma_R=100$.

not affect the transient concentration profile inside membrane even when Pe_R varies over a wider range. It is obvious that the electrophoretic convection in the fluid phase plays an important role in affecting the increase of concentration profile inside the membrane. The dynamic speed of polyelectrolyte in the membrane is significantly reduced in case of $Pe_R/Pe_f \gg 1$ as seen in Figure 3. But transient rate of polyelectrolyte increases in the lower boundary region of fluid phase. Polyelectrolyte reaches the steady-state sooner than the membrane. At low electric field, polyelectrolyte retains a globular shape and relative ratio of mobility ideally approach 1/3 in the polymeric gel[9]. But diffusion coefficient in the membrane is greatly smaller than that on free solution. This indicates that Pe_R/Pe_f can be practically much greater than 1 in only low electric field. Higher value of Pe_R can be considered by slower diffusive transport and/or faster convective transport. In this case, the total flux of equation (6) increases in the membrane. High total flux of polyelectrolyte in the membrane affects fast convective velocity in the lower boundary layer region. This observation is a result of equal flux boundary condition in the lower interphase boundary region of fluid phase. This is caused by convection effect in the membrane. From results of Figures 2-4, the build-up of concentration in the membrane is
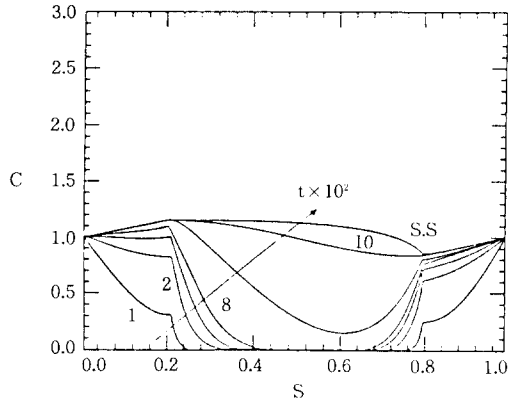
Fig. 5. Porosity effect in M-layered membrane.
1. $\beta_1=1., \beta_2=0.5, \beta_3=0.4, \beta_4=0.3, \beta_5=0.2,$
   $\beta_6=1.$ and $\phi_k=0.5, Pe_k=10.$
2. $\beta_1=1., \beta_2=0.5, \beta_3=0.6, \beta_4=0.7, \beta_5=0.8,$
   $\beta_6=1.$ and $\phi_k=0.5, Pe_k=10.$
3. $\beta_1=1., \beta_5=0.9, \beta_6=1.$ and $\phi_k=0.5, Pe_k=10.$
4. $\beta_1=1., \beta_2=0.5, \beta_6=1.$ and $\phi_k=0.5, Pe_k=10.$

strongly dependent on electric field in the fluid phase as well as convection in the membrane. In order to enhance electrophoretic convection of polyelectrolyte in the membrane, several factors such as the size of polyelectrolyte, the concentration of electrolyte, pH and pore size must be considered.

For example, reduction of polyelectrolyte-to-pore size ratio or dilution of electrolyte concentration must be checked.

The effect of membrane porosity of dynamic speed is closely related to the electrophoretic intra-particle transport. Figure 5 shows how the concentration profiles significantly vary with porosity in the presence of electrophoretic convection. In the case of $Pe_K/Pe_f \gg 1$, polyelectrolyte moves fastly through larger porous membrane with electric field. Transient concentration in the membrane is significantly lower and flatter in large porous membrane. In M-layered membrane, the concentration in each layer can be significantly changed by different membrane porosity in each layer. As porosity of each layer increases gradually in the M-layered membrane, the polyelectrolyte moves faster from layer to layer. Concentration of each layer gradually increases due to faster convection as shown in Figure 5. But in the reverse case of Figure 5, concentration significantly increases with larger porosity in comparison when membrane porosity has constant value in any membrane layer. Polyelectrolyte in each layer is stacked due to smaller porosity of each layer. Also when porosity in each membrane layer is irregularly changed, concentration profiles

Table 1. Steady State Solution of M-layered Membrane

$$C_m = a_m \exp\left(\frac{Pe_m s}{2}\right) + b_m \exp\left(-\frac{Pe_m s}{2}\right)$$

$$a_m = \alpha_m + N y_m \; ; \; m=2, 3, 4, \cdots\cdots, M \text{ and } \alpha_1 = 1$$

$$b_1 \kappa_1 = b_2 \kappa_2 = \cdots\cdots = b_m \kappa_m = N$$

$$\kappa_m = \phi_m Pe_m / \beta_m$$

$$N = \frac{\beta_1 \exp(-Pe_M) - \alpha_M}{\beta_2 \exp(-Pe_M) - \delta_M}$$

$$y_1 = \frac{1}{\kappa_1} + \frac{\beta_0 q_0}{p_0}$$

$$p_0 = \frac{x'^2_L}{D_0}, \quad p_L = \frac{x'^2_L}{D_0}, \quad q_0 = \frac{a_1 x'_L}{D_0}, \quad q_L = \frac{a_1 x'_L}{D_0}$$

$$\alpha_m = \alpha_1 \exp\left[\sum_{i=1}^{m-1} (Pe_i - Pe_{i+1}) s_i\right] \; ; \; m=2, 3, \cdots\cdots, M$$

$$y_m = y_1 \exp\left[\sum_{i=1}^{m-1} (Pe_i - Pe_{i+1}) s_i\right] - \left[\sum_{i=1}^{m-1} \left(\frac{1}{\kappa_i} - \frac{1}{\kappa_{i+1}}\right) \exp\left(\sum_{i=1}^{m-1} Pe_i - Pe_{i+1}) s_k\right) \exp(-Pe_i s_i)\right] \; ; \; m=2, 3, \cdots\cdots, M$$

have optimal profiles as seen in Figure 3(a). The variation of porosity in composite membrane plays an important role to enhance concentrations. This may be utilized to design the membrane device for ele-trophoretic separation.

4. Conclusion

A complete analysis of the multi-layered membrane in the transient state, and a full description of the effects of system parameters including diffusion coefficient, electrophoretic convection velocity, and porosity, on the dynamic problem has been presented. The methodology is complete *a priori* characterization of the solution with minimal computations. Furthermore, these calculations can be greatly guided for dynamic effect of membrane transport. The advantge of the intraconvection is to make possible the acceleration of the speed of polyelectrolyte in the separation process. The speed of polyelectrolyte in the membrane can be controlled by the electrophoretic fluid velocity in the external space of the separation system. Transport in M-layered membrane can be significantly varied by continuously varying properties of each layer. Convection effect in multilayer membrane is found to be enhanced by different physical properties of each layer as polyelectro-lyte penetrates from layer to layer. The variation of permeate fluxes with membrane is much more influenced by membrane porosity. Therfore, the diffusion and electrophoretic convection of polyelec-trolyte into and out of pores of membrane can be determined for efficient separation. This separation is a function of the ratio of Pe_f /Pe_k. The study in this paper is useful in guiding the analysis and the design of devices on laboratory and other scales required for a variety of separations.

Nomenclatures

A_k, B_k Integration constants
$c.$ Species molar concentration

C_k Dimensionless species concentration
d Length of membrane layer
D_k Species diffusion coefficient
D_l Diffusion coefficient of electrolyte
D_s Diffusion coefficient of polyelectrolyte
$D(L)$ Domain of the differential operation L
F Faraday constant
H Direct-sum Hilbert space
I Electric current
$\mathbf{I}$ Unit matrix
k Layer of the composite media
L Total length of M-composite membrane layers
$\mathbf{L}$ Matrix form defined in equation(12)
L_k M differential operations in each membrane
M Layer number of multilayer membrane
Pe_k Peclet number
R_k Expression defined by equation(18)
s_i Dimensionless length of each layer
U Matrix form defined in equation(12)
V Electric field
x' Dimensional spacial coordinate
x Dimensionless spacial coordinate
z Valence of polyelectrolyte

Greek Symbols

ϕ Relative ratio of diffusion coeffients(D_m/D_o)
β Porosity of the membrane
γ_k Variable defined in equation(17)
τ Dimensionless time in three layer problem
λ Eigenvalue
κ Normalization factor of the eigenvector
ψ Electrostatic potential
Ω Electric resistence
$<, >$ Composite inner product

Subscripts

k, m Layer of the membrane
o Upper boundary layer of membrane
L Lower boundary layer of membrane
M Total number of membrane layers

References

1. D. Rodbard and A. Chrambach, *Analytical Bio-chemistry*, **40**, 95(1971).

2. D. A. Saville and O. A. Paulusinski, *AIChE Journal*, **32**, 207(1986).

3. W. S. Opong and A. L. Zydney, *AIChE Journal*, **37**, 1497(1991).

4. Z. Lu and A. Rodrigus, *AIChE Journal*, **38**, 416 (1992).

5. W. C. McGregor, Membrane Separations in Biotechnology, Marcel Dekker, Inc., New York (1986).

6. D. Ramkrishina and N. R. Amundson, Linear Operator Methods in Chemical Engineering with Applications to Transport and Chemical Reaction Sys-tems, Prentice–Hall, Englewood Cliffs(1985).

7. J. Newman, Electrochemical Systems, Prentice Hall, Englewood Cliffs(1973).

8. Y. Park and H. Lim, *Mathl. Comput. Modelling*, in press(1993).

9. G. W. Slater and J. Noolandi, *Biopolymer*, **28**, 1781(1989).

Appendix I

The M differential operations in each membrane layer are defined from equation(11) by

$$L_k \equiv -\phi_k \left(\frac{d^2}{ds^2} - \frac{Pe_k^2}{4} \right) \quad \text{where } k = 1, 2, 3, \cdots, M.$$

The domain associated with this differential operation is given by

$$D(L) \equiv \{ w \in H \text{ and } Lw \in H : u_1(0) = 0 ;$$

$$u_{k+1}(s_k) r_{k+1}(s_k) ;$$

$$\frac{\beta_k \phi_{k+1}}{\beta_{k+1} \phi_k} \left(\frac{d u_{k+1}}{ds} - Pe_{k+1} \frac{u_{k+1}}{2} \right) r_{k+1}(s_k)$$

$$= \left(\frac{d u_k}{ds} - Pe_k \frac{u_k}{2} \right) r_k(s_k) ;$$

$$k = 1, 2, 3, \cdots, M-1 ; u_M(1) = 0 \}$$

The composite differential operator defined in the Hilbert space, *H*, is given by $L = \{L, D(L)\}$. *H* is a direct sum of Hilbert spaces defined as

$$\mathbf{H} \equiv \oplus \sum_{k=1}^{M} \boldsymbol{H}_k$$

with inner product of the form

$$< w_1, w_2 > \equiv \sum_{j=1}^{M} \delta_j (u_1, u_2)_j \qquad (16)$$

In the above equation $u_i = \{u_j\}$, $j = 1, 2$ are vectors in each Hilbert space, the δ's given by

$$\delta_{k+1} = \delta_k \left(\frac{r_{k+1}(s_k)}{r_k(s_k)} \right)^2 \frac{\beta_k}{\beta_{k+1}}, \quad k = 1, 2, \cdots, M-1$$

with $\delta_1 = 1$ and $\delta_j > 0$ for all $j = 2, 3, 4, \cdots, n$.

The eigenvalue problem associated with the operator **L** is given by $LU = \lambda U$. The above equation yields

$$\frac{d^2 u_k}{dx^2} + Q^2_k(\lambda) u_k = 0$$

where

$$Q_k = \sqrt{\lambda - \gamma_k}, \quad \gamma_k = \phi_k \frac{Pe_k}{4} \qquad (17)$$

Eigenfunctions of **L** that belong to different eigenvalues are orthogonal each other. The general solution of equation(16) can be written as

$$u_k = \kappa \{ A_k \zeta_k(Q_k, x) + B_k \zeta_k(Q_k, x) \}$$

where $\zeta_k(Q_k, x)$ and $\zeta_k(Q_k, x)$ are either trigonometric function(when the arguments are real) to hyperbolic function(when the arguments are imaginary). With no loss of generality, we can take $\zeta_k(Q_k, x) = \sin(Q_k \omega_k)$ and $\zeta_k(Q_k, x) = \cos(Q_k \omega_k)$. u_k are eigenfunctions in the fluid phase when $k = 1, M$, while u_k are eigenfunction in the solid phase when $k = 2, 3, \cdots, M-1$. the value of κ can be calculated by normalizing the eigenfunctions in *H*. The coefficient 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 $D(L)$.

For the particular case a single membrane surrounded by two equal sized stagnant fluid layers is considered, in equation(12) given by $M=3$, $\omega_k=s_1$, $\phi_k=1$, $Pe_k=Pe_f$ for $k=1$, and $\omega_k=s_2-s_1$, $\phi_k=\phi_1$, $Pe_k=Pe_g$ for $k=2$, $\omega_k=1-s_2$, $\phi_k=1$, $Pe_k=Pe_f$ for $k=3$. And R_k in equation(12) is given for $M=3$ by

$$R_k=Q_1[1+\exp[Pe_g-Pe_f)(s_1-s_2)](A_3)\exp(-Pe_f)$$

(18)

The eigenvalues for equation(17) are obtained from the characteristic equation yielded by the transport operator $\mathbf{L}$ as

$$\beta\phi\left(\frac{Pe_f}{Pe_g}\left[Q^2_2+\frac{Pe^2_g}{4}(1-\frac{1}{\beta\phi})\right]^2=\frac{Q_1}{\tan(Q_1s_1)}\right.$$

$$\left[\frac{Pe_gQ_1}{Pe_f\beta\phi\tan(Q_1s_1)}+\frac{2Q_2}{\tan\{Q_2(s_2-s_1)\}}\right]$$

(19)

Each cotangent function of equation(19) has a group of asymptotic vertical lines. These vertical lines play an important role in the calculation of eigenvalues of the composite operator $\mathbf{L}$ since they are bounds between which the eigenvalues of the composite operator $\mathbf{L}$ are located. The asymptotic vertical lines are indicated as $F=(n\pi/s_1)^2+Pe_f^2/4$ and $S_k=(n\pi/s_{k+1}-s_k)^2\phi+Pe_g^2/4$. The bisection numerical method is used to calculate the eigenvalues and the asymptotic lines, between which is defined the range over which to search for roots. There are either one or two roots in each region bounded by consecutive asymptotic lines.