Lumen Mass Transfer in Hollow-Fiber Membrane Processes with Nonlinear Boundary Conditions

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Hollow-fiber membrane separation or reaction processes, with a nonlinear boundary condition at the lumen interface, are analyzed numerically. Sixteen different nonlinear boundary conditions in the literature were simplified to four dimensionless boundary conditions, in which only two parameters are needed to incorporate the effect on mass transport of membrane and shell resistances, lumen inlet concentration, shell concentration, phase and/or chemical equilibria, and interface reaction kinetics. The lumen mass-transfer coefficients were obtained by solving the continuity mass-conservation equation with the corresponding boundary conditions. The calculated results demonstrate that the lumen mass-transfer coefficient is a function of lumen-inlet concentration and shell concentration, as opposed to the case when a linear boundary condition occurs at the lumen interface. By using the empirical correlations of the lumen local mass-transfer coefficient, an ordinary differential equation substituting a partial differential equation can be applied to obtain the lumen dimensionless mixed-cup concentration with an absolute error of less than 0.005 in most cases, thus making it possible to design and evaluate the hollow-fiber membrane separation or reaction processes.

Introduction

Hollow-fiber modules have been found in almost all membrane applications, because of their high surface area per unit volume and other advantages (Qin et al., 1996). The analysis of mass transfer for hollow-fiber processes has been carried out by using two different approaches. An accurate approach to model hollow-fiber processes consists of considering the velocity and concentration profiles along the hollow fiber by means of the continuity mass-conservation equation and the associated boundary conditions. When a linear boundary condition exists at the wall, analytical solutions are available in the literature (Qin and Cabral, 1997, and references cited therein). The numerical methods and analytical approach have been used to solve the problem of nonlinear boundary conditions (Kim and Stroeve, 1988, 1989; Urtiaga et al., 1992a,b; Alonso et al., 1994; Alonso and Pantelides, 1996; Qin and Cabral, 1996; Qin et al., 1996). The complexity of solving the partial differential equations has been avoided by assuming plug-flow and lumped-lumen mass-transfer effects into a film-type mass-transfer coefficient to describe mass transfer to the membrane lumen wall (Qin and Cabral, 1997, and references cited therein).

In a previous study (Qin and Cabral, 1997), numerical simulations were performed in order to calculate the lumen Sherwood number for a linear boundary condition at the wall. Correlations for the lumen Sherwood number were also provided, which allow for the use of an algebraic equation to determine the lumen mixed-cup concentration, thus avoiding the complexity introduced by the partial differential equation. However, there are several membrane processes presenting nonlinear boundary condition at the wall, for example, (1) dependence of the diffusivity or the solubility of the component on its concentration in a nonporous membrane (Fleming and Slater, 1992). Thus a nonlinear boundary condition may occur for membrane processes such as: permabsorption, gas permeation, pervaporation, perstraction. (2) The nonideality of liquid–vapor equilibrium; thus a nonlinear boundary condition may occur in supported gas membrane (SGM) processes or membrane distillation (Sarti et al., 1993). (3) The nonideality of liquid–liquid equilibrium in supported liquid membrane (SLM) processes or membrane extraction

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(ME) (Urtiaga et al., 1992a, b; Yun et al., 1992; Tompkins et al., 1992). (4) A carrier-facilitated SLM or ME process (Alexander and Callahan, 1987; Kim and Stroeve, 1988, 1989; Haan et al., 1989; Yun et al., 1993; Qin and Cabral, 1996). (5) A nonlinear reaction kinetics at the wall (Guit et al., 1991).

Although the Leveque equation and Skelland's solution of the Graetz problem, strictly valid for a constant lumen-wall concentration and a concentration profile rarely developed, have been used to describe the lumen mass-transfer coefficient for a nonlinear boundary condition at the wall (Alexander and Callahan, 1987; Haan et al., 1989; Tompkins, 1992; Yun et al., 1992, 1993; Sarti et al., 1993; Brookes and Livingston, 1995; Daiminger et al., 1996), their validity has never been analyzed theoretically. Furthermore, the results of accurate numerical analysis (Kim and Stroeve, 1988, 1989; Urtiaga et al., 1992a,b; Qin and Cabral, 1996) show that the exit concentrations are usually given under limited simulating conditions. Thus, these results cannot be directly used to design a hollow-fiber module under other operational conditions, unless the procedure is repeated to solve a partial differential equation.

In this study, we describe a compromise between these two approaches. Numerical simulations are performed to calculate the lumen Sherwood number for hollow-fiber processes with several types of nonlinear boundary conditions at the membrane wall that occur in the literature. By the use of the correlations of the lumen Sherwood number, an ordinary differential equation substituted for a partial differential equation can be applied to calculate the lumen dimensionless mixed-cup concentration, and thus the real concentration.

Theory

Mass-transfer model for the hollow-fiber membrane process with a nonlinear boundary condition at the wall

The membrane separation or reaction processes analyzed in this article, though referenced in the literature using a variety of terms as previously stated, fall in one of two basic categories: Mode A, where there is a phase interface at the lumen surface, which occurs in the SGM or ME process, when the porous membrane is wetted by the shell phase; and Mode B, where there are two phase interfaces at the lumen and shell surfaces of the hollow fiber, respectively. This may be found in SGM and SLM processes, when the porous membrane is impregnated by the third (gas or liquid phase), or pervaporation, gas permeation, permabsorption, and perstraction, when a nonporous membrane is used. The following assumptions are made to describe the fluid flow and the transport of a single component in the lumen of the hollow fibers: (1) the fluid in the lumen is Newtonian and has constant physical properties; (2) the fluid flow through the lumen is a steady, fully developed laminar flow; (3) the concentration of the component of interest in the lumen phase is low, so the mass transport does not affect the volumetric flow rate; (4) the radial transfer of the component follows Fickian diffusion, and the axial diffusion is neglected; (5) the bulk concentration of the component in the shell side and the shell mass-transfer resistance, if not negligible, are treated as constants, which is valid when:

(i) The fluid flow in the shell is in excess (Kim and Stroeve, 1988, 1989);

(ii) The distribution coefficient of the component between the lumen and shell phases is quite small (Alexander and Callahan, 1987; Yun et al., 1992; Tompkins et al., 1992);

(iii) The shell is kept under vacuum (Sarti et al., 1993);

(iv) When an instantaneously irreversible reaction with a concentrated solution of a strong acid or base occurs in the shell (Urtiaga et al., 1992a,b; Qin and Cabral, 1996);

(6) The characteristic of the mass transport at the membrane wall is as described individually in the literature and will be discussed later. Therefore the concentration profiles in the lumen can be established as

$$2u\left[1-\left(\frac{r}{R}\right)^2\right]\frac{\partial C_A}{\partial z}=D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right)\right] \tag{1}$$

$$\text{B.C.1: } C_A=C_{A,0},\qquad z=0,\text{ for all } r \tag{2}$$

$$\text{B.C.2: } \frac{\partial C_A}{\partial r}=0,\qquad r=0,\text{ for all } z. \tag{3}$$

The third boundary condition at the lumen interface (B.C.3) for various practical membrane reaction or separation processes is given in the following section.

Third boundary condition at the lumen interface

Distribution Coefficient Varies Linearly with the Concentration in the Lumen Phase.

Case 1. In some ME or SLM processes, the phase distribution coefficient, m, varies with the concentration in the lumen phase and the relationship can be considered approximately linear (Yun et al., 1992; Urtiaga et al., 1992a,b; Tompkins et al., 1992):

$$m=m_0(1+m_1C_A), \tag{4}$$

where, m_0 and m_1 are empirical parameters. Thus, for Mode B and when the shell resistance is negligible, B.C.3 can be expressed as:

$$\begin{aligned}-D\frac{\partial C_A}{\partial r}&=k_{m,A}(C_{A,m,l}-C_{A,m,s})\\&=k_{m,A}\left[m_0(1+m_1C_{A,R})C_{A,R}-m_0(1+m_1C_{A,s})C_{A,s}\right]\\&=k_{m,A}m_0(C_{A,R}-C_{A,s})\left[1+m_1(C_{A,R}+C_{A,s})\right]\\&\qquad(r=R),\end{aligned} \tag{5}$$

where, $C_{A,m,l}$ and $C_{A,m,s}$ are concentration of A in the membrane phase at lumen surface and in the membrane phase at outside surface, respectively; and $k_{m,A}$ is mass transfer coefficient of A through the membrane wall. Assuming

$$r'=r/R \tag{6}$$

$$z'=zD/4uR^2 \tag{7}$$

$$C'=(C_A-C_{A,s})/(C_{A,0}-C_{A,s}), \tag{8}$$

then, Eq. 5 can be further expressed as

$$\frac{\partial C'}{\partial r'} = -\frac{Rk_{m,A}m_0(1+2m_1C_{A,s})}{D}\left[1+\frac{m_1(C_{A,0}-C_{A,s})}{1+2m_1C_{A,s}}C'\right]C' \qquad (r'=1). \quad (9)$$

Defining:

$$Sh_w = 2Rk_{m,A}m_0(1+2m_1C_{A,s})/D \qquad (10)$$

$$\alpha_1 = m_1(C_{A,0}-C_{A,s})/(1+2m_1C_{A,s}) = (1+2m_1C_{A,0})/2(1+2m_1C_{A,s})-0.5, \qquad (11)$$

where Sh_w is called as wall Sherwood number as in the literature (Kim and Stroeve, 1988, 1989; Urtiaga et al., 1992a,b), and α_1 is a dimensionless parameter. Therefore the dimensionless concentration profiles in the lumen can thus be established as

$$(1-r'^2)\frac{\partial C'}{\partial z'} = \frac{2}{r'}\frac{\partial}{\partial r'}\left(r'\frac{\partial C'}{\partial r'}\right) \qquad (12)$$

$$\text{B.C.1: } C'=1, \qquad z'=0, \text{ for all } r' \qquad (13)$$

$$\text{B.C.2: } \frac{\partial C'}{\partial r}=0, \qquad r'=0, \text{ for all } z' \qquad (14)$$

$$\text{B.C.3: } \frac{\partial C'}{\partial r'} = -\frac{Sh_w}{2}(1+\alpha_1C')C', \qquad r'=1, \text{ for all } z'. \qquad (15)$$

For the other cases discussed later, the definition of r' and z' will be the same, and by the individual definitions of C' as below, the dimensionless form of the differential equation and B.C.1 and B.C.2 do not vary and are given as in Eqs. 12–14.

Urtiaga et al. (1992a,b) obtained dimensionless equations similar to Eqs. 12–15 for an SLM process, assuming, however, that $C_{A,s}=0$. The effect of $C_{A,s}$ on the mass-transfer rate can actually be reflected in the definition of Sh_w and α_1 as in Eqs. 10 and 11.

As seen from Eq. 5, whenever $C_{A,0} > C_{A,s}$ or $C_{A,0} < C_{A,s}$, the value of m_1 is limited by

$$1+m_1(C_{A,R}+C_{A,s}) > 0. \qquad \text{(i)}$$

Since the values of $C_{A,0}$ and $C_{A,s}$, and hence that of $C_{A,R}$, are given freely, it can be established that

$$1+2m_1C_{A,0} > 0, \qquad \text{(ii)}$$

$$1+2m_1C_{A,s} > 0. \qquad \text{(iii)}$$

Therefore, $Sh_w > 0$ and $\alpha_1 > -0.5$. Urtiaga et al. (1992a) have given the numerical results of mixed-cup concentration for $\alpha_1 = 0.9$. This case does not exist practically, however, and the numerical calculations give some misleading results, which are discussed later.

Case 2. When the process just discussed is operated by Mode A, and the effect of shell resistance is included, B.C.3 can be expressed as

$$-D\frac{\partial C_A}{\partial r} = k_{m,A}(C_{A,m,l}-C_{A,m,s}) = k_{s,A}(C_{A,m,s}-C_{A,s}) = \frac{1}{k_{m,A}^{-1}+k_{s,A}^{-1}}(C_{A,m,l}-C_{A,s}) = \frac{1}{k_{m,A}^{-1}+k_{s,A}^{-1}}[m_0(1+m_1C_{A,R})C_{A,R}-C_{A,s}] \qquad (r=R). \quad (16)$$

Assuming

$$C_{A,s} = m_0(1+m_1C'_{A,s})C'_{A,s} \qquad (17)$$

$$C' = (C_A - C'_{A,s})/(C_{A,0}-C'_{A,s}) \qquad (18)$$

$$K_A = 1/(k_{m,A}^{-1}+k_{s,A}^{-1}), \qquad (19)$$

where $C'_{A,s}$ is a supposed concentration of A in equilibrium with $C_{C,s}$. When operated as in Mode B, it does not really exist but can be obtained from Eq. 17. Then, Eq. 16 can be further expressed as

$$\frac{\partial C'}{\partial r'} = -\frac{RK_Am_0(1+2m_1C'_{A,s})}{D}\left[1+\frac{m_1(C_{A,0}-C'_{A,s})}{1+2m_1C'_{A,s}}C'\right]C' \qquad (r'=1). \quad (20)$$

Defining:

$$Sh_w = 2RK_Am_0(1+2m_1C'_{A,s})/D \qquad (21)$$

$$\alpha_1 = m_1(C_{A,0}-C'_{A,s})/(1+2m_1C'_{A,s}). \qquad (22)$$

Thus, the dimensionless form of B.C.3 can also be expressed as by Eq. 15.

Diffusion Coefficient Varies with the Concentration in the Membrane Phase.

Case 3. For some cases of Mode B, a mass-transfer process using a nonporous membrane, the diffusion coefficient of the component in the membrane is usually a function of its concentration in the membrane. When the concentration is low, a linear correlation can be used to describe the relationship between the diffusion coefficient in the membrane, D_m, and the concentration in the membrane (Fleming and Slater, 1992):

$$D_m = D_0(1+D_1C_{A,m}). \qquad (23)$$

By mass balance in the membrane wall:

$$2\pi RN + 2\pi rD_0(1+D_1C_{A,m})\frac{dC_{A,m}}{dr}, \qquad (R \le r \le R_1) \quad (24)$$

where N is the mass-transfer rate through the lumen surface of the hollow-fiber membrane.

Integrating Eq. 24 yields

$$N = \frac{D_0}{R\ln(R_1/R)}\left[(C_{A,m,l}-C_{A,m,s})+\frac{1}{2}D_1(C_{A,m,l}^2-C_{A,m,s}^2)\right]. \qquad (25)$$

Note that $C_{A,m,l} = mC_{A,R}$, and when the shell resistance is negligible, that is, $C_{A,m,s} = mC_{A,s}$, B.C.3 can be expressed as

$$-D\frac{\partial C_A}{\partial r} = N = \frac{mD_0}{R\ln(R_1/R)}(C_{A,R} - C_{A,s}) \times\left[1+\frac{mD_1}{2}(C_{A,R}+C_{A,s})\right] \quad (r=R). \quad (26)$$

Defining C' as by Eq. 8, then the dimensionless form of Eq. 26 is

$$\frac{\partial C'}{\partial r'} = -\frac{mD_0(1+mD_1C_{A,s})}{D\ln(R_1/R)}\left[1+\frac{mD_1(C_{A,0}-C_{A,s})}{2(1+mD_1C_{A,s})}C'\right]C', \quad (r'=1) \quad (27)$$

and defining,

$$Sh_w = 2mD_0(1+mD_1C_{A,s})/D\ln(R_1/R) \quad (28)$$

$$\alpha_1 = mD_1(C_{A,0}-C_{A,s})/2(1+mD_1C_{A,s}) = (1+mD_1C_{A,0})/2(1+mD_1C_{A,s}) - 0.5. \quad (29)$$

Thus, Eq. 27 can be reduced to Eq. 15. From Eq. 26 it can be seen that whenever $C_{A,0} > C_{A,s}$ or $C_{A,0} < C_{A,s}$, the value of D_1 is limited by

$$1 + 0.5mD_1(C_{A,R} + C_{A,s}) > 0. \quad \text{(iv)}$$

As the values of $C_{A,0}$ and $C_{A,s}$, and hence that of $C_{A,R}$, are given freely, we get

$$1 + mD_1C_{A,0} > 0 \quad \text{(v)}$$

$$1 + mD_1C_{A,s} > 0, \quad \text{(vi)}$$

and so $Sh_w > 0$ and $\alpha_1 > -0.5$ by their definition.

Facilitated Transport (viz., Carrier) Through the Membrane while the Phase and/or Chemical Equilibrium Is Maintained at the Interface(s). When a carrier is used to facilitate the mass transport through a porous or nonporous membrane, the following assumptions are added to ensure the validity of Eq. 1: (1) the carrier and the carrier–solute complex formed are present only in the membrane phase; (2) the interfacial reaction rate is so fast compared to the mass-transfer rate that the local chemical equilibrium is maintained—several examples of this case are referred to in the literature (Lee et al., 1993; Alonso et al., 1994; Youn et al., 1995; Daiminger et al., 1996; Qin and Cabral, 1996); (3) distribution of the component in the membrane phase without the carrier is small and thus the passive diffusion through the membrane can be ignored, which is valid for many species, such as the inorganic ions, organic acid ions, and Penicillin G (Alexander and Callahan, 1987; Haan et al., 1989; Basu and Sirkar, 1991; Yun et al., 1993; Lee et al., 1993; Alonso et al., 1994; Youn et al., 1995; Daiminger et al., 1996; Qin and Cabral, 1996); (4) the mass transport of the component in the lumen is not affected by the others.

The symbolic representation of reversible equilibrium interfacial complexation reactions under consideration are, respectively,

$$A + nB = C \qquad K_1 \quad (30)$$

$$A^a + \left|\frac{a}{d}\right|D^d + nB = C \qquad K_2 \quad (31)$$

$$A^a + nB = C + \frac{a}{e}E^e. \qquad K_3 \quad (32)$$

Examples of Eqs. 30–32 can be found in the literature (for Eq. 30: Kim and Stroeve, 1988; Basu and Sirkar, 1991; Sikdar and Sawant, 1994; for Eq. 31: Kim and Stroeve, 1989; Lee et al., 1993; Yun et al., 1993; for Eq. 32: Yun et al., 1993; Alonso et al., 1994; Youn et al., 1995; Qin and Cabral, 1996). In Eqs. 30–32 A is the permeate species of interest in the lumen fluid, B is the carrier in the membrane, C is the complex in the membrane formed from A and B, D is the component in the lumen fluid taking part in the interface reaction, and E is the component in the lumen formed by the interface reaction, and superscripts, a, d, and e are the charge of the species A, D, and E, respectively. If the process is an SLM, permabsorption, or perstraction process, the reverse reaction of Eqs. 30–32 occurs in the shell interface.

The interfacial chemical equilibria can be expressed as

$$K_1 = C_C/C_AC_B^n \quad (33)$$

$$K_2 = C_C/C_AC_B^nC_D^{|a/d|} \quad (34)$$

$$K_3 = C_CC_E^{|a/e|}/C_AC_B^n. \quad (35)$$

Furthermore, for an SLM process, the following relationship is valid (Qin and Cabral, 1998):

$$(C_{B,m,l} + nC_{C,m,l}) + [(C_{B,m,s} + nC_{C,m,s}) - (C_{B,m,l} + nC_{C,m,l})]\left[\frac{R_1^2}{R_1^2 - R^2} - \frac{1}{2}\,\frac{1}{\ln(R_1/R)}\right] = C_{B.0}, \quad (36)$$

where $C_{B,0}$ is the initial concentration of the carrier without complexion. When the molecular weight of B is far higher than that of A, and when $n = 1$, B and C can be assumed to have the same diffusivity in the membrane phase. Thus Eq. 36 reduced to (Qin and Cabral, 1998)

$$C_{B,m,l} + C_{C,m,l} = C_{B,m,s} + C_{C,m,s} = C_{B,0}. \quad (37)$$

Case 4. In the case of Eq. 30, when $n = 1$ for Mode B, and the shell resistance is negligible, combining with Eqs. 33 and 37, B.C.3 can be expressed and rearranged as

$$-D\frac{\partial C_A}{\partial r} = k_{m,C}(C_{C,m,l} - C_{C,s}) = k_{m,C}K_1C_{B,0}\left(\frac{C_{A,R}}{1+K_1C_{A,R}} - \frac{C_{A,s}}{1+K_1C_{A,s}}\right). \quad (38)$$

Defining the dimensionless concentration as by Eq. 8, Eq. 38 can be further expressed as

$$\frac{\partial C'}{\partial r'} = -\frac{Rk_{m,C}K_1C_{B,0}}{D(1+K_1C_{A,s})^2}\,\frac{C'}{1+\dfrac{C_{A,0}-C_{A,s}}{1+K_1C_{A,s}}K_1C'} \qquad (r'=1), \tag{39}$$

and defining

$$Sh_w = 2Rk_{m,C}K_1C_{B,0}/D(1+K_1C_{A,s})^2 \tag{40}$$

$$\alpha^2 = K_1(C_{A,0}-C_{A,s})/(1+K_1C_{A,s})$$
$$= (C_{A,0}/C_{A,s}-1)/(1+1/K_1C_{A,s}). \tag{41}$$

Thus, the dimensionless form of B.C.3 can be expressed as

$$\frac{\partial C'}{\partial r'} = -\frac{Sh_w}{2}\,\frac{C'}{1+\alpha_2 C'}. \tag{42}$$

From Eqs. 40 and 41 it can be seen that $Sh_w > 0$, and when $C_{A,0} < C_{A,s}$, $\alpha_2 < 0$ and the minimum value of α_2 is -1 when $C_{A,s} \to \infty$.

Case 5. When the process just discussed is operated by Mode A, B.C.3 can be expressed as

$$-D\frac{\partial C_A}{\partial r} = k_{m,C}(C_{C,m,l}-C_{C,m,s})$$
$$= k_{s,C}(C_{C,m,s}-C_{C,s}) = \frac{1}{k_{m,C}^{-1}+k_{s,C}^{-1}}(C_{C,m,l}-C_{C,s})$$
$$= \frac{1}{k_{m,C}^{-1}+k_{s,C}^{-1}}\left(\frac{K_1C_{B,0}C_{A,R}}{1+K_1C_{A,R}}-C_{C,s}\right). \tag{43}$$

Assuming

$$C_{C,s} = K_1C_{B,0}C'_{A,s}/(1+K_1C'_{A,s}) \tag{44}$$

$$K_C = 1/(k_{m,C}^{-1}+k_{s,C}^{-1}), \tag{45}$$

$C'_{A,s}$ does not really exist, it can be obtained from Eq. 44. By replacing $C_{A,s}$ with $C'_{A,s}$, $k_{m,C}$ with K_C in the definition of C', Sh_w, and α_2 as in Eqs. 8, 40 and 41, respectively, the dimensionless form of Eq. 43 can be expressed exactly as in Eq. 42.

Kim and Stroeve (1988) obtained the same B.C.3 as Eq. 42 for an ME process, assuming, however, that $C_{A,s} = 0$. The effect of $C_{A,s}$ on the mass-transfer rate can actually be reflected in the definition of Sh_w and α_1 as in Eqs. 40 and 41.

Case 6. Considering Eqs. 31 and 34 when $|a| = |d| = n = 1$, for Mode B, when C_D is constant and the shell resistance is negligible, B.C.3 can be expressed as

$$-D\frac{\partial C_A}{\partial r} = k_{m,C}(C_{C,m,l}-C_{C,s})$$
$$= k_{m,C}K_2C_{B,0}\left(\frac{C_DC_{A,R}}{1+K_2C_DC_{A,R}}-\frac{C_{D,s}C_{A,s}}{1+K_2C_{D,s}C_{A,s}}\right). \tag{46}$$

Equation 46 is valid when subscript D represents either H^+ or OH^-, and the feed is at an extreme pH value or it contains a concentrated buffer (Lee et al., 1993; Qin and Cabral, 1998). Assuming

$$C' = (C_A - C_{A,s}C_{D,s}/C_D)/(C_{A,0}-C_{A,s}C_{D,s}/C_D) \tag{47}$$

then

$$\frac{\partial C'}{\partial r'} = -\frac{Rk_{m,C}K_2C_{B,0}C_D}{D(1+K_2C_{A,s}C_{D,s})^2}\,\frac{C'}{1+\dfrac{C_{A,0}-C_{A,s}C_{D,s}/C_D}{1+K_2C_{A,s}C_{D,s}}K_2C'}. \tag{48}$$

Defining

$$Sh_w = 2Rk_{m,C}K_2C_{B,0}C_D/D(1+K_2C_{A,s}C_{D,s})^2 \tag{49}$$

$$\alpha_2 = K_2(C_{A,0}-C_{A,s}C_{D,s}/C_D)/(1+K_2C_{A,s}C_{D,s})$$
$$= (C_{A,0}C_D/C_{A,s}C_{D,s}-1)/(1+C_D/K_2C_{A,s}C_{D,s}). \tag{50}$$

Thus, the dimensionless form of B.C.3 can exactly be expressed as in Eq. 42. From Eq. 49 it can be seen that $Sh_w > 0$, and from Eq. 50 it can be seen that when $C_DC_{A,0} < C_{D,s}C_{A,s}$, $\alpha_2 < 0$, and that the minimum value of α_2 is -1 when $C_D/C_{D,s}C_{A,s} \to 0$.

Case 7. When the process just discussed is operated by Mode A, B.C.3 can be expressed as

$$-D\frac{\partial C_A}{\partial r} = k_{m,C}(C_{C,m,l}-C_{C,m,s})$$
$$= k_{s,C}(C_{C,m,s}-C_{C,s}) = \frac{1}{k_{m,C}^{-1}+k_{s,C}^{-1}}(C_{C,m,l}-C_{C,s})$$
$$= K_C\left(\frac{K_2C_{B,0}C_DC_{A,R}}{1+K_2C_DC_{A,R}}-C_{C,s}\right) \qquad (r=R). \tag{51}$$

Assuming

$$C_{C,s} = K_2C_{B,0}C_DC'_{A,s}/(1+K_2C_{D,s}C'_{A,s}), \tag{52}$$

and replacing $C_{A,s}$ with $C'_{A,s}$, $k_{m,C}$ with K_C in the definition of C', Sh_w, and α_2 in Eqs. 47, 49, and 50, the dimensionless form of Eq. 51 can be expressed exactly as in Eq. 42.

Case 8. Considering Eq. 32, when $|a| = |e| = n = 1$, for Mode B, when C_E is constant and the shell resistance is negligible, B.C.3 can be expressed and rearranged as

$$-D\frac{\partial C_A}{\partial r} = k_{m,C}(C_{C,m,l}-C_{C,s})$$
$$= k_{m,C}K_3C_{B,0}\left(\frac{C_{A,R}/C_E}{1+K_3C_{A,R}/C_E}-\frac{C_{A,s}/C_{E,s}}{1+K_3C_{A,s}/C_{E,s}}\right). \tag{53}$$

Assuming

$$C' = (C_A - C_{A,s}C_E/C_{E,s})/(C_{A,0}-C_{A,s}C_E/C_{E,s}), \tag{54}$$

then

$$\frac{\partial C'}{\partial r'} = -\frac{Rk_{m,C}K_3C_{B,0}/C_E}{D(1+K_3C_{A,s}/C_{E,s})^2}\,\frac{C'}{1+\dfrac{C_{A,0}-C_{A,s}C_E/C_{E,s}}{1+K_3C_{A,s}C_E/C_{E,s}}K_3C'}. \qquad (r'=1) \quad (55)$$

Defining

$$Sh_w = 2Rk_{m,C}K_3C_{B,0}/DC_E(1+K_3C_{A,s}/C_{E,s})^2 \quad (56)$$

$$\alpha^2 = \frac{K_3(C_{A,0}-C_{A,s}C_E/C_{E,s})}{1+K_3C_{A,s}/C_{E,s}} = \frac{C_{A,0}C_{E,s}/C_{A,s}C_E - 1}{C_{E,s}/K_3C_{A,s}C_E + 1}. \quad (57)$$

Thus, the dimensionless form of B.C.3 can also be expressed as in Eq. 42. From Eq. 56 it can be seen that $Sh_w > 0$. From Eq. 57 it can be seen that when $C_{E,s}C_{A,0} < C_EC_{A,s}$, $\alpha_2 < 0$ and the minimum value of α_2 is -1 when $C_{E,s}/C_{A,s}C_E \to 0$.

Case 9. When the process just discussed is operated by Mode A, B.C.3 can be expressed as

$$\begin{aligned} -D\frac{\partial C_A}{\partial r} &= k_{m,C}(C_{C,m,l}-C_{C,m,s}) = k_{s,C}(C_{C,m,s}-C_{C,s}) \\ &= K_C(C_{C,m,l}-C_{C,s}) \\ &= K_C\left(\frac{K_3C_{B,0}C_{A,R}/C_E}{1+K_3C_{A,R}/C_E} - C_{C,s}\right) \qquad (r=R). \quad (58) \end{aligned}$$

Assuming

$$C_{C,s} = (K_3C_{B,0}C'_{A,s}/C_{E,s})/(1+K_3C'_{A,s}/C_{E,s}), \quad (59)$$

from Eq. 59, $C'_{A,s}$ can be obtained. By replacing $C_{A,s}$ with $C'_{A,s}$, and $k_{m,C}$ with K_C in the definition of C', Sh_w, and α^2 as in Eqs. 54, 56, and 57, the dimensionless form of Eq. 58 can exactly be expressed as in Eq. 42.

Case 10. Considering Eq. 31, when $|a| = |d| = n = 1$, $C_{A,s} = 0$, $C_{A,0} = C_{D,0}$ (Kim and Stroeve, 1989a), the diffusion coefficient of D is equal to that of A as a result of Nernst–Planck diffusion (Qin and Cabral, 1998), and $C_A = C_D$ in the lumen feed. When the shell resistance and shell concentration of A are negligible, B.C.3 can be expressed as

$$-D\frac{\partial C_A}{\partial r} = k_{m,C}C_{C,m,l} = \frac{k_{m,C}K_2C_{B,0}C_{A,R}^2}{1+K_2C_{A,R}^2} \qquad \text{(for Modes A and B)}. \quad (60)$$

Assuming

$$C' = C_A/C_{A,0}, \quad (61)$$

then

$$\frac{\partial C'}{\partial r'} = -\frac{Rk_{m,C}K_2C_{A,0}C_{B,0}}{D}\,\frac{C'^2}{1+K_2C_{A,0}^2C'^2}. \quad (62)$$

Defining:

$$Sh_w = 2Rk_{m,C}K_2C_{A,0}C_{B,0}/D \quad (63)$$

$$\alpha_3 = K_2C_{A,0}^2. \quad (64)$$

Thus, the dimensionless form of B.C.3 can also be rewritten as

$$\frac{\partial C'}{\partial r'} = -\frac{Sh_w}{2}\,\frac{C'^2}{1+\alpha_3C'^2}. \quad (65)$$

From Eqs. 63 and 64 it can be seen that $Sh_w > 0$, and $\alpha_3 > 0$.

Case 11. For case of Eq. 32 when operated as an SLM process, $|a| = 2$, $|e| = 1$, $n = 2$, $C_E =$ constant, the shell resistance is negligible, and $C_{A,s} = 0$, B.C.3 can be expressed as:

$$-D\frac{\partial C_A}{\partial r} = k_{m,C}C_{C,m,l}. \quad (66)$$

By mass balance

$$k_{m,B}(C_{B,s}-C_{B,m,l}) = 2k_{m,C}C_{C,m,l}. \quad (67)$$

From Eqs. 35, 36, and 67, $C_{C,m,l}$ can be solved. Thus Eq. 66 can be expressed as (Qin and Cabral, 1998)

$$-D\frac{\partial C_A}{\partial r} = \frac{2k_{m,C}K_3C_{B,0}^2C_{A,R}/C_E^2}{1+2\beta K_3C_{B,0}C_{A,R}/C_E^2+\sqrt{1+4\beta K_3C_{B,0}C_{A,R}/C_E^2}}, \quad (68)$$

where,

$$\beta = 2+\chi(\gamma-2) \quad (69)$$

$$\chi = \frac{R_1^2}{R_1^2-R^2} - \frac{1}{2}\,\frac{1}{\ln(R_1/R)} \quad (70)$$

$$\gamma = \frac{2k_{m,C}}{k_{m,B}}. \quad (71)$$

Assuming

$$C' = C_A/C_{A,0} \quad (72)$$

$$Sh_w = 2Rk_{m,C}K_3C_{B,0}^2C_{A,0}/DC_E^2 \quad (73)$$

$$\alpha_4 = 2\beta K_3C_{A,0}C_{B,0}/C_E^2. \quad (74)$$

Thus, B.C.3 can also be expressed as

$$\frac{\partial C'}{\partial r'} = -\frac{Sh_w}{2}\,\frac{C'}{\left(1+\alpha_4C'+\sqrt{1+2\alpha_4C'}\right)/2}. \quad (75)$$

From Eq. 73 it can be seen $Sh_w > 0$. Usually, $k_{m,B} > k_{m,C}$ (Youn et al., 1995; Daiminger et al., 1996). Thus $0 < \gamma < 2$, $-2 < \gamma - 2 < 0$, and from Eq. 70, it can be concluded that

$1 > \chi > 0.5$, so, $2 + \chi(\gamma - 2) > 0$, $\beta > 0$. So $\alpha_4 > 0$, as seen from Eq. 74.

Case 12. When the process just discussed is operated by Mode A, the shell resistances are constants, $C_{C,s} = 0$, and $C_{B,s}$ = constant, B.C.3 can be expressed as

$$-D\frac{\partial C_A}{\partial r} = k_{m,C}(C_{C,m,l} - C_{C,m,s}) = k_{s,C}C_{C,m,s} = K_C C_{C,m,l}. \tag{76}$$

By mass balance,

$$K_B(C_{B,s} - C_{B,m,l}) = 2K_C C_{C,m,l}. \tag{77}$$

Combining with Eq. 35, B.C.3 can be rewritten as

$$-D\frac{\partial C_A}{\partial r} = \frac{2K_C K_3 C_{B,s}^2 C_{A,R}/C_E^2}{1 + 2\eta K_3 C_{B,s} C_{A,R}/C_E^2 + \sqrt{1 + 4\eta K_3 C_{B,s} C_{A,R}/C_E^2}}, \tag{78}$$

where

$$\eta = 2K_C/K_B. \tag{79}$$

Equations 1–3 and 78 are valid when Cu^{2+} are separated by an ME process (Daiminger et al., 1996), when a concentrated buffer is used, or when CrO_4^{2-} are separated by an MBE process (Alonso et al., 1994) when concentrations of Cl^- and ion strength are high. Since Fick's law is valid in these cases (Qin and Cabral, 1988). By defining C', Sh_w, and α_4 as in Eqs. 72–74, respectively, but replacing $k_{m,C}$ with K_C, β with η, the dimensionless form of Eq. 78 can be exactly expressed by Eq. 75.

Case 13. One case of the ME process may include a porous hydrophilic membrane and an organic phase containing a carrier that passes through the lumen while an aqueous phase passes through the shell. Taking Eq. 30 as an example, when $n = 1$, Eqs. 1–3 are valid as well, but in which C_A should be replaced by C_C, B.C.3 can be expressed and arranged as

$$\begin{aligned} -D\frac{\partial C_C}{\partial r} &= k_{m,A}(C_{A,m,l} - C_{A,m,s}) = k_{s,A}(C_{A,m,s} - C_{A,s}) \\ &= \frac{1}{k_{m,A}^{-1} + k_{s,A}^{-1}}(C_{A,m,l} - C_{A,s}) \\ &= K_A\left(\frac{C_{C,R}}{K_1(C_{B,0} - C_{C,R})} - C_{A,s}\right). \end{aligned} \tag{80}$$

Assuming

$$C_{A,s} = C'_{C,s}/K_1(C_{B,0} - C'_{C,s}) \tag{81}$$

$$C' = (C_C - C'_{C,s})/(C_{C,0} - C'_{C,s}), \tag{82}$$

then, Eq. 80 can be further expressed as

$$\frac{\partial C'}{\partial r'} = -\frac{RK_A C_{B,0}}{DK_1(C_{B,0} - C'_{C,s})^2}\,\frac{C'}{1 - \dfrac{C_{C,0} - C'_{C,s}}{C_{B,0} - C'_{C,s}}C'}, \tag{83}$$

and defining

$$Sh_w = 2RK_A C_{B,0}/DK_1(C_{B,0} - C'_{C,s})^2 \tag{84}$$

$$\begin{aligned} \alpha_2 &= -(C_{C,0} - C'_{C,s})/(C_{B,0} - C'_{C,s}) \\ &= (C_{B,0} - C_{C,0})/(C_{B,0} - C'_{C,s}) - 1. \end{aligned} \tag{85}$$

Thus, the dimensionless form of B.C.3 can be exactly expressed as in Eq. 42 and $Sh_w > 0$, $\alpha_2 > -1$ (because $C_{B,0} > C_{C,0}$ and $C_{B,0} > C'_{C,s}$).

Nonlinear Chemical Reaction Kinetics at the Membrane Lumen Surface.

Case 14. A hydrophilic hollow-fiber module can be used as a bioreactor. Using a lipase immobilized on the lumen surface, the organic phase containing the substrate flows through the lumen while the aqueous phase flows through the shell side. The hydrolysis kinetics of triglycerides can be described by the Michaelis–Menten equation (Guit et al., 1991). When the resistance in both the membrane and shell is negligible, B.C.3 can be expressed as

$$-D\frac{\partial C_A}{\partial r} = \frac{V_{\max} C_{A,R}}{K_M + C_{A,R}}, \tag{86}$$

where $V_{\max}$ is the maximum reaction rate and K_M is the Michaelis–Menten constant. By using definition of dimensionless concentration as in Eq. 61, then,

$$\frac{\partial C'}{\partial r'} = -\frac{RV_{\max}}{DK_M}\,\frac{C'}{1 + \dfrac{C_{A,0}}{K_M}C'} \tag{87}$$

Defining

$$Sh_w = 2RV_{\max}/DK_M \tag{88}$$

$$\alpha_2 = C_{A,0}/K_M. \tag{89}$$

Hence B.C.3 can be expressed as in Eq. 42. From Eqs. 88 and 89 it can be seen that $Sh_w > 0$, and $\alpha_2 > 0$.

Case 15. When C_u^{2+} is separated from an aqueous solution through the lumen by an ME or SLM process, the interfacial reaction can be expressed by Eq. 32 ($a = n = 2$, $e = 1$), and kinetics can be expressed as (Haan et al., 1989; Yun et al., 1993)

$$r = k'(C_{A,R}C_{B,m,l}/C_{E,R} - C_{C,m,l}C_{E,R}/K_3 C_{B,m,l}). \tag{90}$$

When the reverse reaction is negligible and the pH value in the feed is maintained constant by a concentrated buffer, Fick's law is valid, and the interfacial reaction rate can be rewritten as

$$r = kC_{A,R}C_{B,m,l}. \tag{91}$$

When the preceding process is operated as an SLM process and the effect of shell side is negligible, the boundary condition at the lumen interface is

$$-D\frac{\partial C_A}{\partial r} = kC_{A,R}C_{B,m,l} = k_{m,C}C_{C,m,l} \qquad \text{(for Mode B).} \tag{92}$$

Combined with Eqs. 36 and 67, Eq. 92 can be arranged as

$$-D\frac{\partial C_A}{\partial r} = \frac{k_{m,C}kC_{A,R}C_{B,0}}{k_{m,C}+\beta kC_{A,R}} \tag{93}$$

where β is defined by Eq. 69. By assuming C' as in Eq. 61 and defining

$$Sh_w = 2RkC_{B,0}/D \tag{94}$$

$$\alpha_2 = \beta kC_{A,0}/k_{m,C}, \tag{95}$$

Eq. 93 can be reduced to Eq. 42, and $Sh_w > 0$, and $\alpha_2 > 0$.

Case 16. When the process just discussed is operated as an ME process, and $C_{B,s} =$ constant, $C_{C,s} =$ constant, B.C.3 can be expressed as

$$-D\frac{\partial C_A}{\partial r} = kC_{A,R}C_{B,R} = K_C(C_{C,m,l} - C_{C,s}), \tag{96}$$

and by mass balance,

$$2K_C(C_{C,m,l} - C_{C,s}) = K_B(C_{B,s} - C_{B,m,l}). \tag{97}$$

Thus, Eq. 96 can be rewritten as

$$-D\frac{\partial C_A}{\partial r} = \frac{K_B kC_{A,R}C_{B,s}}{K_B + 2kC_{A,R}}. \tag{98}$$

From Eq. 98 it can be seen that when the reverse reaction at the lumen interface can be neglected, the mass transfer rate of A is independent of the values of K_C and $C_{C,s}$. By definition of C', Sh_w and α_2 as by Eqs. 61, 94, and 95 (but β in Eq. 95 is replaced by unit 1), Eq. 98 can be reduced to Eq. 42, and $Sh_w > 0$, and $\alpha_2 > 0$.

If only one phase interface is present at the outside surface of the hollow fibers, and if the shell resistance is negligible and the concentration of the components in the shell is zero, B.C.3 at the lumen surface is linear whether or not a carrier is used in the shell. This case has been described in an earlier article (Qin and Cabral, 1997). If the shell resistance and the shell concentration are treated as constants, while the phase distribution coefficient is not a constant or a carrier is used in the shell phase, three or more parameters are needed in the dimensionless form of B.C.3, which is beyond the scope of the present article.

Results and Discussion

As a summary, the dimensionless boundary conditions and the examples suitably described by them are listed in Table 1. From the definition of five dimensionless parameters r', z', C', Sh_w, and α_i $(i = 1, 2, 3, 4)$, it can be seen that all the effects of the hollow-fiber characteristics and operation conditions on the mass-transfer rate, such as the lumen diameter and wall thickness of the hollow fiber, the module length, the mass-transfer coefficients through the membrane wall and the shell side, the phase and chemical equilibrium constants or kinetics constants, the flow rate through the lumen; the entrance concentration of the permeate species, the diffusion coefficient of the component in the lumen, the concentration of the facilitating carrier in the membrane phase, the concentration of the permeate component in the shell, and the concentration of another reactant or product in the lumen and shell, were included.

The preceding equation cannot be solved analytically, and the method of orthogonal collocation on finite elements in the r' direction was applied to convert the partial differential equation into a set of coupled ordinary differential equations. Solving these equations in the z'-direction by the Runge-Kutta method yields C' at any point within the lumen or on the lumen surface of the hollow fiber (Qin and Cabral, 1997). Other interesting values, for example, the dimensionless mixed-cup concentration C'_z, the local lumen Sherwood number, Sh_z, at any z', can be obtained as follows (Kim and Stroeve, 1988; Qin et al., 1997):

$$C'_z = 4\int_0^1 (1 - r'^2)r'C'\,dr' \tag{99}$$

$$Sh_z = \frac{2RK_z}{D} = -2\frac{\partial C'}{\partial r'}\bigg|_{r'=1} \Big/ (C'_z - C'_R) = Sh_w C'_R/(C'_z - C'_R). \tag{100}$$

From Eqs. 12–14 and Eqs. 1–4 in Table 1, it can be seen that C' is a function of r', z', Sh_w, and α_i. Thus C'_z and Sh_z are functions of z', Sh_w, and α_i, and thus functions of $C_{A,0}$ and $C_{A,s}$. This is compared to the case where a linear boundary condition exists at the lumen interface, and C'_z and Sh_z are independent of $C_{A,0}$ and $C_{A,s}$ (Qin and Cabral, 1997). It can also be concluded that, for a certain type of hollow fiber and given lumen and shell fluids (i.e., R, D, Sh_w, and α_i remain unchanged), C'_z will be the same for the same mean retention time, z/u (thus an unvaried z'). This conclusion remains true for a system where B.C.3 at the wall is a more complex function of concentrations, but independent of z.

Effect of α_i on lumen mass-transfer coefficient Sh_z

The effective wall Sherwood number, $Sh'_{w,i}$, is introduced to describe the effect of wall concentration on the wall resistance, and is defined for four types as

$$Sh'_{w,1} = Sh_w(1 + \alpha_1 C'_R) \tag{101}$$

$$Sh'_{w,2} = Sh_w/(1 + \alpha_2 C'_R) \tag{102}$$

$$Sh'_{w,3} = Sh_w C'_R/(1 + \alpha_3 C'^2_R) \tag{103}$$

$$Sh'_{w,4} = 2Sh_w/\left(1 + \alpha_4 C'_R + \sqrt{1 + 2\alpha_4 C'_R}\right). \tag{104}$$

Table 1. Various Dimensionless Boundary Conditions at the Hollow-Fiber Wall and Some Examples Suitable to be Described by Them

Type	Boundary Condition at $r = R$	Operation Mode	Examples*	Remark
1	$-\frac{Sh_w}{2}(1+\alpha_1 C')C'$	SLM	Urtiaga et al., 1992a,b	$\alpha_1 > -0.5$
		MD	Sarti et al., 1993	
		MBE	Yun et al., 1992; Tompkins et al., 1992	
		SGM**		
		Pervaporation**		
		Vapor permeation**		
		Premaborption**		
		Perstraction**	Brookes and Livingston, 1995	
2	$-\frac{Sh_w}{2}\frac{C'}{1+\alpha_2 C'}$	SLM	Haan et al., 1989; Lee et al., 1993; Qin and Cabral, 1996	$\alpha_2 > -1$
		MBE	Kim and Stroeve, 1988; Yun et al., 1993	
		Bioreactor pervaporation		
		Gas permeation		
		Premaborption		
		Perstraction	Sikdar and Sawant, 1994	
		Facilitated transport through fixed carrier membranes or a solvent swollen membranes		
3	$-\frac{Sh_w}{2}\frac{C'^2}{1-\alpha_3 C'^2}$	MBE	Kim and Stroeve, 1989	$\alpha_3 > 0$
4	$-\frac{Sh_w}{2}\frac{C'}{1+\alpha_4 C'+\sqrt{1+2\alpha_4 C'}}$	SLM	Youn et al., 1995	$\alpha_4 > 0$
		MBE	Alonso et al., 1994; Yun et al., 1993; Daiminger et al., 1996	

*Only if the membrane is used as a hollow-fiber module.

**Diffusion coefficient in the membrane is a linear function of its concentration in the membrane, or the phase-distribution equilibrium constant is a linear function of its concentration in the lumen phase.

From Eqs. 101–104, $Sh'_{w,i,0}$, the value of $Sh'_{w,i}$ at $z' = 0$, $C' = C'_R = 1$, and $Sh'_{w,i,\infty}$, the value of $Sh'_{w,i}$ at $z' = +\infty$, $C' = C'_R = 0$, can be obtained, respectively.

The typical variation of Sh_z with Sh_w and α_i are given in Figures 1–6. It must be noticed that the difference of Sh_z for a given value of Sh_w and α_i to Sh_z at $Sh_w = +\infty$ and $\alpha_i = 0$ instead of Sh_z is used as the Y-axis, in order to make the figures more clear. It can be seen that, for all four types, Sh_z tends to a constant, $Sh_{i,\infty}$, when z' is large, and the value of z' where Sh_z tends to the constant varies from 0.1 to 10 depending on the type of B.C.3 and the values of Sh_w and α_i. $Sh_{i,\infty}$ is equal to $Sh_\infty(Sh'_{w,i,\infty})$, the Sherwood number for linear boundary condition at the wall when $Sh_w = Sh'_{w,i,\infty}$, even when $Sh'_{w,3,\infty} = 0$ (type 3, as seen from Figure 5).

It can be seen from Figures 2, 3, 5, and 6 that, when $\alpha_i > 0$ for types 2, 3, and 4, and when $\alpha_1 < 0$ for type 1, Sh_z is higher than that when $\alpha_i = 0$. This is similar to the linear

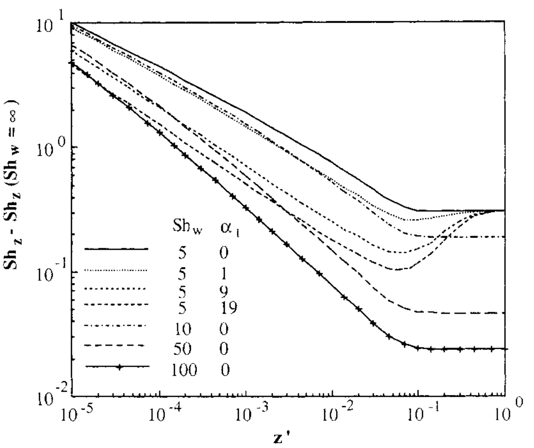

Figure 1. Variation of Sh_z with z' at various values of α_1.

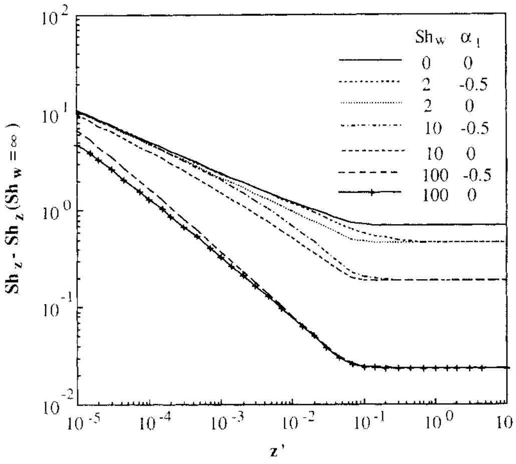

Figure 2. Variation of Sh_z with z' at various values of α_1.

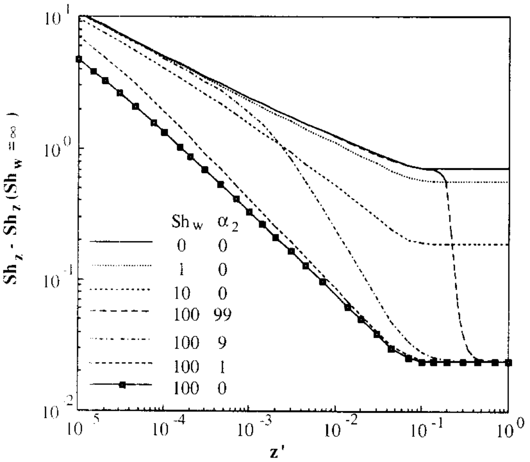

Figure 3. Variation of Sh_z with z' at various values of α_2.

case that, for a certain z', Sh_z increases when Sh_w decreases (Qin and Cabral, 1997), because $Sh'_{w,i}$ is lower than Sh_w. Furthermore, it can be seen that within a certain distance from the entrance, for some cases, Sh_z is even higher than $Sh_z(Sh'_{w,i,0})$, the local Sherwood number for linear boundary condition when $Sh_w = Sh'_{w,i,0}$, but it is always lower than $Sh_z(0)$, the local Sherwood number for linear boundary condition when $Sh_w = 0$ (see Figures 2, 3, 5, and 6). In contrast, when $\alpha_i > 0$ for type 1 and $\alpha_2 < 0$ for type 2. Sh_z is lower than that when $\alpha_i = 0$ (see Figures 1 and 4). This is similar to the linear case that, for a certain z', Sh_z decreases when Sh_w increases. Besides, it is also noticeable that within a certain distance from the entrance, in some cases, Sh_z is even lower than $Sh_z(Sh'_{w,i})$, but higher than $Sh_z(+\infty)$, the local Sherwood number for the linear boundary condition when $Sh_w = \pm\infty$. Thus, it can be concluded that for types 1, 2, 3, and 4, the values of Sh_z are always between $Sh_z(0)$ and $Sh_z(+\infty)$ for any given valid values of Sh_w and α_i ($i = 1, 2, 3, 4$). If a value less than -0.5 is taken for α_1, the value of Sh_z is higher than $Sh_z(0)$. However, this case is not found in practice, as indicated before.

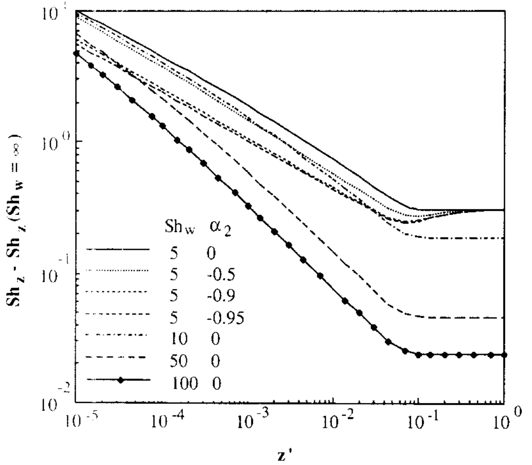

Figure 4. Variation of Sh_z with z' at various values of α_2.

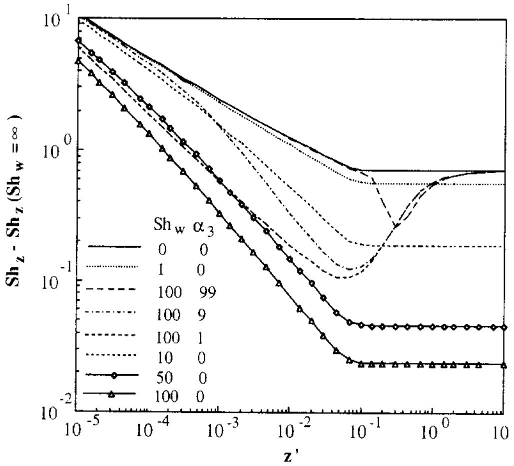

Figure 5. Variation of Sh_z with z' at various values of α_3.

Simplified model for calculating the mixed-cup concentration

By solving the dimensionless form of the partial differential equation and the corresponding nonlinear boundary conditions, the dimensionless mixed-cup concentration can be obtained at a set of given values of z', Sh_w, and α_i. Thus a real mixed-cup concentration can be obtained for a given operation. In order to ensure an accurate solution for the entrance region, however, many finite elements in the radial direction and the very small size of the step in the z'-direction have to be used (Kim and Stroeve, 1988; Urtiaga et al., 1992a,b; Qin and Cabral, 1997). In an earlier article (Qin and Cabral, 1997), for the linear case, the logarithmic averaged lumen Sherwood number is introduced as a function of z' and Sh_w. An algebraic equation can thus be used to substitute the partial differential equation to obtain the lumen mixed-cup concentration. For the nonlinear cases, however, the preliminary calculation results demonstrate that it is difficult to describe the average Sherwood number as a function of z', Sh_w, and α_i. Nevertheless, by the use of the local Sher-

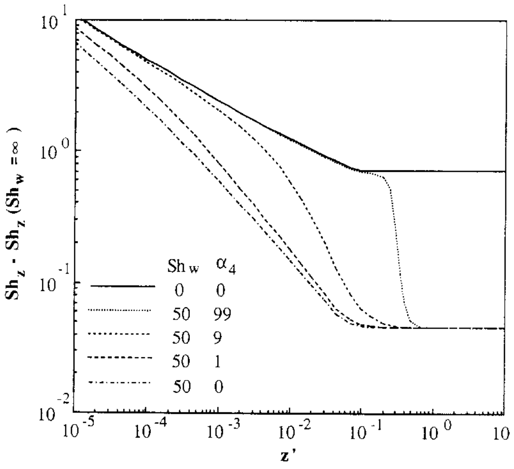

Figure 6. Variation of Sh_z with z' at various values of α_4.

wood number, Sh_z, the ordinary differential equation can substitute for the partial differential equation to obtain the lumen mixed-cup concentration. By macroscopic mass balance, the dimensionless form of the mass conservative equation suitable for all 16 cases mentioned earlier is established:

$$\frac{dC'}{dz'} = -4Sh_z(C' - C'_R). \tag{105}$$

By mass balance,

$$Sh_z(C' - C'_R) = Sh_w C'_R(1 + \alpha_1 C'_R) \qquad \text{(Type 1)} \tag{106}$$

$$Sh_z(C' - C'_R) = Sh_w C'_R/(1 + \alpha_2 C'_R) \qquad \text{(Type 2)} \tag{107}$$

$$Sh_z(C' - C'_R) = Sh_w C'^2_R/(1 + \alpha_3 C'^2_R) \qquad \text{(Type 3)} \tag{108}$$

$$Sh_z(C' - C'_R) = Sh_w C'_R/0.5\left(1 + \alpha_4 C'_R + \sqrt{1 + 2\alpha_4 C'_R}\right) \qquad \text{(Type 4)}. \tag{109}$$

The initial condition is

$$C' = 1, \quad \text{when} \quad z' = 0 \tag{110}$$

From Eqs. 106–109 C'_R can be expressed as an explicit function of C' or can be obtained numerically. The key lies on the calculation of Sh_z, since it is a function of z', Sh_w, and α_i as concluded before. For linear cases, Sh_z is correlated as (Qin and Cabral, 1997):

$$Sh_z = \left[\left(\alpha z'^{\beta}\right)^{5.1} + Sh_\infty^{5.1}\right]^{1/5.1}, \tag{111}$$

where

$$Sh_\infty = -0.288\ \mathrm{arctg}\{1.56[\log(Sh_w) - 0.583]\} + 4.01, \tag{112}$$

when $0.1 \leq Sh_w \leq 1{,}000$,

$$\begin{aligned}\alpha = {} & 1.20 - 7.57\times10^{-2}\log(Sh_w) - 1.14\times10^{-1}[\log(Sh_w)]^2 \\ & - 1.45\times10^{-2}[\log(Sh_w)]^3 + 4.55\times10^{-2}[\log(Sh_w)]^4 \\ & - 9.46\times10^{-3}[\log(Sh_w)]^5\end{aligned} \tag{113}$$

$$\begin{aligned}\beta = {} & -0.338 - 5.52\times10^{-3}\log(Sh_w) - 9.71\times10^{-3}[\log(Sh_w)]^2 \\ & - 8.02\times10^{-4}[\log(Sh_w)]^3 + 4.591\times10^{-3}[\log(Sh_w)]^4 \\ & - 1.04\times10^{-3}[\log(Sh_w)]^5.\end{aligned} \tag{114}$$

when $Sh_w \leq 0.1$, $\alpha = 1.23$, $\beta = -0.337$, and when $Sh_w \geq 1{,}000$, $\alpha = 0.954$, $\beta = -0.342$.

$Sh'_{w,i}$ is used to replace Sh_w in the preceding correlations to calculate Sh_z as a function of z', but since C'_R is not known in advance, a trial-and-error method has to be used. Nevertheless, if the fourth-order varied-step Runge-Kutta method is used, the trial-and-error method does not provide additional difficulty in integrating Eq. 105. However, as concluded in the previous section, when $\alpha_i > 0$ for types 2, 3, and 4, and when $\alpha_1 < 0$ for type 1, Sh_z is even higher than $Sh_z(Sh'_{w,i,0})$ at the entrance. In this case, the values of C' obtained by solving the ordinary differential equation is higher than those obtained by solving the partial differential equation; and when $\alpha_2 < 0$ for type 2 and when $\alpha_1 > 0$ for type 1, Sh_z is even lower than $Sh_z(Sh'_{w,i,0})$ at the entrance. In this case, the values of C' obtained by solving the ordinary differential equation are lower than those obtained by solving the partial differential equation. So it seems that a higher value should be used to substitute C'_R in Eqs. 101–104 to calculate $Sh'_{w,i}$. The following correlations greatly improve the accuracy of Sh_z, and thus of C'_z, when $Sh''_{w,i}$ replaces Sh_w in Eqs. 111–114 to calculate Sh_z:

$$Sh''_{w,1} = Sh_w\left(1 + \alpha_1\sqrt{C'_R}\right) \qquad \text{(Type 1)} \tag{115}$$

$$Sh''_{w,2} = Sh_w/\left(1 + \alpha_2\sqrt{C'_R}\right) \qquad \text{(Type 2)} \tag{116}$$

$$Sh''_{w,3} = Sh_w\sqrt{C'_R}/(1 + \alpha_3 C'_R) \qquad \text{(Type 3)} \tag{117}$$

$$Sh''_{w,4} = Sh_w/0.5\left(1 + \alpha_4\sqrt{C'_R} + \sqrt{1 + 2\alpha_4\sqrt{C'_R}}\right) \qquad \text{(Type 4)} \tag{118}$$

Using the preceding correlations, the calculation of C'_z for a wide range of Sh_w and α_i shows that the error of C'_z obtained by solving the ordinary differential equation as compared to the one obtained when solving the partial differential equation is very small. For types 1, 2, 3, and 4, the maximum absolute error of C' is usually less than 0.005. Only in some particular situations, for example, when $Sh_w > 1{,}000$ and $\alpha_i > 100$ ($i = 2,3,4$), the maximum absolute error is higher than 0.005 but still less than 0.01. Some results of the mixed-cup concentration calculated for different values of Sh_z and α_i are shown in Table 2. As a comparison, the local form of the Leveque equation and the correlation of $Sh_z(+\infty)$ obtained in an earlier work (Qin and Cabral, 1997) are also used to calculate Sh_z. It can be seen that the use of Eqs. 115–118 greatly improved the accuracy of C'_z.

Conclusion

Among the applications of hollow-fiber membrane processes, are some cases where a nonlinear boundary condition exists at the membrane wall. By introducing dimensionless parameters, 16 different nonlinear boundary conditions found in the literature are simplified to 4 dimensionless boundary conditions. Furthermore only two parameters are needed to incorporate the effect of membrane and shell resistances, the lumen inlet concentration, the carrier concentration, the shell concentration, the phase or/and chemical equilibria, and the interface reaction kinetics, on mass transport. The lumen mass-transfer coefficients are obtained by solving numerically the continuity mass-conservation equation with the corresponding boundary conditions. The results demonstrate that the lumen mass-transfer coefficient is a function of lumen inlet concentration and shell concentration as well as wall and shell resistances, as opposed to the case where a linear boundary condition occurs at the lumen interface. The lumen local Sherwood number Sh_z is soundly influenced by the second parameter α_i, for example, and even Sh_z increases with

Table 2. The Simulation Results of Mixed-Cup Concentration for Various Values of Sh_w and α_i

	$Sh_w = 5,\ \alpha_1 = 19$				$Sh_w = 1000,\ \alpha_2 = 100$				$Sh_w = 100,\ \alpha_3 = 9$				$Sh_w = 50,\ \alpha_4 = 9$			
z'	*	**	***	****	*	**	***	****	*	**	***	****	*	**	***	****
0.001	0.9577	0.9572	0.9596	0.9579	0.9611	0.9614	0.9619	0.9615	0.9693	0.9695	0.9711	0.9704	0.9755	0.9755	0.9762	0.9759
0.002	0.9313	0.9307	0.9343	0.9312	0.9253	0.9278	0.9299	0.9280	0.9453	0.9455	0.9489	0.9473	0.9533	0.9536	0.9553	0.9546
0.004	0.8897	0.8892	0.8942	0.8891	0.8710	0.8762	0.8798	0.8750	0.9059	0.9060	0.9122	0.9089	0.9132	0.9142	0.9181	0.9162
0.007	0.8400	0.8399	0.8463	0.8391	0.8102	0.8172	0.8214	0.8136	0.8577	0.8577	0.8670	0.8619	0.8608	0.8629	0.8698	0.8664
0.010	0.7982	0.7981	0.8060	0.7977	0.7609	0.7689	0.7733	0.7640	0.8170	0.8168	0.8284	0.8222	0.8149	0.8179	0.8274	0.8229
0.015	0.7389	0.7401	0.7483	0.7401	0.6928	0.7017	0.7057	0.6966	0.7588	0.7584	0.7725	0.7664	0.7485	0.7526	0.7652	0.7606
0.020	0.6879	0.6895	0.6982	0.6919	0.6356	0.6445	0.6482	0.6414	0.7087	0.7079	0.7237	0.7191	0.6913	0.6957	0.7104	0.7073
0.025	0.6429	0.6444	0.6535	0.6502	0.5857	0.5941	0.5974	0.5945	0.6643	0.6629	0.6797	0.6779	0.6407	0.6449	0.6609	0.6608
0.030	0.6022	0.6036	0.6128	0.6133	0.5413	0.5489	0.5518	0.5537	0.6241	0.6222	0.6396	0.6414	0.5952	0.5989	0.6157	0.6195
0.035	0.5651	0.5662	0.5754	0.5804	0.5012	0.5079	0.5105	0.5177	0.5874	0.5849	0.6027	0.6086	0.5538	0.5569	0.5741	0.5826
0.040	0.5310	0.5317	0.5409	0.5505	0.4646	0.4703	0.4727	0.4855	0.5536	0.5506	0.5684	0.5788	0.5159	0.5181	0.5356	0.5491
0.045	0.4994	0.4997	0.5088	0.5233	0.4311	0.4359	0.4381	0.4566	0.5222	0.5187	0.5366	0.5516	0.4810	0.4823	0.4999	0.5187
0.050	0.4700	0.4700	0.4790	0.4984	0.4002	0.4042	0.4061	0.4303	0.4931	0.4892	0.5069	0.5266	0.4487	0.4492	0.4666	0.4909
0.060	0.4171	0.4165	0.4254	0.4541	0.3454	0.3479	0.3495	0.3843	0.4406	0.4359	0.4532	0.4821	0.3908	0.3901	0.4069	0.4416
0.070	0.3708	0.3699	0.3784	0.4157	0.2983	0.2998	0.3012	0.3454	0.3944	0.3895	0.4062	0.4436	0.3341	0.3389	0.3550	0.3994
0.080	0.3302	0.3291	0.3373	0.3823	0.2577	0.2585	0.2596	0.3119	0.3538	0.3488	0.3647	0.4098	0.2970	0.2946	0.3098	0.3627
0.090	0.2944	0.2932	0.3011	0.3527	0.2275	0.2231	0.2240	0.2829	0.3180	0.3131	0.3282	0.3799	0.2590	0.2561	0.2703	0.3306
0.100	0.2627	0.2617	0.2691	0.3265	0.1925	0.1925	0.1932	0.2575	0.2863	02.816	0.2959	0.3532	0.2258	0.2227	0.2359	0.3023
0.120	0.2101	0.2092	0.2159	0.2817	0.1438	0.1435	0.1440	0.2152	0.2333	0.2293	0.2418	0.3078	0.1716	0.1685	0.1756	0.2546
0.140	0.1687	0.1681	0.1741	0.2451	0.1074	0.1070	0.1074	0.1816	0.1915	0.1882	0.1991	0.3271	0.1304	0.1276	0.1367	0.2165
0.160	0.1360	0.1358	0.1411	0.2147	0.0825	0.0798	0.0801	0.1545	0.1583	0.1557	0.1652	0.2395	0.0991	0.9066	0.1042	0.1853
0.200	0.0895	0.0897	0.0938	0.1675	0.0448	10.0445	0.0446	0.1139	0.1108	0.1092	0.1164	0.1911	0.0571	0.0554	0.0604	0.1382
0.250	0.0541	0.0545	0.0575	0.1256	0.0216	0.0214	0.0215	0.0799	0.0740	0.0733	0.0784	0.1480	0.0287	0.0277	0.0305	0.0982
0.300	0.0333	0.0338	0.0359	0.0961	0.0104	0.0103	0.0104	0.0574	0.0517	0.5158	0.0552	0.1173	0.0144	0.0138	0.0154	0.0713
0.400	0.0131	0.0134	0.0146	0.0586	0.0024	0.0024	0.0024	0.0312	0.0286	0.2883	0.0307	0.0778	0.0036	0.0035	0.0039	0.0394
Δ		0.0008	0.0067	0.0342		0.0034	0.0051	0.0330		0.0022	0.0097	0.0381		0.0022	0.0112	0.0424
$\Delta_{\max}$		0.0016	0.0106	0.0787		0.0089	0.0129	0.0742		0.0050	0.0152	0.0812		0.0044	0.0206	0.0862

*Solving partial differential equations.

**Solving ordinary differential equation using Eqs. 116–122.

***Using correlation of Sh_z when $Sh_w = +\infty$.

****Using the local form of Leveque equation $Sh_z = 1.007z'^{-1/3}$; Δ: the average error of C'; $\Delta_{\max}$: the maximum error of C'.

z'. However, it can be concluded from the results that for types 1, 2, 3, and 4, the values of Sh_z for any given valid value of Sh_w and α_i are always between the values of local mass-transfer coefficients when the wall Sherwood number tends to zero and when the wall Sherwood number tends to infinite. By the use of the empirical correlations for Sh_z, the ordinary differential equation can be used instead of the partial differential equation in order to obtain the lumen dimensionless mixed-cup concentration with an absolute error of less than 0.005 in most cases, thus facilitating the design and evaluation of the hollow-fiber membrane separation or reaction processes.

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Notation

C' = dimensionless concentration of the permeate component A in fiber lumen
$C_{A,0}$ = inlet concentration of component A in the lumen at fiber entrance, M
$C_{A,R}$ = concentration of component A in the lumen fluid at lumen interface, M
C_i = concentration of component i ($i = A$, D, or E) in the fluid through the lumen, M
$C_{i,m}$ = concentration of component i ($i = A$, B, C) in the membrane phase, M
$C_{i,s}$ = bulk concentration of component i ($i = A$, B, C, D, or E) in the shell fluid, M
C_z = mixed-cup concentration of the component in fiber lumen at z, M
C'_z = dimensionless lumen mixed-cup concentration of the component at z'
D = molecular diffusion coefficient of component A in the lumen fluid, m^2/s
$k_{s,i}$ = mass-transfer coefficient of component i through the shell, m/s
K_i = mass-transfer coefficient of component i through the membrane wall and shell, m/s
K_z = local lumen film-transfer coefficient at z, m/s
n = stoichiometry
r = radial coordinate, m
r' = dimensionless radial coordinate
R = fiber lumen radius, m
Sh_∞ = Sherwood number when $z' \to +\infty$
u = average velocity in the lumen, m/s
z = axial coordinate, m
z' = dimensionless axial coordinate

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