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EFFECT OF VARIABLE DIFFUSIVITY AND SOLUBILITY UNDER DIFFERENT FLOW CONDITIONS ON MASS TRANSFER IN HOLLOW FIBERS

Summary. The mixing-cup concentration for hollow-fiber membrane is investigated under different flow conditions (parabolic flow and plug flow) and at different concentration dependent diffusivity and solubility. The results show significant effect of flow conditions on the concentration in the hollow fiber. Similarly the variable diffusivity and solubility have significant influence on the process.

WPŁYW ZMIAN DYFUZYJNOŚCI I ROZPUSZCZALNOŚCI W RÓŻNYCH WARUNKACH PRZEPŁYWU NA TRANSPORT MASY W MEMBRANACH KAPILARNYCH

Streszczenie. Badano rozkłady stężenia z uwzględnieniem mikromieszania w modułach kapilarnych dla różnych warunków przepływu (laminarny i burzliwy) oraz przy różnych stężeniach zależnych od dyfuzyjności i rozpuszczalności. Wyniki pokazały znaczący wpływ warunków przepływowych na stężenie w modułach kapilarnych. Podobnie, zmienna dyfuzyjność i rozpuszczalność mają istotny wpływ na proces membranowy.

Introduction

Membrane based mass separation processes are of considerable interest in the areas of dialysis, extraction, membrane distillation, pervaporation, pertraction, gas separation, etc. Mass transfer rates attainable in membrane separation devices are, in most cases, limited by solute transport through the membrane layer. It is assumed in this paper that the mass transport oc-

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curs by diffusion through the membrane layer. Efficiency of a membrane separation thus depends on the flow conditions inside the membrane tube and the diffusion conditions, i.e. on membrane structures, interaction between membrane material and the solute, etc. The velocity and concentration profiles along the hollow fiber can be obtained by means of the continuity mass-conservation equation and the associated boundary conditions. When linear boundary conditions exists at the wall, analytical solutions are available in the literature. For non-linear conditions, those are our cases, only numerical solution can be obtained [1, 2].

For modeling the flow conditions and mass transport through the membrane it is assumed that:

- axial diffusion in the lumen side can be neglected,
- diffusion coefficient in the membrane (D_m) is concentration dependent,
- equilibrium distribution coefficient (H_m) can linearly change as a function of solute concentration,
- shell side mass transfer resistance is neglected,
- concentration in the shell side is equal to zero for our simulation
- two flow conditions are to be taken into account:

Model A: the flow through the cylindrical core is laminar with a parabolic velocity on radial position,

Model B: plug flow in the cylindrical tube.

Practically, the most of literature use the parabolic velocity profile in the whole length of fibers. From chemical engineering point of view the plug flow would be desired, because this is more effective. Otherwise, form of the parabolic profile needs a part of the fiber length. Comparison of these two models seems to be very useful for the cases investigated in this paper. Similar results we do not know in the literature.

Theory

The continuity mass conservation equation is generally used with given velocity profile along the hollow fiber for the analysis of mass transfer in hollow-fiber processes.

The mass balance equations for the lumen side and for the membrane are as follows, respectively (dimensionless form, steady-state conditions):

$$\frac{1}{R}\frac{\partial}{\partial R}\left(R\frac{\partial A}{\partial R}\right) = t\left(1-R^2\right)\frac{\partial A}{\partial Z}$$
(1)

$$\frac{1}{R}\frac{\partial}{\partial R}\left(RD_{m}\frac{\partial A_{m}}{\partial R}\right) = 0$$
⁽²⁾

where

$$R = \frac{r}{R^*}; \qquad Z = \frac{z}{L}; \qquad t = \frac{2u_{max}R^{+2}}{DL} \qquad A = \frac{a}{a_{in}} \qquad A_m = \frac{a_m}{H_m a_{in}}$$

In the case of plug flow:

$$\frac{1}{R}\frac{\partial}{\partial R}\left(R\frac{\partial A}{\partial R}\right) = u_{ave}\frac{\partial A}{\partial Z}$$
(3)

where

$$u_{ave} = 2 \int_{0}^{R^{*}} u_{max} \left(1 - R^{2} \right) \frac{2R\pi}{R^{*2}\pi} dR = u_{max}$$
(4)

Boundary conditions for differential equations (1) and (3):

$$A=1, Z=0, \text{ for all } R$$
(5a)

$$\frac{\partial A}{\partial R} = 0$$
, R=0, for all Z (5b)

$$D\frac{\partial A}{\partial R} = D_m H_m \frac{\partial A_m}{\partial R}$$
, R=1, for all Z (5c)

Determination on the third boundary condition (Eq. 5c) can be obtained by means of Eq. (2) Four different types of concentration dependence will be discussed below:

D_m(A) with two given functions and one with general function,

 $H_m(A)$ with a given function.

Let us look the mass transfer rates at the membrane interface, at R=1 for the five different cases:

Case 1.: linear dependency of the diffusion coefficient on the solute concentration in the membrane:

$$D_m = D_{mo}(1 + pA_m) \tag{6}$$

When the concentration is low, a linear correlation can often be used to describe the relationship between the concentration in the membrane (Qin and Cabral, 1998). The parameter p is the dimensionless slope of Eq. (6), it takes into account the dependency of the diffusion coefficient on the solute concentration in the membrane. The mass transfer rate through the lumen surface, j, can be obtained by solving the following equation:

$$-2\pi R^{*} j = 2\pi R a_{in} H_{m} \left(D_{mo} \left[1 + pA_{m} \right] \right) \frac{\partial A_{m}}{\partial R}$$
(7)

This equation is valid for every point of the membrane. Integrating of Eq. (7) yields:

$$j = k_{m} s H_{m} \left(A_{N} - A_{\delta} \right) \left(1 + \frac{p}{2} \left(A_{N} + A_{\delta} \right) \right) a_{in}$$
(8)

According to the third boundary condition in Eq. (5c), you can get it as follows:

$$-\frac{\partial A}{\partial R} = j\frac{R^*}{D} = Sh_W sq(A_N - A_\delta)$$
(9)

where

$$\operatorname{Sh}_{\mathbf{w}} = \frac{\operatorname{k}_{\mathrm{m}}\operatorname{sRH}}{\operatorname{D}}; \ \operatorname{s} = \frac{\delta}{\operatorname{R}\ln\left(1 + \frac{\delta}{\operatorname{R}}\right)}; \ \operatorname{k}_{\mathrm{m}} = \frac{\operatorname{D}_{\mathrm{mo}}}{\delta};$$

and

$$q = \frac{H_m}{H} \left(1 + \frac{p}{2} (A_N + A_\delta) \right)$$

Note that $H_m/H=1$ when p =0 (see Eq. 12), i. e. if the distribution coefficient is constant.

Case 2 .: exponential function of diffusion coefficient on concentration:

$$D_m = D_{mo} e^{pA_m} \tag{10}$$

After integrating Eq. (7) with the use of Eq. (10) we obtained:

$$-\frac{\partial A}{\partial R} = Sh_{w}s\frac{H_{m}}{Hp}\left(e^{pA}N - e^{pA}\delta\right)$$
(11)

Case 3.:the linear dependency of the distribution coefficient in dimensionless form can be given as:

$$H_{m}=H(1+p^{*}A_{N})$$
(12)

For the concentration gradient at membrane interface one can get in this case as:

$$-\frac{\partial A}{\partial R} = Sh_{W}s\left(1 + p^{*}A_{N}\right)A_{N}$$
(13)

Case 4: $D_m(A_m)$ is a general function, thus, integration of Eq. (7) is not possible analytically. In this case the differential quotient at the membrane interface can only be given after numerical solution of Eq. (2). For it the concentration distribution inside the membrane shall also be calculated. One needs it for the calculation of the $D_m(A_m)$ function.

An analytical approach is developed for the solution the differential Eq. (2) with nonlinear, boundary conditions. Essential of the method is that the membrane layer is divided into M sections in the directions of r. In these sections the above differential equations are regarded as ordinary differential equation with constant parameters. The boundary conditions at the border between sections:

$$A_{m,n} = A_{m,n+1}$$
 as well as $D_{m,n} \frac{\partial A_{m,n}}{\partial R} = D_{m,n+1} \frac{\partial A_{m,n+1}}{\partial R}$, at $R = R_n$ (14)

Indexes n, n+1 represent two neighboring sections. For the sake of simplicity we give here the concentration distribution for plane membrane layer (if $R \rightarrow \infty$, here $R=r/\delta$):

$$A_{m,n} = T_n R + B_n, R_i \leq R \leq R_{i+1}$$
(15)

where

$$T_{n} = \frac{A_{N} - A_{\delta}}{D_{m,n} \sum_{i=1}^{N} \frac{1}{D_{m,i}}}; B_{n} = A_{N} - T_{n} (n-1)\Delta R + \sum_{i=1}^{n-1} T_{i};$$

The value of A_m can also be obtained in the case of cylindrical coordinate though its function is much complex in the membrane layer.

From Eq. (15) the differential quotient can be obtained as follows:

$$-\frac{\mathrm{dA}}{\mathrm{dR}} = \frac{\mathrm{D}_{\mathrm{m},\mathrm{l}}}{\mathrm{D}}\mathrm{T}_{\mathrm{l}} \tag{16}$$

Knowing the $D_m(A_m)$ function, one calculates the concentration distribution through the membrane, using Eq. (15), repeatedly until the correct diffusion coefficients are used for the calculation.

The other possibility here is the integration of Eq. (7) as it was made in the former cases [3]:

$$-\frac{\partial A}{\partial R} = \frac{R^*}{\delta D} H_m s \int_{A_m} \frac{A_m (R^* + \delta)}{D_m (A_m) \partial A_m}$$
(17)

 $A_m(R^*)$ and $A_m(R^*+\delta)$ represent the membrane concentration on membrane interfaces at R=R^{*} and R=R+ δ , respectively. The above integration can be carried out numerically. Disadvantage of this method is that the concentration distribution can not be determined.

Results and discussion

Knowing the mass transfer rates on the membrane interface in the lumen side (Eqs. 9, 11, 123, 16, 17) the solute concentration in the hollow fiber can now be calculated by the solution of the differential equation (1) or (3) with the boundary conditions (5a) to (5c). The solution was made by numerical integration using finite difference method [4]. The concentration dependency of the diffusivity and the distribution coefficient was taken into account by iteration. The parameter values used for calculations are listed in Table 1.

Table 1

R [*] =100 μm	$u_{max} = 5 \times 10^{-2} \text{ m/s}$	H=1-5	δ=100 μm
L=0.6 m	$D=1x10^{-9} m^2/s$	$k_m = 5 \times 10^{-6} \text{ m/s}$	Sh _w =0.5

Parameter values used for calculations



Fig.1. Mixing-cup concentration with Z for Sh_w=0.5 (k_m=5x10⁻⁶ m/s) as a function of p for the diffusion coefficient given by Eq. (6) (D_m=D_{mo}(1+pA_m); H_m==H=1 since p*=0; parabolic flow; ---- plug flow)



Fig. 2. The effect of the varying diffusion coefficient with p on the value of the mixing cup concentration, A_{ave} obtained for parabolic flow (continuous lines) and on the value of Q (broken lines). (D_m=D_{mo}exp(pA_m),k_m=5x10⁻⁴ m/s, Sh_w=0.5; H_m=H=1, Q=(A_{ave})_{plug}/(A_{ave})_{parabolic})

Effect of the linear dependency of the diffusion coefficient (Eq. 6) on the mixing cup concentration is illustrated in Fig. 1. The definition of this concentration is well known [1, 2]. The mixing cup concentration, A_{ave} , was calculated at four different values of parameter p.

For comparison, the values of A_{ave} obtained for plug flow is also shown (broken lines) in this figure. The volumetric velocity was the same in both cases (see Eq. 4). There is an increasing difference between them, which increases with the increase of the p value up to about 20% in the range investigated. The mixing-cup concentration as a function of diffusion coefficient with an exponential function on the concentration (Eq. 10) is plotted in Fig. 2 for parabolic flow (continuous lines). The role of p is, here, as in Fig. 1, again, essential.

How the ratio of the mixing-cup concentrations obtained under different flow conditions, Q, $(Q=A_{ave})_{plug}/(A_{ave})_{parabolic}$ change in axial direction is plotted in this figure (broken lines). It can be seen that the ratio can lower to about 75% which means that the effect of the flow conditions is not negligible. How the varying distribution coefficient (see Eq. 12) influences the mixing cup concentration is shown in Fig. 3 for both the parabolic flow and the plug flow.



Fig. 3. The effect of the varying distribution coefficient with p* on the value of A_{ave} as a function of Z obtained under parabolic flow profile (continuous lines) and for plug one (broken lines); (k_m=5x10⁻⁶ m/s, Sh_w=0.5, H=1, H_m=H(1+p*A), D_m=D_{mo})

The effect of dimensionless parameter, p^* , is essential. The outlet values of A_{ave} decreases about 70% as a function of p^* between 1 to 10. The effect of constant distribution coefficients ($p^*=0$) is shown in Fig. 4. Here again the ratio of $(A_{ave})_{plug}/(A_{ave})_{parabolic}$ is also plotted as a function of Z (broken lines). As it can be seen the Q value can essentially be decreased with increasing value of H (H_m=H). In the reality that is almost the case since the membrane has, in practice, much larger values of distribution coefficient than unity, i.e. H>>1.



Fig. 4. The effect of the constant distribution coefficient (p^{*}=0) on the mixing cup concentration, A_{ave} (continuous lines) and on the ratio of mixing cup concentrations, Q (broken lines); (k_m=5x10⁻⁴ m/s, Sh_w=0.5, H_m=H, D_m=D_{mo})

Notation

A dimensionless concentration in the solution, A=a/ain Aave dimensionless mixing cup concentration -(Aave)plug mixing cup concentration with plug flow condition (Aave)parabolic - mixing cup concentration with parabolic flow condition dimensionless concentration in the membrane, $A_m = a_m/(H_m a_m)$ Am A_N solute concentration in the lumen membrane interface solute concentration on membrane interface in the shell side As solute concentration, mol/m³ a - inlet solute concentration, mol/m³ ain - concentration in the membrane, mol/m³ am D - diffusion coefficient in the solute phase, m²/s - diffusivity of solute in the membrane, m²/s Dm - diffusion coefficient in membrane for infinite solute dilution, m²/s D_{mo} distribution coefficient of solute concentration in the membrane to that in fluid H_m distribution coefficient for infinite diluted solution Η - mass transfer rate, mol/m²s i

- k_m membrane permeability coefficient, m/s
- L length of hollow fiber, m
- p dimensionless parameter in Eqs. (6) and (10) for diffusion coefficient
- p^{*} dimensionless parameter in Eq. (12) for the distribution coefficient
- umax maximum velocity, m/s
- uave average fluid velocity, m/s
- r radial coordinate, m
- R^{*} inner radius of hollow fiber, m
- Z dimensionless axial coordinate
- δ thickness of the cylindrical membrane layer, m
- Q the ratio of A_{ave} for plug and for parabolic flows $(A_{ave})_{plug}/(A_{ave})_{parabolic}$

Literature

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