Influence of Nernst-Planck Diffusion on Hollow-Fiber Mass-Transfer Processes

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Hollow-fiber membrane reactive extraction and facilitated supported liquid membrane processes for the separation of charged species are analyzed theoretically. A mathematical model incorporating laminar flow, Nernst-Planck diffusion, buffer effect, ion strength, interfacial reaction kinetics and/or equilibria, diffusivity of species in the membrane phase, shell resistances, and shell concentration is developed and solved numerically. When the lumen mass-transfer resistance is dominant, the predicted removal rate of a single ion or the separation rate of a mixture of ions by a simplified model with Fickian diffusion deviates greatly from the prediction with the present model. For instance, when the concentration of trivalent ions in the feed decreases to half of its initial value, the membrane length calculated using Fickian diffusion is 75% higher than the length predicted by Nernst-Planck diffusion. Thus, the Leveque equation based on Fick's law does not adequately describe the mass transfer of the charged species in the lumen feed. The effect of buffer ions and diffusivity of species in the membrane phase on the mass transfer of the species is also discussed.

Introduction

Microporous hollow-fiber membranes have been increasingly used for liquid-liquid extraction in recent years. The advantages of membrane extraction (ME) include high throughput capacity, independence of phase densities and interfacial tension, no flooding or entrainment, high mass-transfer areas, and the possibility to operate at extreme phase ratios. Furthermore, membrane processes can be carried out in a single apparatus incorporating extraction of the species of interest from a solution into an immiscible phase impregnated within the porous membrane wall and its stripping to another solution. This process is known as supported liquid membrane (SLM) separation.

Various mathematical models have been proposed to describe the mass-transfer rate in ME and SLM processes. In many cases, a plug flow through the hollow-fiber lumen has been assumed and the mass transfer rate has been described by the use of an overall permeability coefficient (Alexander and Callahan, 1987; Haan et al., 1989; Yun et al., 1993; Guha et al., 1994; Yang et al., 1996; Ortiz et al., 1996; Daiminger et al., 1996). A more accurate approach for the modeling of hollow-fiber separations considers the steady laminar flow and radial Fickian diffusion for the species of interest in the lumen. Analytical and numerical methods have been used to study the problem of linear or nonlinear boundary conditions for hollow fiber ME or SLM processes (Yoshizuka et al., 1986; Kim and Stroeve, 1988, 1989a,b, 1990; Alonso et al., 1994; Kubota et al., 1995; Yi and Tavlarides, 1995; Alam et al., 1996; Alonso and Pantelides, 1996; Qin et al., 1996; Qin and Cabral, 1996, 1997, 1998).

In many ME or SLM processes, more than two charged species may exist in the feed. For example, when metal cations are extracted by a carrier in the organic phase, counter ions (usually H^+) and couple ions (usually Cl^- or SO_4^{2-}) exist in the feed in addition. When organic acid anions are extracted by a carrier in the organic phase, counter ions (usually Cl^-) and couple ions (usually Na^+) are also present. Other ions may also be present when a buffer (usually NaAc/HAc) and/or inert salts (usually Na^+ and SO_4^{2-}) are used. In these cases, the Nernst-Planck diffusion should be used instead of the Fickian diffusion to describe the radial flux of species in the fiber lumen (Qin et al., 1996; Qin and Cabral, 1996).

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However, most researchers have used the Fickian diffusion in establishing the mass conservation equation and the associated boundary conditions. Although the Leveque equation and Skelland's solution of Graetz's problem, strictly valid for the case where Fick's law is sound, have been used to describe the lumen mass-transfer coefficient where more than two ions exist in the lumen phase (Alexander and Callahan, 1987; Haan et al., 1989; Yun et al., 1993; Guha et al., 1994; Yang et al., 1996; Daiminger et al., 1996), their validity has never been theoretically analyzed. In some theoretical models, the influence of the diffusion of couple ions on the transport of the species of interest is neglected (Haan et al., 1989; Alonso et al., 1994; Yi and Tavlarides, 1995). However, experimental data demonstrated that the hydrogen ion transfer resistance in the feed phase can be a significant retarding factor on metal permeation under some experimental conditions (Youn et al., 1995).

When a complex is formed between an ion and more than one carrier molecule, the diffusion coefficient of the complex in the organic phase is usually lower than that of the free carrier (Yoshizuka et al., 1986; Haan et al., 1989; Kubota et al., 1995; Youn et al., 1995; Yang et al., 1996; Daiminger et al., 1996). Thus the total concentration of the carrier in all its forms is not a constant at the lumen interface as claimed in the literature (Basu and Sirkar, 1991; Alonso et al., 1995). However, only Youn et al. (1995) considered the nonuniform distribution of the carrier in a flat SLM process.

Even though buffers are used to increase the extraction of ions (Danesi, 1986; Yoshizuka et al., 1986; Alexander and Callahan, 1987; Hano et al., 1991), the nonuniform distribution of the buffer species in the feed or in the stripping solution, and their concomitant effect on the interface kinetics, have never been mentioned in the literature.

In this article, hollow-fiber membrane reactive extraction and carrier-facilitated supported liquid membrane processes are studied theoretically. A mathematical model incorporating Nernst-Planck flux, buffer effect, ion strength, interfacial reaction kinetics and equilibria, diffusivity of species in the membrane phase, shell resistances, and shell concentration is developed and solved numerically. The effect of Nernst-Planck flux in the lumen on mass-transfer rate is emphatically discussed.

Theory

Mass conservation equations for hollow-fiber ME and SLM processes

The symbolic representation of the reversible interfacial complexation reactions for countertransport is given by

$$A^a + nB = C + \frac{a}{e}E^e \qquad K_1 \qquad \text{(countertransport)} \quad (1)$$

A^a is the ion of interest that migrates from the lumen side through the membrane wall to the shell side, and superscript a denotes its charge. B is the carrier present in the membrane phase, and C is the complex formed between A and B. E^e is the counter ion (when A^a is cation, E^e is usually H^+; when A^a is anion, E^e is usually Cl^-). K_1 is the reactive extraction equilibrium constant. The buffer reaction is represented as:

$$E^e + G^{-e} = EG \qquad K_2 \qquad (2)$$

where G^{-e}/EG is a buffer couple. Though not appearing in the above equations, D^d is the couple ion of A^a, superscript d is its charge, and J^j and L^l represent the inert cations and anions in the feed, respectively.

The cases of hollow-fiber ME or SLM processes discussed here are those with an interfacial reaction as given by Eq. 1 and with an operational mode such that an aqueous feed passes through the lumen and the membrane wall is impregnated with the organic phase. The following assumptions are made to describe the fluid flow in the lumen side and the transport of species of interest in the lumen side, in the membrane wall, and in the shell side:

- The fluid in the lumen of the hollow-fiber modules is Newtonian and has constant physical properties.
- The fluid flow through the lumen of hollow fibers is steady, fully developed laminar flow.
- The concentration of the ion of interest in the lumen phase is low (e.g., < 0.5 M), and therefore mass transport does not affect the volumetric flow rate.
- The radial diffusion of the species in the lumen feed is described by Nernst-Planck diffusion, and the axial diffusion is neglected.
- The species in the aqueous solution in the lumen side do not dissolve by themselves in the membrane organic phase.
- The carrier and the carrier-solute complex formed are present only in the membrane phase and the complexing (or discomplexing) reaction occurs only at the phase interface(s).
- The diffusion coefficients of the free carrier and the complex in the membrane phase are considered to be constant, independent of their concentrations.
- Shell-side mass-transfer resistance and the concentration of all species in the shell, if not equal to zero, do not change along the axial direction.

Therefore, the concentration profiles in the lumen can be established (Qin et al., 1996; Qin and Cabral, 1996) as:

$$u_z \frac{\partial C_i}{\partial z} + \frac{1}{r}\frac{\partial}{\partial r}(rN_i) = R_i \qquad (i = 1, 7) \qquad (3)$$

where

$$u_z = 2u\left[1 - \left(\frac{r}{R}\right)^2\right] \qquad (4)$$

$$N_i = -D_i\frac{\partial C_i}{\partial r} + \frac{z_i D_i C_i}{\sum z_j^2 D_j C_j}\sum z_j D_j \frac{\partial C_j}{\partial r} \qquad (i, j = 1, 7) \quad (5)$$

Subscripts $i, j = 1, 2, 3, 4, 5, 6, 7$ are the species existing in the feed solution, A^a, D^d, E^e, G^{-e}, EG, J^j, and L^l, respectively. R_i is the local instantaneous reaction rate that ensures local equilibrium in Eq. 2. According to the total balance for the buffer in all the forms, the net chemical reaction rate of the buffer is zero at any point within the hollow-fiber lumen solution. Therefore, the continuity equations can be linearly combined to eliminate the rates of ionic reactions, leading to the following expressions:

$$u_z \frac{\partial C_A}{\partial z} = -\frac{1}{r}\frac{\partial}{\partial r}(rN_A) \tag{6}$$

$$u_z \frac{\partial C_D}{\partial z} = -\frac{1}{r}\frac{\partial}{\partial r}(rN_D) \tag{7}$$

$$u_z \frac{\partial (C_E + C_{EG})}{\partial z} = D_{EG}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{EG}}{\partial r}\right)\right] - \frac{1}{r}\frac{\partial}{\partial r}(rN_E) \tag{8}$$

$$u_z \frac{\partial (C_G + C_{EG})}{\partial z} = D_{EG}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{EG}}{\partial r}\right)\right] - \frac{1}{r}\frac{\partial}{\partial r}(rN_G) \tag{9}$$

$$u_z \frac{\partial C_J}{\partial z} = \frac{1}{r}\frac{\partial}{\partial r}(rN_J) \tag{10}$$

$$u_z \frac{\partial C_L}{\partial z} = -\frac{1}{r}\frac{\partial}{\partial r}(rN_L) \tag{11}$$

There are seven variables in six partial differential equations, thus an ionic equilibrium equation is needed:

$$K_2 = C_{EG}/C_E C_G \tag{12}$$

Boundary conditions:

$$\text{B.C.1:} \quad C_i = C_{i,0} \qquad z = 0,\ 0 \le r \le R \quad (i = 1, 7) \tag{13}$$

To comply with the demand of electroneutrality:

$$\Sigma z_i C_{i,0} = 0 \qquad (i = 1, 7) \tag{14}$$

$$\text{B.C.2:} \quad \frac{\partial C_i}{\partial r} = 0 \qquad r = 0,\ 0 \le z \le Z \quad (i = 1, 7) \tag{15}$$

Boundary conditions at the lumen surface (B.C.3) for impermeable species, D^d, J^j, and L^l are:

$r = R,\ 0 \le z \le Z$:

$$-D_D \frac{\partial C_D}{\partial r} + \frac{z_D D_D C_D}{\Sigma z_j^2 D_j C_j}\Sigma z_j D_j \frac{\partial C_j}{\partial r} = 0 \tag{16}$$

$$-D_J \frac{\partial C_J}{\partial r} + \frac{z_J D_J C_J}{\Sigma z_j^2 D_j C_j}\Sigma z_j D_j \frac{\partial C_j}{\partial r} = 0 \tag{17}$$

$$-D_L \frac{\partial C_L}{\partial r} + \frac{z_L D_L C_L}{\Sigma z_j^2 D_j C_j}\Sigma z_j D_j \frac{\partial C_j}{\partial r} = 0 \tag{18}$$

When a buffer couple exists in the feed, in order to ensure the local equilibrium in the feed at the lumen interface, B.C.3 for EG and G is:

$$-D_{EG}\frac{\partial C_{EG}}{\partial r} - D_G \frac{\partial C_G}{\partial r} + \frac{z_G D_G C_G}{\Sigma z_j^2 D_j C_j}\Sigma z_j D_j \frac{\partial C_j}{\partial r} = 0 \tag{19}$$

B.C.3 for A^a and E^e is given for various practical membrane reaction or separation processes later. Nevertheless, the following relationship is always valid as a result of electroneutrality:

$$aN_A|_{r=R} + eN_E|_{r=R} = 0 \tag{20}$$

Note that $N_E|_{r=R}$ is the total transfer rate of E through the lumen interface and into the liquid membrane, thus by mass balance:

$$N_E|_{r=R} = -D_E \frac{\partial C_E}{\partial r} + \frac{z_E D_E C_E}{\Sigma z_j^2 D_j C_j}\Sigma z_j D_j \frac{\partial C_j}{\partial r} - D_{EG}\frac{\partial C_{EG}}{\partial r} \tag{21}$$

thus,

$$-D_A \frac{\partial C_A}{\partial r} + \frac{z_A D_A C_A}{\Sigma z_j^2 D_j C_j}\Sigma z_j D_j \frac{\partial C_j}{\partial r} = -\frac{e}{a}\left(-D_E \frac{\partial C_E}{\partial r} + \frac{z_E D_E C_E}{\Sigma z_j^2 D_j C_j}\Sigma z_j D_j \frac{\partial C_j}{\partial r} - D_{EG}\frac{\partial C_{EG}}{\partial r}\right) \tag{22}$$

Equations 6–19 and B.C.3 for A^a and E^e for various practical SLM or ME processes, which will be shown later, constitute a whole initial problem.

B.C. 3 from the literature

Interfacial Chemical Reaction Equilibrium Maintained. Some experimental data in the literature show that the interfacial reaction rate can be so fast compared to the mass-transfer rate that local chemical equilibrium is maintained. This is the case for NH_4^+ extraction by DTPA (Qin and Cabral, 1996), Co^{2+} by HEH (Youn et al., 1995), Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} by DEHPA (Daiminger et al., 1996), and metal anions or organic acid anions by ammonium salts (Hano et al., 1991; Basu and Sirkar, 1991; Alonso et al., 1994).

From Eq. 1, the chemical equilibrium at the interfaces can be expressed as:

$$K_1 = \frac{C_{C,m,L} C_{E,R}^{a/e}}{C_{A,R} C_{B,m,L}^{n}} \quad \text{(for ME and SLM processes at lumen surface)} \tag{23}$$

$$K_1 = \frac{C_{C,m,s} C_{E,s,s}^{a/e}}{C_{A,s,s} C_{B,m,s}^{n}} \quad \text{(for SLM processes at fiber outside surface)} \tag{24}$$

Whether operated as an SLM process or an ME process, B.C.3 for A^a and E^e at $r = R$ can be expressed as:

$$-D_A \frac{\partial C_A}{\partial r} + \frac{z_A D_A C_A}{\Sigma z_j^2 D_j C_j}\Sigma z_j D_j \frac{\partial C_j}{\partial r} = k_{m,C}(C_{C,m,L} - C_{C,m,s}) \tag{25}$$

$$- D_E \frac{\partial C_E}{\partial r} + \frac{z_E D_E C_E}{\Sigma z_j^2 D_j C_j} \Sigma z_j D_j \frac{\partial C_j}{\partial r} - D_{EG} \frac{\partial C_{EG}}{\partial r} = \frac{ne}{a} k_{m,B} (C_{B,m,L} - C_{B,m,s}) \quad (26)$$

SLM Process. When $n > 1$, the molecular weight of the complex, C, is considerably different from that of the free carrier, B. Thus, the diffusion coefficient of the complex differs from that of the free carrier. As a result, the total concentration of carrier in all forms is not constant along the radial direction in the membrane. Nevertheless, for SLM processes, the total concentration of carrier in the membrane phase is conserved. Referring to the case where a flat membrane was used (Youn et al., 1995), the relationship for hollow-fiber SLM processes is given by

$$C_{B,0} = \frac{\int_R^{R_1} 2\pi (C_{B,m,r} + nC_{C,m,r}) r dr}{\int_R^{R_1} 2\pi r dr} = \frac{2}{R_1^2 - R^2} \int_R^{R_1} (C_{B,m,r} + nC_{C,m,r}) r dr \quad (27)$$

where $C_{B,mr}$ and $C_{C,mr}$ are the concentrations of B and G in the membrane phase, respectively, and $C_{B,0}$ is the total initial carrier concentration without complexation. The mass conservation equations for B and C in the membrane phase can be expressed as:

$$D_{m,B} \frac{\epsilon}{\tau} \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_B}{\partial r} \right) = 0 \quad (28)$$

$$D_{m,C} \frac{\epsilon}{\tau} \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_C}{\partial r} \right) = 0 \quad (29)$$

where ϵ and τ are the porosity and the tortuosity of the membrane wall, respectively.

The integration of Eqs. 28 and 29 yields:

$$C_{B,m,r} = C_{B,m,L} - \frac{\ln(r/R)}{\ln(R_1/R)} (C_{B,m,L} - C_{B,m,s}) \quad (R \le r \le R_1) \quad (30)$$

$$C_{C,m,r} = C_{C,m,L} - \frac{\ln(r/R)}{\ln(R_1/R)} (C_{C,m,L} - C_{C,m,s}). \quad (R \le r \le R_1) \quad (31)$$

The integration of Eq. 27 yields:

$$(C_{B,m,L} + nC_{C,m,L}) + [(C_{B,m,s} + nC_{C,m,s}) - (C_{B,m,L} + nC_{C,m,L})] \left[\frac{R_1^2}{R_1^2 - R^2} - \frac{1}{2} \frac{1}{\ln(R_1/R)} \right] = C_{B,0}. \quad (32)$$

From Eqs. 30 and 31, the mass transfer rate at the lumen interface can be expressed as:

$$N_B|_{r=R} = - D_{m,B} \frac{\epsilon}{\tau} \frac{dC_B}{dr}\bigg|_{r=R} = \frac{D_{m,B} \frac{\epsilon}{\tau}}{R \ln(R_1/R)} (C_{B,m,L} - C_{B,m,s}) = k_{m,B} (C_{B,m,L} - C_{B,m,s}) \quad (33)$$

$$N_C|_{r=R} = - D_{m,C} \frac{\epsilon}{\tau} \frac{dC_C}{dr}\bigg|_{r=R} = \frac{D_{m,C} \frac{\epsilon}{\tau}}{R \ln(R_1/R)} (C_{C,m,L} - C_{C,m,s}) = k_{m,C} (C_{C,m,L} - C_{C,m,s}) \quad (34)$$

and by mass balance,

$$k_{m,B} (C_{B,m,s} - C_{B,m,L}) = \frac{ne}{a} k_{m,C} (C_{C,m,L} - C_{C,m,s}) \quad (35)$$

For SLM processes, at least three kinds of ions, A^a, D^d, and E^e, exist in the shell-stripping phase. The difficulty is how to calculate the mass-transfer rate of the charged species in the shell-stripping phase. Referring to the film coefficient for spherical particles (Hu et al., 1992), the mass-transfer rate can be expressed as:

$$N_A|_{r=R} = k_{m,A} (C_{A,m,L} - C_{A,m,s}) = \frac{R_1}{R} \left[k_{s,A} (C_{A,s,s} - C_{A,s}) - \frac{z_A k_{s,A} C_{A,s,s}}{\Sigma z_j^2 k_{s,j} C_{j,s,s}} \Sigma z_j k_{s,j} (C_{j,s,s} - C_{j,s}) \right] \quad (36)$$

$$N_E|_{r=R} = k_{m,E} (C_{E,m,L} - C_{E,m,s}) = \frac{R_1}{R} \left[k_{s,E} (C_{E,s,s} - C_{E,s}) - \frac{z_E k_{s,E} C_{E,s,s}}{\Sigma z_j^2 k_{s,j} C_{j,s,s}} \Sigma z_j k_{s,j} (C_{j,s,s} - C_{j,s}) \right]. \quad (37)$$

$k_{s,i}$ can be obtained from correlations of shell mass-transfer coefficient found in the literature (Yun et al., 1993; Daiminger et al., 1996) using the molecular diffusion coefficient of species i. In most SLM processes, nevertheless, the concentrations of D^d and E^e are far higher than the concentration of A^a in the stripping phase; their influence on the diffusion of A is negligible, as can be seen from Eq. 5. It can be thought as well that the influence of A on the diffusion of D and E is negligible and thus the ion couple of D and E has a diffusion coefficient equivalent to that of the corresponding molecule (Cussler, 1984), that is,

$$D'_D = D'_E = \frac{D_D D_E (|d| + |e|)}{|d| D_D + |e| D_E}. \quad (38)$$

Hence, Eqs. 36 and 37 are reduced respectively to:

$$k_{m,C} (C_{C,m,L} - C_{C,m,s}) = \frac{R_1}{R} k_{s,A} (C_{A,s,s} - C_{A,s}) \quad (39)$$

$$k_{m,B}(C_{B,m,L}-C_{B,m,s})=\frac{R_1}{R}k_{s,E}(C_{E,s,s}-C_{E,s}) \quad (40)$$

where $k_{s,A}$ can be obtained from the correlations in which the molecular diffusion coefficient of A is used, and $k_{s,E}$ can also be obtained from the correlations in which the diffusion coefficient is calculated as by Eq. 38.

From Eqs. 23, 24, 32, 35, 39, and 40, $C_{B,m,L}$, $C_{C,m,L}$, $C_{B,m,s}$, $C_{C,m,s}$, $C_{A,s,s}$, and $C_{E,s,s}$ can be expressed as functions of $C_{A,R}$, $C_{A,s}$, $C_{E,R}$, and $C_{E,s}$. Thus, B.C.3 for A and E only contains $C_{A,R}$ and $C_{E,R}$ as variables. In other words, B.C.3 for A and E is given by Eqs. 23–26, 32, 35, 39 and 40.

When $a=e$ and $|a|=n=1$ (for example, in the extraction of amino acid anions or metal anions, such as $Au(CN)_2^-$, $Au(CN)_4^-$, and VO_3^-, by ammonium salts), the molecular size of A is usually far smaller than that of B and C. The diffusion coefficients of B and C can thus be treated as being equal to each other (Qin and Cabral, 1996), that is, $D_{m,B}=D_{m,C}$, $k_{m,B}=k_{m,C}$. Eq. 32 is therefore reduced to

$$C_{B,m,L}+C_{C,m,L}=C_{B,m,s}+C_{C,m,s}=C_{B,0} \quad (41)$$

B.C.3 for A and E can be further expressed by Eqs. 42–45:

$$-D_A\frac{\partial C_A}{\partial r}+\frac{z_AD_AC_A}{\Sigma z_j^2D_jC_j}\Sigma z_jD_j\frac{\partial C_j}{\partial r}=k_{m,C}K_1C_{B,0}\left(\frac{C_{A,R}}{C_{E,R}+K_1C_{A,R}}-\frac{C_{A,s,s}}{C_{E,s,s}+K_1C_{A,s,s}}\right) \quad (42)$$

$$-D_E\frac{\partial C_E}{\partial r}+\frac{z_ED_EC_E}{\Sigma z_j^2D_jC_j}\Sigma z_jD_j\frac{\partial C_j}{\partial r}-D_{EG}\frac{\partial C_{EG}}{\partial r}=-k_{m,C}K_1C_{B,0}\left(\frac{C_{A,R}}{C_{E,R}+K_1C_{A,R}}-\frac{C_{A,s,s}}{C_{E,s,s}+K_1C_{A,s,s}}\right) \quad (43)$$

$$k_{m,C}K_1C_{B,0}\left(\frac{C_{A,R}}{C_{E,R}+K_1C_{A,R}}-\frac{C_{A,s,s}}{C_{E,s,s}+K_1C_{A,s,s}}\right)=\frac{R_1}{R}k_{s,A}(C_{A,s,s}-C_{A,s}) \quad (44)$$

$$k_{m,C}K_1C_{B,0}\left(\frac{C_{A,R}}{C_{E,R}+K_1C_{A,R}}-\frac{C_{A,s,s}}{C_{E,s,s}+K_1C_{A,s,s}}\right)=-\frac{R_1}{R}k_{s,E}(C_{E,s,s}-C_{E,s}). \quad (45)$$

When $a=2e$, $|a|=n=2$, $C_{A,s}=0$, and the shell resistances are negligible, B.C.3 for A and E can be further expressed explicitly by Eqs. 46 and 47:

$$-D_A\frac{\partial C_A}{\partial r}+\frac{z_AD_AC_A}{\Sigma z_j^2D_jC_j}\Sigma z_jD_j\frac{\partial C_j}{\partial r}=\frac{2k_{m,C}K_1C_{B,0}^2C_{A,R}/C_{E,R}^2}{1+2\beta K_1C_{B,0}C_{A,R}/C_{E,R}^2+\sqrt{1+\frac{4\beta K_1C_{B,0}C_{A,R}}{C_{E,R}^2}}} \quad (46)$$

$$-D_E\frac{\partial C_E}{\partial r}+\frac{z_ED_EC_E}{\Sigma z_j^2D_jC_j}\Sigma z_jD_j\frac{\partial C_j}{\partial r}-D_{EG}\frac{\partial C_{EG}}{\partial r}=-\frac{4k_{m,C}K_1C_{B,0}^2C_{A,R}/C_{E,R}^2}{1+2\beta K_1C_{B,0}C_{A,R}/C_{E,R}^2+\sqrt{1+\frac{4\beta K_1C_{B,0}C_{A,R}}{C_{E,R}^2}}} \quad (47)$$

where

$$\beta=2+\chi(\gamma-2) \quad (48)$$

$$\chi=\frac{R_1^2}{R_1^2-R^2}-\frac{1}{2}\frac{1}{\ln(R_1/R)} \quad (49)$$

$$\gamma=\frac{2k_{m,C}}{k_{m,B}}=\frac{2D_{m,C}}{D_{m,B}}. \quad (50)$$

ME Processes. For ME processes, B.C.3 can be expressed as:

$$-D_A\frac{\partial C_A}{\partial r}+\frac{z_AD_AC_A}{\Sigma z_j^2D_jC_j}\Sigma z_jD_j\frac{\partial C_j}{\partial r}=k_{m,C}(C_{C,m,L}-C_{C,m,s}) \quad (51)$$

$$-D_E\frac{\partial C_E}{\partial r}+\frac{z_ED_EC_E}{\Sigma z_j^2D_jC_j}\Sigma z_jD_j\frac{\partial C_j}{\partial r}-D_{EG}\frac{\partial C_{EG}}{\partial r}=\frac{ne}{a}k_{m,B}(C_{B,m,L}-C_{B,m,s}). \quad (52)$$

Eq. 35 is still valid for ME processes, though Eq. 32 is no longer valid. A reasonable assumption is that the concentrations of B and C in the bulk shell phase can be treated as constants. By mass balance:

$$k_{m,C}(C_{C,m,L}-C_{C,m,s})=\frac{R_1}{R}k_{s,C}(C_{C,m,s}-C_{C,s}) \quad (53)$$

$$k_{m,B}(C_{B,m,L}-C_{B,m,s})=\frac{R_1}{R}k_{s,B}(C_{B,m,s}-C_{B,s}). \quad (54)$$

From Eqs. 23, 35, 53, and 54, $C_{B,m,L}$, $C_{C,m,L}$, $C_{B,m,s}$, and $C_{C,m,s}$ can be expressed as functions of $C_{A,R}$, $C_{E,R}$, $C_{B,s}$, and $C_{C,s}$. Thus, B.C.3 only contains $C_{A,R}$ and $C_{E,R}$ as variables.

When $a=e$ and $|a|=n=1$, B.C.3 for A and E can be further expressed explicitly as:

$$-D_A\frac{\partial C_A}{\partial r}+\frac{z_AD_AC_A}{\Sigma z_j^2D_jC_j}\Sigma z_jD_j\frac{\partial C_j}{\partial r}=K_{m,C}\left(\frac{K_1C_{A,R}C_{B,0}}{C_{E,R}+K_1C_{A,R}}-C_{C,s}\right) \quad (55)$$

$$-D_E\frac{\partial C_E}{\partial r}+\frac{z_ED_EC_E}{\Sigma z_j^2D_jC_j}\Sigma z_jD_j\frac{\partial C_j}{\partial r}-D_{EG}\frac{\partial C_{EG}}{\partial r}=-K_{m,C}\left(\frac{K_1C_{A,R}C_{B,0}}{C_{E,R}+K_1C_{A,R}}-C_{C,s}\right) \quad (56)$$

$K_{m,C}$ and $K_{m,B}$ are defined by:

$$K_{m,B} = \frac{1}{\frac{1}{k_{m,B}} + \frac{R_1}{R k_{s,B}}} \tag{57}$$

$$K_{m,C} = \frac{1}{\frac{1}{k_{m,C}} + \frac{R_1}{R k_{s,C}}} \tag{58}$$

Also, when $a = 2e$ and $|a| = n = 2$, B.C.3 can be further explicitly expressed as:

$$k\left(\frac{C_{A,R}C_{B,m,L}}{C_{E,R}} - \frac{C_{C,m,L}C_{E,R}}{K_1 C_{B,m,L}}\right) = k_{m,C}(C_{C,m,L} - C_{C,m,s}) \tag{64}$$

$$2k\left(\frac{C_{A,R}C_{B,m,L}}{C_{E,R}} - \frac{C_{C,R}C_{E,R}}{K_1 C_{B,m,L}}\right) = -k_{m,B}(C_{B,m,L} - C_{B,m,s}) \tag{65}$$

$C_{B,m,L}$, $C_{C,m,L}$, $C_{B,m,s}$, and $C_{C,m,s}$ can be obtained from Eqs. 53, 54, 64, and 65 as functions of $C_{A,R}$, $C_{E,R}$, $C_{B,s}$, and $C_{C,s}$. Thus, B.C.3 only contains $C_{A,R}$ and $C_{E,R}$ as variables.

$$-D_A\frac{\partial C_A}{\partial r} + \frac{z_A D_A C_A}{\Sigma z_j^2 D_j C_j}\Sigma z_j D_j \frac{\partial C_j}{\partial r} = K_{m,C}(C_{C,m,L} - C_{C,s})$$

$$= \frac{4K_1 K_{m,B} C_{A,R} C_{B,s} + K_{m,B} C_{E,R}^2 - \sqrt{K_{m,B}^2 C_{E,R}^4 + 8K_1 K_{m,B} K_{m,C} C_{A,R} C_{B,s} C_{E,R}^2 + 16 K_1 K_{m,C}^2 C_{A,R} C_{C,s} C_{E,R}^2}}{4K_1 C_{A,R}} \tag{59}$$

$$-D_E\frac{\partial C_E}{\partial r} + \frac{z_E D_E C_E}{\Sigma z_j^2 D_j C_j}\Sigma z_j D_j \frac{\partial C_j}{\partial r} - D_{EG}\frac{\partial C_{EG}}{\partial r} = -2K_{m,C}(C_{C,m,L} - C_{C,s})$$

$$= -\frac{4K_1 K_{m,C} C_{A,R} C_{B,s} + K_{m,B} C_{E,R}^2 + \sqrt{K_{m,B}^2 C_{E,R}^4 + 8K_1 K_{m,B} K_{m,C} C_{A,R} C_{B,s} C_{E,R}^2 + 16 K_1 K_{m,C}^2 C_{A,R} C_{C,s} C_{E,R}^2}}{2K_1 C_{A,R}} \tag{60}$$

ME or SLM Processes with an Interfacial Reactive Extraction Equilibrium. For some reactive extractions, for example, Cu^{2+} with LIX 84 (Haan et al., 1989; Yun et al., 1993; Yi and Tavlarides, 1995), or rare earth metals with PC-88A (Kubota et al., 1995), the interfacial extractive reaction rates are slower than the mass-transfer rate. Thus the reaction kinetics need to be considered.

The extraction of Cu^{2+} with LIX 84 in a buffer-free feed can be expressed by Eq. 1 with $a = n = 2$, $E^e = H^+$. Interfacial chemical reaction kinetics can be expressed (Haan et al., 1989; Yun et al., 1993; Yi and Tavlarides, 1995) as:

$$R = k\left(\frac{C_A C_B}{C_E} - \frac{C_C C_E}{K_1 C_B}\right) \tag{61}$$

Thus, without assuming any controlling step, B.C.3 for A^a (Cu^{2+}) and E^e (H^+) can be expressed for an ME process as:

$$-D_A\frac{\partial C_A}{\partial r} + \frac{z_A D_A C_A}{\Sigma z_j^2 D_j C_j}\Sigma z_j D_j \frac{\partial C_j}{\partial r} = k\left(\frac{C_{A,R}C_{B,m,L}}{C_{E,R}} - \frac{C_{C,m,L}C_{E,R}}{K_1 C_{B,m,L}}\right) \tag{62}$$

$$-D_E\frac{\partial C_E}{\partial r} + \frac{z_E D_E C_E}{\Sigma z_j^2 D_j C_j}\Sigma z_j D_j \frac{\partial C_j}{\partial r} = -2k\left(\frac{C_{A,R}C_{B,m,L}}{C_{E,R}} - \frac{C_{C,m,L}C_{E,R}}{K_1 C_{B,m,L}}\right) \tag{63}$$

For an SLM process, Eqs. 62–65 are still valid, and Eqs. 53 and 54 are substituted by:

$$k_{m,B}(C_{B,m,L} - C_{B,m,s}) = k\left(\frac{C_{A,s,s}C_{B,m,s}}{C_{E,s,s}} - \frac{C_{C,m,s}C_{E,s,s}}{K_1 C_{B,m,s}}\right) \tag{66}$$

$$k_{m,C}(C_{C,m,L} - C_{C,m,s}) = -2k\left(\frac{C_{A,s,s}C_{B,m,s}}{C_{E,s,s}} - \frac{C_{C,m,s}C_{E,s,s}}{K_1 C_{B,m,s}}\right) \tag{67}$$

$C_{B,m,L}$, $C_{C,m,L}$, $C_{A,s,s}$, $C_{B,s,s}$, $C_{C,m,s}$, and $C_{E,m,s}$ can be obtained from Eqs. 32, 39, 40, and 64–66 as functions of $C_{A,R}$, $C_{E,R}$, $C_{A,s}$, and $C_{E,s}$. Thus, B.C.3 only contains $C_{A,R}$ and $C_{E,R}$ as variables.

The extraction of rare earth metals with PC-88A can be expressed by Eq. 1 with $a = n = 3$, $E^e = H^+$. Interfacial chemical reaction kinetics can be expressed (Kubota et al., 1995) as:

$$R = k\left(\frac{C_A C_B^3}{C_E^3} - \frac{C_C}{K_1}\right)\Big/\sigma \tag{68}$$

where

$$\sigma = 1 + 4.65(1 + 4.79/C_E)\sqrt{C_B/3} + 1.8C_B \tag{69}$$

Thus, without assuming any controlling step, B.C.3 for the trivalent metal ions and H^+ can be expressed for an ME process as:

$$-D_A\frac{\partial C_A}{\partial r}+\frac{z_A D_A C_A}{\Sigma z_j^2 D_j C_j}\Sigma z_j D_j\frac{\partial C_j}{\partial r}=R|_{r=R} \tag{70}$$

$$-D_E\frac{\partial C_E}{\partial r}+\frac{z_E D_E C_E}{\Sigma z_j^2 D_j C_j}\Sigma z_j D_j\frac{\partial C_j}{\partial r}=-3R|_{r=R} \tag{71}$$

$$R|_{r=R}=k_{m,C}(C_{C,m,L}-C_{C,m,s}) \tag{72}$$

$$3R|_{r=R}=-k_{m,B}(C_{B,m,L}-C_{B,m,s}) \tag{73}$$

$C_{B,m,L}$, $C_{C,m,L}$, $C_{B,m,s}$, and $C_{C,m,s}$ can be obtained from Eqs. 53, 54, 72, and 73 as functions of $C_{A,R}$, $C_{E,R}$, $C_{B,s}$, and $C_{C,s}$. Therefore, B.C.3 for A and E only contains $C_{A,R}$ and $C_{E,R}$ as variables.

For an SLM process, Eqs. 70–73 are still valid, and, at the outer surface of the fibers, the mass-transfer rate can be expressed as:

$$k_{m,B}(C_{B,m,L}-C_{B,m,s})=R|_{r=R_1} \tag{74}$$

$$k_{m,C}(C_{C,m,L}-C_{C,m,s})=-3R|_{r=R_1} \tag{75}$$

$C_{B,m,L}$, $C_{C,m,L}$, $C_{A,s,s}$, $C_{B,m,s}$, $C_{C,m,s}$ and $C_{E,s,s}$ can be obtained from Eqs. 32, 39, 40, and 72–74 as functions of $C_{A,R}$, $C_{E,R}$, $C_{A,s}$, and $C_{E,s}$. So, B.C.3 only contains $C_{A,R}$ and $C_{E,R}$ as variables.

ME or SLM processes are also used for the separation of ions based on the difference in their reactive extraction equilibrium constants or reaction extraction kinetics (Marr and Draxler, 1992; Kubota et al., 1995; Yang et al., 1996). In these cases, in addition to Eqs. 6–11, one or more partial differential equations are needed, and B.C.3 for this set of equations can be given according to the equilibrium or kinetic expressions. However, Eq. 20 should be replaced by a new expression in which the total transfer rate of all the complexes of ions from lumen to shell equals that of the free carrier from the shell to the lumen.

The discussion above deals with countertransport of charged species through the membrane. Another case in ME or SLM processes is cotransport of charged species through the membrane. The symbolic representation of the reversible interfacial complexion reactions for cotransport is given by Eq. 76:

$$A^a+\left|\frac{a}{d}\right|D^d+nB=C \qquad K_3 \qquad \text{(cotransport)} \tag{76}$$

Examples of Eq. 76 are the reactive extraction of metal anions, organic acids, or penicillin G by ME or SLM processes using amines, or the extraction of metal ions by crown ethers. If A^a and D^d are the only ions in the feed solution, by the limitation of electroneutrality, the ion couple of A and D has a diffusion coefficient equivalent to that of the corresponding molecule diffusion coefficient similar to Eq. 38. Therefore, Fick's law is valid and the problem reduces to the case previously described (Qin and Cabral, 1998).

When hydrophilic porous membranes are used for ME processes (Yi and Tavlarides, 1995), the Nernst-Planck flux also occurs in the micropores in the membrane wall, which are wetted by the aqueous phase. Partial differential equations have to be formulated to describe the mass transfer in the wall. The concentration fields in the lumen and in the membrane wall are coupled through mutual boundary conditions at the lumen and shell interfaces of the fibers and the problem should be treated as a coupled boundary problem. However, this situation will not be considered in this paper.

Results and Discussion

The partial differential equation with nonlinear boundary conditions given above cannot be solved analytically. Therefore, the method of orthogonal collocation on finite elements in the r direction was applied to convert these partial differential equations into a set of coupled ordinary differential equations (Finlayson, 1980). By use of the orthogonal collocation methods, B.C.3 is reduced to a set of nonlinear algebraic equations as a result of Nernst-Planck flux. Therefore B.C.3 expressed by a group of equations instead of explicit expressions does not make solving the equations more difficult. Solving these equations in the z direction by the Runge-Kutta method yields C_i at any point within the lumen or on the lumen surface of the hollow fiber. Other interesting values, for example, the mixed cup concentration $C_{z,i}$ and the local lumen $Sh_{z,i}$ for each species are obtained (Qin et al., 1996, and reference cited herein) as:

$$C_{z,i}=\frac{\int_0^R 2\pi ruC_i dr}{\int_0^R 2\pi rudr}=\frac{4}{R^2}\int_0^R\left[1-\left(\frac{r}{R}\right)^2\right]rC_i dr$$

$$(i=A,\ D,\ E,\ EG,\ G,\ J,\ \text{or}\ L) \tag{77}$$

$$Sh_{z,i}=\frac{2Rk_{z,i}}{D}=\frac{2R}{D}\frac{N_i|_{r=R}}{C_{z,i}-C_{i,R}} \qquad (i=A\ \text{or}\ E) \tag{78}$$

Referring to the definition of dimensionless length when Fick's law is valid (Qin and Cabral, 1997, and references cited herein), dimensionless length for species i is defined as:

$$z_i'=zD_i/4uR^2 \qquad (i=A\ \text{or}\ E) \tag{79}$$

In the simulation calculations, the following characteristics of the hollow-fiber membrane are used: $R=0.12$ mm, $R_1=0.15$ mm, $\epsilon=0.30$, $\tau=2.6$. Thus, mass-transfer coefficients through the membrane wall can be calculated by:

$$k_{m,i}=\frac{D_{m,i}\frac{\epsilon}{\tau}}{R\ln(R_1/R)} \qquad (i=B,\ C) \tag{80}$$

The values of diffusion coefficients of the ions, as listed in Table 1, are obtained from the *Handbook of Physics and Chemistry*.

Separation of Monovalent Ions. Ammonium salts are used as the extractant when amino acids and hydroxyl acids exist

in the feed as monovalent ions. The extraction of tryptophan by quaternary ammonium salts, with a high extractive equilibrium constant of $K_1 = 8.89$ (Hano et al., 1991) and thus a relatively smaller membrane resistance, is given as an example. The membrane mass-transfer coefficients calculated by Eq. 80 are listed in Table 1. When the shell resistance is neglected and no buffer and other inert salts are present, the partial differential equations with boundaries can be further expressed as:

$$u_z \frac{\partial C_A}{\partial z} = -\frac{1}{r}\frac{\partial}{\partial r}(rN_A) \tag{81}$$

$$u_z \frac{\partial C_D}{\partial z} = -\frac{1}{r}\frac{\partial}{\partial r}(rN_D) \tag{82}$$

$$u_z \frac{\partial C_E}{\partial z} = -\frac{1}{r}\frac{\partial}{\partial r}(rN_E) \tag{83}$$

Boundary conditions:

$$\text{B.C.1:}\quad C_i = C_{i,0} \quad z = 0,\ 0 \le r \le R \quad (i = A, D, E) \tag{84}$$

$$\text{B.C.2:}\quad \frac{\partial C_i}{\partial r} = 0 \quad r = 0,\ 0 \le z \le Z \quad (i = A, D, E) \tag{85}$$

B.C.3 at $r = R$, $0 \le z \le Z$:

$$-D_A\frac{\partial C_A}{\partial r} + \frac{z_A D_A C_A}{\sum z_j^2 D_j C_j}\sum z_j D_j \frac{\partial C_j}{\partial r} = k_{m,C} K_1 C_{B,0}\left(\frac{C_{A,R}}{C_{E,R} + K_1 C_{A,R}} - \frac{C_{A,s}}{C_{E,s} + K_1 C_{A,s}}\right) \tag{86}$$

$$-D_D\frac{\partial C_D}{\partial r} + \frac{z_D D_D C_D}{\sum z_j^2 D_j C_j}\sum z_j D_j \frac{\partial C_j}{\partial r} = 0 \tag{87}$$

$$-D_E\frac{\partial C_E}{\partial r} + \frac{z_E D_E C_E}{\sum z_j^2 D_j C_j}\sum z_j D_j \frac{\partial C_j}{\partial r} - D_{EG}\frac{\partial C_{EG}}{\partial r} = -k_{m,C} K_1 C_{B,0}\left(\frac{C_{A,R}}{C_{E,R} + K_1 C_{A,R}} - \frac{C_{A,s}}{C_{E,s} + K_1 C_{A,s}}\right) \tag{88}$$

The simulated variation of lumen concentration along the axial direction is shown in Figure 1. The simplification using Fick's law produces a positive error, that is, for a given lumen exit concentration of A, the needed membrane length calculated by Fickian diffusion (curve 3) is higher than that calculated by Nernst-Planck diffusion (curve 1). For instance, when $C_{z,A} = 0.5C_{A,0}$, the error is around 12%.

When other ions existed in the feed, for example, KOH or NaOH was added to maintain the pH at 10 ~ 12 in order to shift amino acids to the extractable anion type (Hano et al., 1991), the ion strength in the feed was actually increased. The effect of Nernst-Planck diffusion decreases with the increase of ion strength (Hu et al., 1992), as shown in Figure 1 (curve 2 to curve 3) and in Figures 2 and 3.

The extraction of Ag^+ by DEHPA, which has a K_1 value of 0.1 (Lee et al., 1996), is an example of separation of monovalent cations. The simulation conditions are: ME process,

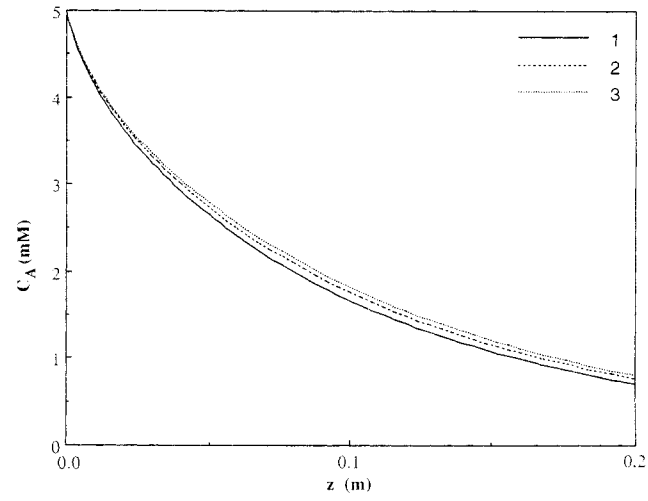

Figure 1. Variation of lumen concentration of tryptophan along the axial direction.

Simulation conditions: SLM process, neglecting shell resistance, $k_{m,B} = k_{m,C} = 1.8 \times 10^{-6}$ m/s, $C_{A,0} = 5$ mM, $C_{A,s} = 0$, $C_{B,0} = 100$ mM, $C_{E,0} = C_{Cl^-,0} = 0.5$ mM, $u = 0.02$ m/s, and for Curve 1: Nernst-Planck flux, $C_{D,0} = C_{K^+,0} = 5.5$ mM, no other ions; Curve 2: Nernst-Planck flux, $C_{D,0} = C_{K^+,0} = 15.5$ mM, $C_{L,0} = C_{OH^-,0} = 10$ mM; Curve 3: Fick flux, for above.

$C_{A,0} = C_{Ag^+,0} = 1$ mM, $C_{B,s} = 100$ mM, $C_{C,s} = 0$, $C_{D,0} = C_{NO_3^-,0} = 1.01$ mM, $C_{E,0} = C_{H^+,0} = 0.01$ mM, $K_B = K_C = 4.3 \times 10^{-6}$ m/s, $u = 0.02$ m/s. Using the Nernst-Planck diffusion model, a membrane length of 0.032 m is needed for $C_{z,A} = 0.5C_{A,0}$, whereas the Fickian diffusion model predicts a membrane length of 0.035 m; the relative error is only 9%. Other monovalent cations, such as alkaline metal ions, are hardly extracted by cation exchangers (which are therefore

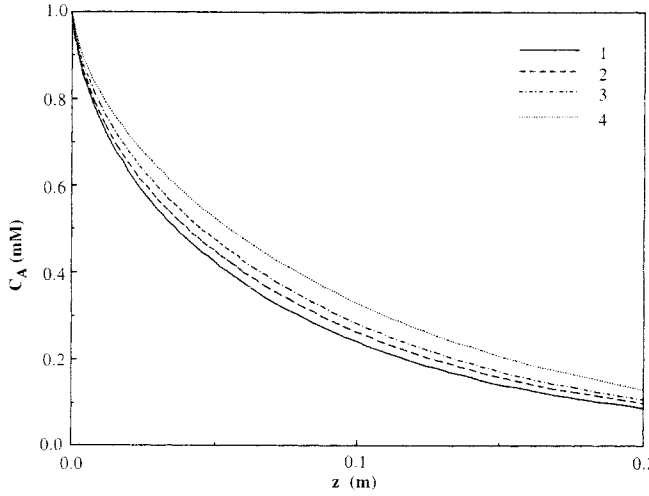

Figure 2. Variation of lumen concentration of Cu^{2+} along the axial direction.

Simulation conditions: SLM process, neglecting shell resistance, $k_{m,B} = 4.3 \times 10^{-6}$ m/s, $k_{m,C} = 2.5 \times 10^{-6}$ m/s, $C_{A,0} = C_{Cu^{2+},0} = 1$ mM, $C_{A,s} = 0.0$, $C_{B,0} = C_{DTPA,0} = 50$ mM, $C_{E,0} = C_{H^+,0} = 0.01$ mM, $u = 0.02$ m/s. For Curve 1: Nernst-Planck flux, $C_{D,0} = C_{Cl^-,0} = 2.01$ mM; Curve 2: Nernst-Planck flux, $C_{D,0} = C_{SO_4^{2-},0} = 1.005$ mM; Curve 3: Nernst-Planck flux, $C_{D,0} = C_{Cl^-,0} = 4.01$ mM, $C_{J,0} = C_{K^+,0} = 2.0$ mM; Curve 4: Fick flux, for all above.

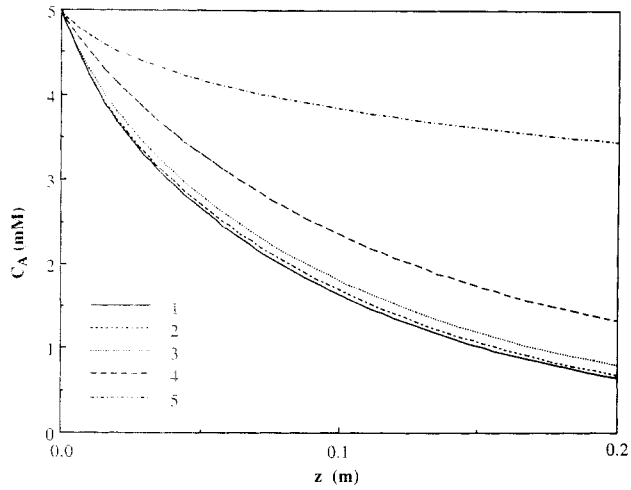

Figure 3. Variation of lumen concentration of Cu^{2+} along the axial direction.

Simulation conditions: ME process, $K_B = 4.3 \times 10^{-6}$ m/s, $K_C = 2.5 \times 10^{-6}$ m/s, $C_{A,0} = 5$ mM, $C_{B,0} = 50$ mM, $C_{C,s} = 0.0$, $C_{E,0} = C_{H^+,0} = 0.01$ mM, $u = 0.02$ m/s. For Curve 1: Nernst-Planck flux, $C_{D,0} = C_{Cl^-,0} = 10$ mM, $C_{G,0} = C_{AC^-,0} = 20$ mM, $C_{J,0} = C_{K^+,0} = 19.99$ mM; Curve 2: as above, Fick flux; Curve 3: Fick flux, $C_{D,0} = C_{Cl^-,0} = 10$ mM, $C_{G,0} = C_{AC^-,0} = 10$ mM, $C_{J,0} = C_{K^+,0} = 9.99$ mM; Curve 4: as with Curve 3, Nernst-Planck flux; Curve 5: no buffer, Nernst-Planck flux or Fick flux.

used in the feed as inert ions to adjust the ion strength), thus the effect of Nernst-Planck diffusion is usually considered negligible as a result of low mass-transfer resistance in the lumen.

As a conclusion, for the practical extraction of monovalent ions, the effect of Nernst-Planck diffusion is small and negligible, and Fick's law can be used to describe the mass transfer in hollow fiber ME or SLM processes with reasonable accuracy.

Separation of Divalent Ions. Many divalent metal cations are easily extracted by cation exchangers, for instance, Zn^{2+} and Pb^{2+} by DEHPA (Daiminger et al., 1996) and most metal ions by DTPA (Marr and Draxler, 1992). The use of anion exchangers for the extraction of anions such as CrO_4^{2-} is also known to be very effective (Alonso et al., 1994). In these cases, the lumen mass-transfer resistance is probably dominant.

DTPA is taken as an example of strange cation exchangers. Though the value of K_1 for the extraction of divalent metal cations by DTPA is not available in the literature, the experimental data given by Marr and Draxler (1992) show that it is 3 orders of magnitude higher than extraction by DEHPA. Therefore, K_1 is taken as 1.0 when referring to the values of K_1 of metal extraction by DEHPA (Daiminger et al., 1996). The membrane mass-transfer coefficients are listed in Table 1. It can be seen from Figure 2 that the simplification using Fick's law produces a positive error. When $C_{z,A} = 0.5C_{A,0}$, the error increases up to around 50% when Cl^- is the couple ion (curve 4 to 1). The error is mainly from the difference in diffusivities of the metal ion and its counter ion, H^+, and not from those of the metal ion and its couple ion. It can also be seen that using SO_4^{2-} instead of Cl^- only results in a small difference (curve 2 to curve 1). Further, when other inert ions exist, the effect of Nernst-Planck diffusion becomes small, as shown in Figure 2 (curves 3 and 4).

It is worth mentioning again that the effect of Nernst-Planck diffusion depends to a large extent on the diffusivity difference of the ions of interest and their counter ions. The extraction of CrO_4^{2-} by Aliquat 336 can be taken as an example (Alonso et al., 1994; Alonso and Pantelides, 1996). According to the data given by those authors: $K_1 = 0.81$, $C_{A,0} = C_{CrO_4^{2-},0} = 0.309$ mM (50 mg/L), $C_{B,s} = 0.2$ M, $C_{C,s} = 0.0$, $C_{D,0} = C_{Na^+,0} = 0.618$ mM, $C_{E,0} = C_{Cl^-,0} = 0.0$, $K_B = K_C = 8.08 \times 10^{-8}$ m/s. It can be calculated that $z = 0.017$ m for $C_A = 0.5C_{A,0}$ if Nernst-Planck diffusion is used, and $z = 0.019$ m for $C_A = 0.5C_{A,0}$ if Fickian diffusion is used, corresponding to an error of 12%. This process is obviously controlled by the lumen mass-transfer rate because $C_{A,R}/C_{z,A} < 0.01$ when $C_A = 0.5C_{A,0}$. The weak effect of Nernst-Planck diffusion can be interpreted by the small difference between D_A and D_E as compared to the extraction of cations by a cation exchanger with H^+ of a high diffusion coefficient as counter ion. As a limitation, when $a = e$ and $D_A = D_E$, the demand of electroneutrality and zero current has naturally been met. Thus, there is no concentration gradient of other inert ions in the radial direction, and the process can be described exactly by Fick's law.

Sometimes a buffer is used to increase the extraction degree in ME or SLM processes (Youn et al., 1995), as for convenient extraction. The extraction of Cu^{2+} by DEHPA from acetic buffered feed is taken as an example. A typical variation of feed concentration in the lumen along the axial direction is given in Figure 3. The simulation using Fick's law almost shows no difference compared to the simulation using Nernst-Planck flux when no buffer is present (curve 4), since the lumen resistance is small due to the low extraction equilibrium coefficient. When a concentrated buffer is used, the extraction rate is high, and the Nernst-Planck diffusion can thus be approximated by a Fickian one (curve 1 to 2) as a result of increasing the ion strength. However, when the buffer concentration is moderate, the effect of Nernst-Planck diffusion becomes significant (curve 3 to 4), and the simplification using Fick's law leads to a negative error of around 45%.

As a result of the Nernst-Planck diffusion, the transport of species with a high molecular diffusion coefficient is retarded while the transport of slower species is accelerated. Usually, D_A is smaller than D_E and the diffusivity of A is enhanced as a result of Nernst-Planck diffusion, thus increasing the amount of A that reaches the interface. The outcome is a higher $C_{C,m,L}$, and therefore a higher mass-transfer rate as compared to that obtained when Fick's law is applied. On the other hand, the diffusivity of E decreases as a result of Nernst-Planck flux. Thus more E builds up at the interface, which leads to a lower $C_{C,m,L}$ and a reduced mass-transfer rate of A as compared to that predicted by Fick's law. The simplification using Fick's law may produce positive errors or negative errors, depending on which effect is dominant, the decrease of $C_{E,R}$ or the increase of $C_{A,R}$.

It must be pointed out that a low extraction equilibrium coefficient does not necessarily imply a large membrane resistance. The resistance that dominates the mass transfer also depends on the relative value of feed concentration to carrier concentration. The extraction of Cd^{2+} by DEHPA is given as an example (Daiminger et al., 1996). The data given by Daiminger et al. (1996) are: $K_1 = 6 \times 10^{-3}$, $C_{A,0} = C_{Cd^{2+},0} =$

0.089 mM (10 mg/L), $C_{C,s} = 0.0$, $u = 0.01$ m/s. When $C_{B,s} = 0.01$ M, it gives $z = 0.0218$ m for $C_{z,A} = 0.5C_{A,0}$ when Nernst-Planck diffusion is used; while $z = 0.0296$ m for $C_{z,A} = 0.5C_{A,0}$ if Fickian diffusion is used, the error is 36%. When $C_{B,s} = 0.02$ M, $z = 0.0195$ m for $C_{z,A} = 0.5C_{A,0}$ according to Nernst-Planck diffusion, whereas $z = 0.028$ m for $C_{z,A} = 0.5C_{A,0}$ if Fickian diffusion is used, the error increases to 44%. Finally when $C_{B,s} = 0.05$ M, Nernst-Planck diffusion leads to $z = 0.0187$ m when $C_{z,A} = 0.5C_{A,0}$, while $z = 0.0276$ m when $C_{z,A} = 0.5C_{A,0}$ for Fickian diffusion, resulting in an error of 48%.

In conclusion, for the extraction of divalent ions, the effect of Nernst-Planck flux is significant when the lumen mass-transfer resistance is dominant. This occurs when the extraction equilibrium constant is high, the extraction equilibrium constant is not high while a buffer of a moderate concentration is used, or the carrier concentration in the membrane phase is high. When the concentrations of other inert ions and buffer are high, or the membrane resistance is high either due to the low extraction equilibrium constant or to the low concentration of carrier impregnated, the effect of Nernst-Planck flux is weak and Fick's law can be used to describe the lumen mass transfer in hollow-fiber ME or SLM processes with a reasonable accuracy.

Trivalent Metal Cation Separation by ME or SLM Processes. The extraction of rare earth metal ions by PC-88A is used as the example of trivalent metal cations. For Er^{3+}, $k = 3.2 \times 10^{-3}$ m/s, $K_1 = 180$, and for Gd^{3+}, $k = 5.7 \times 10^{-6}$ m/s, $K_1 = 3.6$ (Kubota et al., 1995). The membrane mass-transfer coefficients are listed in Table 1. Typical variations of feed concentration in the lumen side along the axial direction are given in Figure 4. It can be seen that the simplification using Fick's law produces a large positive error for Gd^{3+} at a high initial pH value (curves 1 and 2 to curve 3). For instance, when $C_{z,A} = 0.5C_{A,0}$ and Cl^- is the couple ion, the error is around 75%. It can also be seen that using SO_4^{2-} instead of Cl^- provides a lower mass-transfer rate (curve 1 to curve 2, when $C_A = 0.5C_{A,0}$, the difference of z is around 15%). As can be seen from Figure 4, the difference using Nernst-Planck flux and Fick's law for describing the extraction of the highly extractable ion Er^{3+} at a low pH value is small (curve 4 to 5), for instance, when $C_A = 0.5C_{A,0}$, the error is only around 5%. However, the reason is not because the wall resistance becomes significant at a low pH value, which can be seen from high concentration gradient of Er^{3+} in the radial direction, but rather because of the high ion strength relative to Er^{3+} resulting from the high H^+ concentration, thus decreasing the effect of Nernst-Planck diffusion.

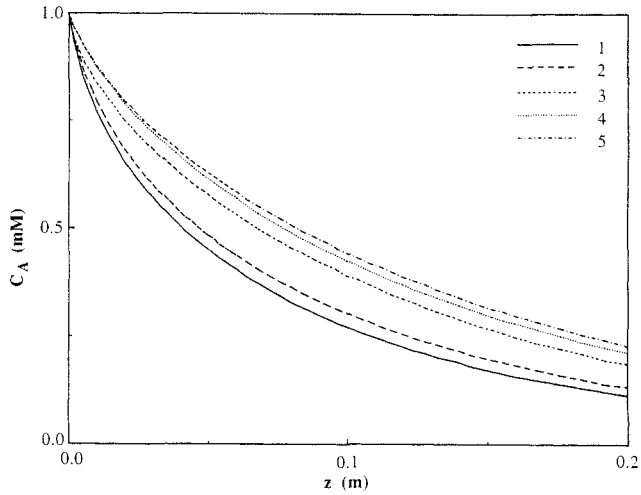

Figure 4. Variation of lumen concentration of rare earth metal ions along the axial direction.

Simulation conditions: ME process, $K_B = 4.3 \times 10^{-6}$ m/s, $K_C = 2.5 \times 10^{-6}$ m/s, $C_{A,0} = 1$ mM, $C_{B,0} = 25$ mM, $C_{C,s} = 0.0$, $u = 0.02$ m/s. For Curve 1: $A = Gd^{3+}$, Nernst-Planck flux, $C_{D,0} = C_{Cl^-,0} = 3.2$ mM, $C_{E,0} = C_{H^-,0} = 0.2$ mM; Curve 2: as above, but $C_{D,0} = C_{SO_4^{2-},0} = 1.6$ mM; Curve 3: as with Curve 1, but Fick flux; Curve 4: $A = Er^{3+}$, Nernst-Planck flux, $C_{D,0} = C_{Cl^-,0} = 18$ mM, $C_{E,0} = C_{H^+,0} = 15$ mM; Curve 5: as with Curve 4, but Fick flux.

As a conclusion, for the practical extraction of rare earth trivalent cations, the effect of Nernst-Planck diffusion is significant because of their low molecular diffusion coefficient and their high charge compared to the counter ions. It is only when the concentration of the other inert ions is very high or the pH value is very low that the effect of Nernst-Planck diffusion can be considered negligible and Fick's law can be used to describe mass transfer in hollow-fiber ME or SLM processes with a reasonable accuracy.

Local Sherwood Number. For hollow-fiber ME or SLM processes where Fick's law is valid, the local Sherwood number of the permeate species through the membrane was described as a function of the dimensionless length z', wall Sherwood number Sh_w, and a third dimensionless parameter (Qin and Cabral, 1998). However, for the cases presented in this paper, Nernst-Planck flux has to be used to describe the diffusion of charged species in the aqueous feed. As a result of the Nernst-Planck flux, the concentration of the counter ion and other charged species in the feed is not uniform in the radial direction. Therefore, the mass transfer of the species of interest in the lumen side is affected by the other

Table 1. Some Values of Parameters Used in the Simulation

i	Ac^-	Ag^+	Cd^{2+}	Cl^-	CrO_4^{2-}	Cu^{2+}	Er^{3+}	Gd^{3+}	HAc
D_i (10^{-9} m^2/s)	1.089	1.648	0.719	2.032	1.132	0.714	0.582	0.597	1.210
i	H^+	Ho^{3+}	K^+	Na^+	NO_3^-	OH^-	Pb^{2+}	SO_4^{2-}	tryptophan
D_i (10^{-9} m^2/s)	9.312	0.589	1.957	1.334	1.902	5.273	0.945	1.065	0.660
n	1	2	3						
$D_{m,B}$ (10^{-9} m^2/s)	0.428	1.0	1.1						
$k_{m,B}$ (10^{-6} m/s)	1.8	4.3	4.7						
$D_{m,C}$ (10^{-9} m^2/s)	0.428	0.584	0.45						
$k_{m,C}$ (10^{-6} m/s)	1.8	2.5	1.9						

The data of D_i are from the *Handbook of Physics and Chemistry*; the data of $D_{m,i}$: $n = 1$ from Coelhoso et al. (1996); $n = 2$ from Daiminger et al. (1996); $n = 3$ from Kubota et al. (1995).

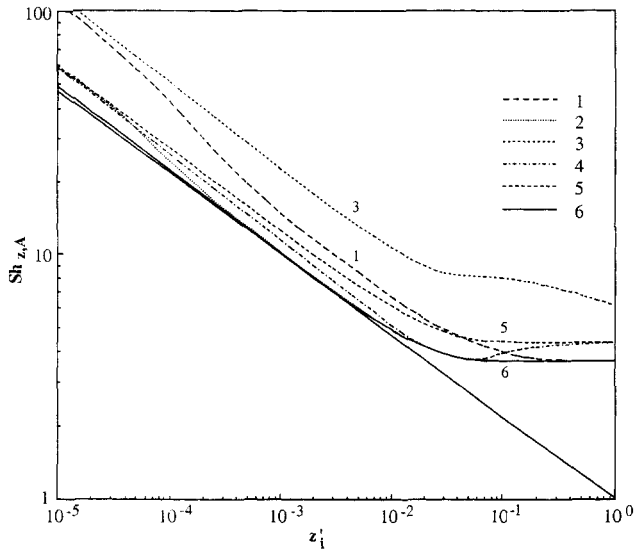

Figure 5. Effect of Nernst-Planck flux on local Sherwood number of Cu^{2+}.

Simulation conditions: ME process, $K_B = 4.7 \times 10^{-6}$ m/s, $K_C = 1.9 \times 10^{-6}$ m/s, $C_{B,0} = 50$ mM, $C_{E,0} = C_{H^+,0} = 0.01$ mM, $C_{C,s} = 0$. For Curve 1: $K_1 = 1.0$, $C_{A,0} = 1$ mM, $C_{D,0} = C_{Cl^-,0} = 2.01$ mM, Nernst-Planck flux; Curve 2: as with Curve 1, Fick flux; Curve 3: $K_1 = 0.01$, $C_{A,0} = 5$ mM, $C_{D,0} = C_{Cl^-,0} = 2.01$ mM, Nernst-Planck flux; Curve 4: as above, Fick flux; Curve 5: linear boundary condition 3, $Sh_w = 0$, Fick flux; Curve 6: linear boundary condition 3, $Sh_w = \infty$, Fick flux, the straight line: the Leveque equation.

charged species, and B.C.3 for the species of interest is coupled with that for the counter ion since the concentration of the counter ion changes along the axial direction. The variations of local Sherwood number of divalent metal cations and of their counter ion, H^+, as a function of their individual dimensionless lengths are shown in Figures 5 and 6, respectively. It can be seen that when Fick's law is used, the values of $Sh_{z,i}$ lie between curves 5 and 6 in both Figures 5 and 6. Curves 5 and 6 are the values of the Sherwood number when Sh_w tends to zero and those when wall Sherwood number Sh_w tends to infinite for linear cases respectively (Qin and Cabral, 1997). However, when the Nernst-Planck diffusion is used, the local Sherwood numbers of the species based on their individual molecular diffusion coefficients are obviously different from those when Fick's law is used (curve 1 to curve 2 and curve 3 to curve 4), whether the wall resistance is low or high (indicated by the used value of extraction equilibrium constant, K_1, in Figure 5). The values obtained by Nernst-Planck diffusion are close to those obtained by Fickian diffusion only when the concentration of the species is low as compared to other charged species. Examples can be found in Figure 5 for divalent metal cations when most of them have been removed at a large z'_i (curve 1 to 2 when $z' > 0.1$), and in Figure 6 for H^+ when its concentration is low at the entrance (curve 3 to 4 when $z' < 10^{-3}$).

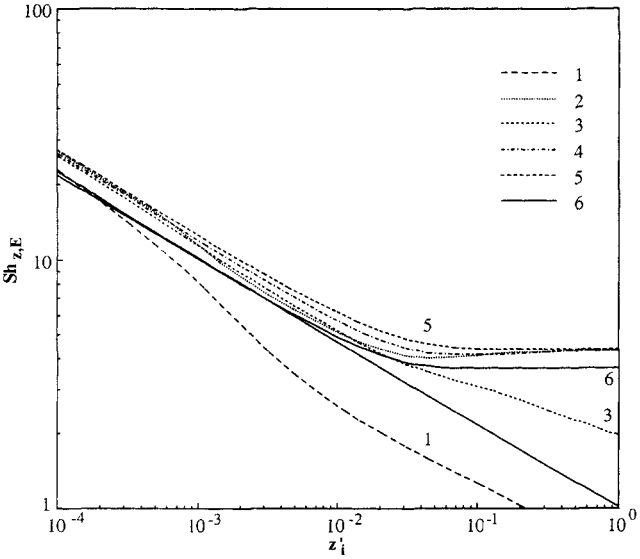

Figure 6. Effect of Nernst-Planck flux on local Sherwood number of H^+.

Simulation conditions are the same as those in Figure 5.

As a conclusion, for ME or SLM processes, when charged species are considered and their molecular diffusion coefficients are significantly different, their local Sherwood numbers, based on their individual molecular diffusion coefficient, even fall out of the scope between the values of the mass-transfer coefficients when Sh_w tends to zero and those when Sh_w tends to infinite for linear cases. Therefore, the correlations such as the Leveque equation do not generally describe the mass transfer of the charged species in the lumen with an appropriate accuracy as shown in Figures 5 and 6.

Influence of Nernst-Planck Diffusion on the Separation of Ion Mixtures. One of the important applications of ME or SLM processes is the separation of ion mixtures (Marr and Draxler, 1992; Kubota et al., 1995). Nernst-Planck diffusion also influences the separation degree. The separation of Pb^{2+} and Cu^{2+} by extraction using DEHPA ($K_1 = 0.1$ for Pb^{2+}, and $K_1 = 0.002$ for Cu^{2+}. Daiminger et al., 1996) can be given as an example, and the separation factor is defined as:

$$\alpha = \frac{N_{Pb^{2+}}|_{r=R} / N_{Cu^{2+}}|_{r=R}}{C_{Pb^{2+},R} / C_{Cu^{2+},R}}. \tag{89}$$

The variation of α along with axial direction as a function of carrier concentration is given in Figure 7. It can be seen that α is largest at the entrance of the module, then rapidly decreases to a minimum value, and gradually increases again. This can be explained as follows: At the entrance, the concentrations of Pb^{2+} and Cu^{2+} are maximum and the pH value is high, thus the carrier is almost saturated with metal ions. Two kinds of metal ions have to compete with each other to be extracted; thus, Pb^{2+} with a high value of K_1 has a higher extraction rate than Cu^{2+}, leading to a higher α. The concentration of Pb^{2+} at the lumen side interface decreases rapidly due to a higher extraction rate of Pb^{2+} to Cu^{2+}, which leads to a minimum value of α; then, when both the concentrations of Pb^{2+} and Cu^{2+} at lumen interface become small, their diffusivity in the lumen feed become relatively important. Since Pb^{2+} has a higher diffusion coefficient than Cu^{2+}, α gradually increases. Therefore, in order to enhance the separation of the ions, the process should be operated in such a mode that the membrane resistance is the rate controlling step. This can be achieved by operating at a low $C_{B,0}$, or a

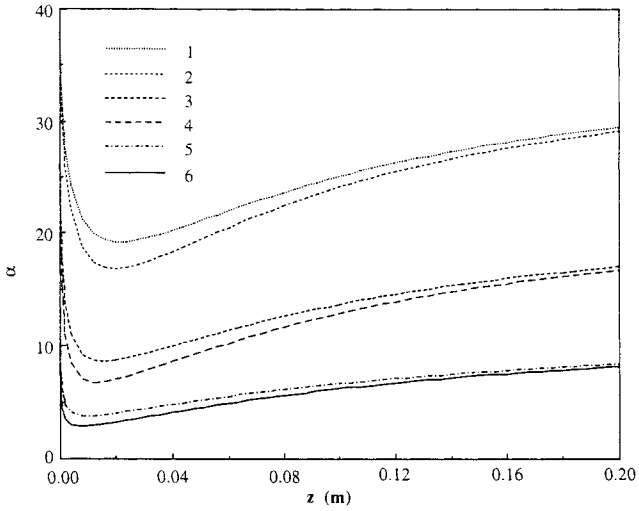

Figure 7. Effect of Nernst-Planck flux on separation factor.

Simulation conditions: ME process, $K_{Pb^{2+}} = 4.3 \times 10^{-6}$ m/s, $K_{Pb\text{-}DEHPA} = K_{Cu\text{-}DEHPA} = 2.5 \times 10^{-6}$ m/s, $C_{Pb^{2+},0} = C_{Cu^{2+},0} = 1$ mM, $C_{E,0} = C_{H^+,0} = 0.01$ mM, $C_{Pb^{2+},s} = C_{Cu^{2+},s} = 0$, $u = 0.02$ m/s. For Curve 1: $C_{B,0} = 25$ mM, Fick flux; Curve 2: as with Curve 1, Nernst-Planck flux; Curve 3: $C_{B,0} = 50$ mM, Fick flux; Curve 4: as above, Nernst-Planck flux; Curve 5: $C_{B,0} = 100$ mM, Fick flux; Curve 6: as above, Nernst-Planck flux.

suitable low pH value, because the separation of ions by ME or SLM processes is based on the difference of their reactive extraction equilibrium or kinetic constants. As shown in Figure 7, when the carrier concentration in the membrane phase decreases, the separation factor increases as a result of the competition metal ions for the carrier. It can also be seen that the prediction of α by Fickian diffusion is obviously deviated from that by Nernst-Planck diffusion. For example, when $C_{z,Pb^{2+}} = 0.5C_{Pb^{2+},0}$, it can be calculated that $z = 0.036$ m and $\alpha = 4.6$ by Nernst-Planck diffusion, while $\alpha = 3.8$ for the same z by Fickian diffusion, the error being around 20%. The simulation results also show that, for a large range of z since the entrance, the concentration of Cu^{2+} ions at the interface is higher than that in the bulk feed in the lumen while Cu^{2+} transfer from the feed in the lumen to the extraction phase in the shell, that is, the ion of a low K_1 value diffuses against its concentration gradient in the feed as a result of Nernst-Planck diffusion, which can not be interpreted by Fickian diffusion.

Conclusions

For hollow-fiber membrane processes such as reactive extraction or carrier-facilitated SLM processes, more than three charged species with significantly different diffusivities are usually considered. For these cases, nonlinear boundary conditions exist at the membrane wall. A mathematical model incorporating Nernst-Planck flux, buffer effect, ion strength, interfacial reaction kinetics and equilibria, diffusivity of species in the membrane phase, shell resistances, and shell concentration, was developed and solved numerically. The studies in the present article led to the following conclusions:

1. Fick's law, which is currently applied widely in the literature, does not properly predict the diffusion behavior of charged species in the aqueous feed through the lumen of hollow-fiber module. When the lumen mass-transfer resistance is dominant, simplification by using Fick's law can result in a large deviation compared to that using Nernst-Planck flux for the prediction of exit concentration or separation factor. For instance, when the feed bulk concentration decreases to half of its initial concentration, the membrane length simulated using Fick's law is 50% higher than that predicted using Nernst-Planck flux for divalent metal cations. The error can be more than 75% for trivalent metal cations.

2. For the above cases, the correlations such as the Leveque equation based on Fick's law do not describe the mass transfer of the charged species in the lumen accurately.

3. When the shell and membrane wall mass-transfer resistances are dominant (e.g., resulting from a low reactive extraction equilibrium constant, a high concentration of counter ion in the lumen feed, a relatively high feed concentration to carrier concentration in the membrane phase), the effect of Nernst-Planck flux in the lumen feed on the mass transport can be ignored.

4. For cotransport processes, when there are only the ions of interest and the couple ions in the feed, Fick's law can be used when an effective diffusion coefficient is used.

5. For the separation of monovalent ions, because of their low charge and/or because the difference between their molecular diffusion coefficients and that of the counter ion is not large, or due to a low reactive equilibrium constant, the effect of Nernst-Planck flux in the lumen feed can be ignored.

6. When the concentration of species of interest is low compared to others (i.e., when there are concentrated buffer or inert ions in the feed), the Fick's law is accurate for describing the lumen mass transfer of species of interest.

7. To improve the mass transfer in the lumen, the use of inert salt ions of high concentration and over-concentrated buffers should be avoided since they can decrease the beneficial effect of the Nernst-Planck diffusion and increase the viscosity of the feed.

8. Couple ions have a significant effect on the mass transfer of the ions. For instance, the couple ions with a high diffusion coefficient increase the lumen mass-transfer rate of the ions of interest. So for the separation of metal cations, chloride or nitrate salts instead of sulfate salts are suggested as the feed due to the higher diffusivity of Cl^- and NO_3^- than that of SO_4^{2-}.

9. The effect of buffer ions on the mass transfer of the species of interest in the radial direction is included in the mathematical model. To our knowledge, this is the first case reported for membrane extractive or supported liquid membrane processes.

10. Due to the size difference of the carrier and the complex formed from the ion and the carrier, they have different diffusion coefficients in the membrane phase. The expression of nonuniform distribution carrier in all the forms is also given for a hollow-fiber SLM process.

11. The consideration of Nernst-Planck diffusion probably improves the accuracy of the reaction extraction equilibrium or kinetic constants obtained from experimental data.

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Notation

C_i = concentration of species i ($i = A, D, E, EG, G, J, L$) in the fluid through the lumen of the hollow fiber module, mM
$C_{i,0}$ = lumen inlet concentration of species i ($i = A, D, E, EG, G, J, L$) at entrance, mM
$C_{i,m,L}$ = concentration of i ($i = B, C$) in membrane phase at lumen interface of the hollow fibers, mM
$C_{i,m,s}$ = concentration of i ($i = B, C$) in membrane phase at outside surface of the hollow fibers, mM
$C_{i,R}$ = concentration of i ($i = A, D, E, EG, G, J, L$) in lumen fluid at lumen interface, mol/m^3 or mM
$C_{i,s}$ = concentration of i ($i = A, D, E$) in bulk shell fluid, mM
$C_{i,s,s}$ = concentration of i ($i = A, D, E$) in shell fluid at fiber outside interface, mM
$C_{z,i}$ = lumen mixed-cup concentration of species i in fiber lumen at z, mM
D_i = molecular diffusion coefficient of species i in lumen fluid, m^2/s
$D_{m,i}$ = molecular diffusion coefficient of species i ($i = B, C$) in membrane phase, m^2/s
k = forward reaction kinetics constant, m/s
$k_{m,i}$ = mass-transfer coefficient of species i ($i = B, C$) through the membrane phase (based on the lumen radius), m/s
$k_{s,i}$ = mass-transfer coefficient of species i ($i = A, B, C, D, E$) through the shell boundary (based on the outside radius of the hollow fiber), m/s
$K_{m,i}$ = mass-transfer coefficient of species i ($i = B, C$) through the membrane and shell boundary (based on the lumen radius of the hollow fiber), m/s
$k_{z,i}$ = local lumen film transfer coefficient of species i ($i = A, E$), m/s
n = stoichiometry
N_i = radial mass-transfer rate, mol/m^2·s
r = radial coordinate, m
R = fiber lumen radius, m
R_1 = fiber outside radius, m
R_i = net reaction rate of species i ($i = E, EG, G$) in the feed, mol/m^3·s
R = interface reaction rate, mol/m^{2}s
u = average velocity in the lumen, m/s
u_z = local velocity in the lumen at r, m/s
z = axial coordinate, m
z_i = charge on species i
z_i' = dimensionless axial coordinate based on the molecular diffusion coefficient of i

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