# Internal Mass Transfer in Hollow Fiber Supported Liquid Membranes

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## Introduction

The study of mass transfer in hollow fiber supported liquid membranes is justified by a large number of separation processes. The analysis starts from the definition of an overall permeability coefficient $P_o$, which is a lumped parameter of a particular system and process conditions which gathers both mass transfer and operation parameters.

By applying the film theory the contribution of the interfacial mass-transfer coefficient due to the inner boundary layer and the contribution of the supported liquid membrane permeability coefficient can be separated and analyzed. The study yields overall permeability coefficients that can be compared with those expected from hollow fiber design equations suggested earlier (Prasad and Sirkar, 1988; Dahuron and Cussler, 1988). The second approach considers the continuity mass conservation equation and the associated boundary conditions for the solute in the inner fluid. The analysis by means of the fundamental equations separates the effects of the operation variables such as the hydrodynamic conditions and length and diameter of the fibers from the mass-transfer properties of the system, described by the wall Sherwood number. The scope of the present work is to compare both methods of describing a hollow fiber supported liquid membrane module, analyzing the influence of the internal mass transfer on the design of such systems (Urtiaga et al., 1992a).

In the experimental system under consideration, the simultaneous separation-concentration of phenol from aqueous solutions with hollow fiber supported liquid membrane modules is performed (Urtiaga, 1990). The influence of the flow rate of the inner aqueous phase on the phenol separation rate has been studied.

## Theoretical Background

The local concentration difference at a particular position of the module gives rise to the commonly called "local permeability coefficient" in contrast to the "average permeability coefficient" (Cussler, 1984). At steady state and assuming uniform velocity and concentration distributions and the lack of backmixing, the local overall permeability coefficient at $z$ is defined by the following differential macroscopic mass balance:

$$\frac{\pi d^2}{4} u dC_A = -P_{o_{\text{Local}}}(\pi d dz)(C_A - C_R) \tag{1}$$

When using an instantaneous stripping reaction, $C_R = 0$. Integration of Eq. 1 gives

$$P_{o_{\text{Local}}} = \frac{ud}{4L} ln \frac{C_{A,z=0}}{C_{A,z=L}} \tag{2}$$

If linear solute concentration profiles at the fiber wall are assumed, the film theory allows us to relate the overall permeability coefficient with each of the resistances to mass transfer coupled in series as follows:

$$\frac{1}{P_o} = \frac{1}{k_i} + \frac{d}{d_{lm}} \frac{1}{P_m} \tag{3}$$

where $k_i$ is the interfacial coefficient corresponding to the inner aqueous boundary layer. In Eq. 3 the contribution of the outer aqueous interface to $P_o$ has been removed due to an instantaneous reaction at the stripping side. $P_m$ is the supported liquid membrane permeability, which is related to the phenol distribution coefficient by

$$P_m = Hk_m \tag{4}$$

Numerous expressions relating the overall permeability coefficient and the properties of the system have been published. The way followed to obtain such expressions is either the dimensional analysis or the solution to the differential equation

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**Table 1. Habitual Mass-Transfer Correlations in Cylindrical Tubes**

| Conditions | Correlations: Diffusion in Hollow Fibers | | Correlations: Heat Transfer in Tubes | |
|---|---|---|---|---|
| Laminar Flow | $\frac{kd}{D}=1.64\left(\frac{d^2u}{LD}\right)^{1/3}$ | (1) | $\frac{kd}{D}=1.64\left(\frac{d^2u}{LD}\right)^{1/3}$ | (5) |
| inside fibers | $\frac{kd}{D}=1.5\left(\frac{d^2u}{LD}\right)^{1/3}$ | (2) | $\frac{kd}{D}=1.86\left(\frac{d^2u}{LD}\right)^{1/3}$ | (6) |
| | $\frac{kd}{D}=1.027\left(\frac{d^2u}{LD}\right)^{1/3}$ | (3) | | |
| | $\frac{kd}{D}=0.5\left(\frac{d^2u}{LD}\right)\theta$ | (4) | | |

(1) Yang and Cussler (1986). Results obtained in gas absorption.
(2) Dahuron and Cussler (1988).
(3) Belfort (1987).

(4) Skelland (1974). $\theta=\dfrac{1-\sum_{j=1}^{j=\infty}\frac{-4Bj}{\beta_j^2}\left(\frac{d\phi_j}{dr^*}\right)_{r^*=1}\exp\frac{-\beta_j^2\left(\frac{2L}{d}\right)}{ReSc}}{1+\sum_{j=1}^{j=\infty}\frac{-4B_j}{\beta_j^2}\left(\frac{d\phi_j}{dr^*}\right)_{r^*=1}\exp\frac{-\beta_j^2\left(\frac{2L}{d}\right)}{ReSc}}$

where $\beta_j=4(j-1)+8/3;\ j=1, 2, 3, \ldots$

$B_j=(-1)^{j-1}\times 2.84606\beta_j^{-2/3}$

$\frac{B_j}{2}\left(\frac{d\phi_j}{dr^*}\right)_{r^*=1}=1.01276\ \beta_j^{-1/3}$

(5) Leveque (1928).
(6) Sieder and Tate (1936).

expressing the overall continuity of matter. For hollow fiber modules, the dimensional analysis relates the permeability coefficient with the system properties:

$$P_o=P_o(u,\rho,\mu,D,d,L) \tag{5}$$

In these correlations, the mass-transfer coefficient is reported as a Sherwood number. For forced convection in tubes the Sherwood number is expressed as a function of the Reynolds number, the Schmidt number, and the geometrical factor $d/L$.

$$Sh=[\text{constant}]Re^{\alpha}Sc^{\beta}(d/L)^{\gamma} \tag{6}$$

where the [constant] and the exponents $\alpha$, $\beta$ and $\gamma$ are adjustable parameters obtained experimentally. Table 1 shows the correlations reported in the literature. The results obtained with hollow fibers are essentially identical with heat-transfer studies in cylindrical tubes (Sieder and Tate, 1936). A direct analogy can be established between heat and mass transfer when the fluids are dilute and natural convection does not take place. All the correlations suggest that the mass-transfer coefficient varies with the cube root of the liquid velocity, so that,

$$Sh=ARe^{1/3}Sc^{1/3}(d/L)^{1/3}=APe^{1/3} \tag{7}$$

For a constant properties fluid flowing in fully developed laminar flow and developing concentration distribution the differential equation expressing the overall continuity of matter in flow through a tube at steady state can be expressed in terms of dimensionless variables (Urtiaga et al., 1992c). Axial diffusion is neglected compared to axial convection. The equations are given by:

$$2(1-r^{*2})\frac{\partial C^*}{\partial z^*}=\frac{1}{r^*}\frac{\partial}{\partial r^*}\left[r^*\frac{\partial C^*}{\partial r^*}\right] \tag{8}$$

$$\text{B.C.1}\quad C^*=1, \qquad z^*=0, \quad \text{all } r^* \tag{9}$$

$$\text{B.C.2}\quad \frac{\partial C^*}{\partial r^*}=0, \qquad r^*=0, \quad \text{all } z^* \tag{10}$$

$$\text{B.C.3}\quad -\frac{\partial C^*}{\partial r^*}=Sh_wC^*, \quad r^*=1, \quad \text{all } z^* \tag{11}$$

where

$$z^*=\frac{4zD}{ud^2}=4\frac{1}{Pe}\quad C^*=\frac{C_A}{(C_A)_{\text{in}}}\quad r^*=\frac{2r}{d}$$

$$Sh_w=\frac{k_mHsd}{2D} \tag{12-15}$$

The problem is similar to the classical Graetz problem with the boundary condition of constant temperature/concentration at the fiber wall (Graetz, 1885), which has been studied by a number of investigators (Leveque, 1928; Brown, 1960; Sideman et al. (1964, 1965); Davis and Parkinson, 1970).

In Eq. 11 the mass-transfer parameter is the wall Sherwood number $Sh_w$, defined as the ratio of the mass-transfer resistance in the inner fluid to that in the membrane. For $Sh_w=\infty$ the supported liquid membrane resistance to mass transfer is negligible and for $Sh_w=0$ the membrane resistance is dominant. The mixing-cup concentration is obtained as follows:

$$C_B^*=\sum_{m=1}^{\infty}E_m\exp\left(-\frac{\lambda_m^2}{2}z^*\right) \tag{16}$$

where the eigenvalue $\lambda_m$ and the associated constant $E_m$ are obtained as a function of the wall Sherwood number $Sh_w$.

By substitution of Eq. 16 into Eq. 1 and integration the overall Sherwood number is obtained as follows:

$$(Sh_o)_{\text{Local}}=\frac{(P_o)_{\text{Local}}d}{D}=\frac{-ln(C_B^*)}{z^*} \tag{17}$$

where $C_B^*$ is taken from the resolution of the system of differential Eqs. 8-11. In this way, following Skelland (1974), Leveque's approximate solution with the boundary condition of constant temperature/concentration at the fiber wall is valid in cases of high mass-transfer velocities through relatively short tubes. Leveque's expressions for local and average Sherwood numbers with uniform concentration along the tube wall are given in Table 1.

## Results and Discussion

A schematic representation of a hollow fiber liquid membrane is shown in Figure 1. The influence of the flow rate of

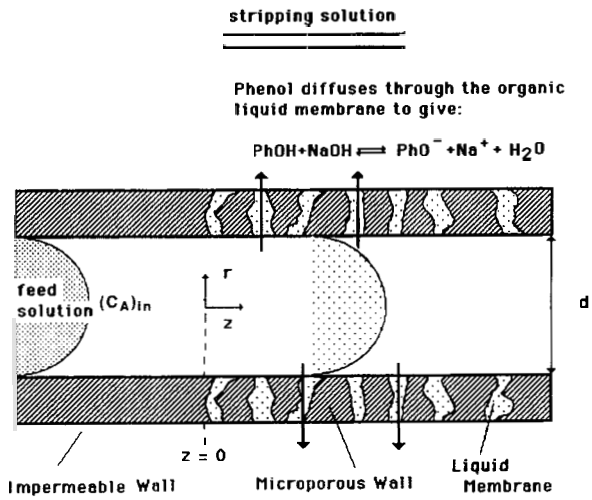


**Figure 1. Diagram of a hollow fiber supported liquid membrane.**

The phenol separation process takes place by diffusion through the liquid membrane and reaction in the outer stripping phase.

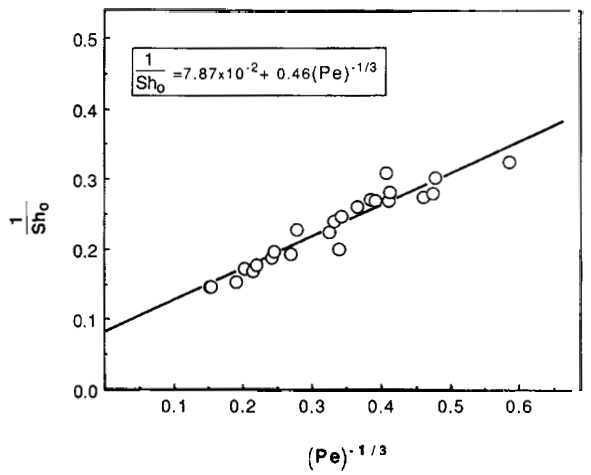


**Figure 2. Influence of the flow rate of the inner fluid.**

Wilson plot of the experimental overall mass-transfer coefficients inside the hollow fiber. The constant $A$ corresponding to Eq. 6 is obtained from the linear regression.

the inner stream on the phenol separation rate has been experimentally investigated. Phenol separation experiments were run in a continuous operation mode. A complete description of the experimental setup, apparatus, reactives and analytical procedures can be found elsewhere (Urtiaga et al., 1992b,c). Feed aqueous solutions with an initial phenol concentration of 5 g/L and caustic stripping solutions with an initial concentration of 1 mol/L were employed. The outer solution was continually recirculated in order to obtain a concentrated stripping solution. The organic solvent used as liquid membranes is a mixture of kerosene and methyl isobutyl ketone (MIBK). The solubility of MIBK in water made necessary to add 1% in volume of MIBK to the aqueous feed and stripping solutions in order to get equilibrium conditions with the membrane composition.

When using the fundamental equations, the influence of the flow rate is included in the dimensionless axial distance $z^*$. The dimensionless axial distance and the Peclet number are related as $Pe = 4(1/z^*)$. Therefore, increasing values of the fluid flow rate will lead to increasing values of $Pe$, when the length and diameter of the fiber and the diffusivity of the solute are held constant. On the other hand, the commonly used correlations determine that the mass-transfer coefficient varies with the cube root of the liquid velocity. The comparison between both analysis will be established in terms of the Wilson plot. The use of Wilson plots have been reported in the literature as a helpful way to obtain the mass-transfer parameters in hollow fiber contactors (Yang and Cussler, 1986; Prasad and Sirkar, 1988). Wilson plots linearize the correlations in Table 1 representing values of $1/Sh_o$ vs. $(Pe)^{-1/3}$. If the permeability coefficients are expressed in terms of Sherwood numbers, Eq. 3 can be written as follows

$$\frac{1}{Sh_o} = \frac{1}{2Sh_w} + \frac{1}{Sh_i} \tag{18}$$

The intercept on the $1/Sh_o$ axis is a function of the supported liquid membrane resistance to mass transfer, $1/2Sh_w$ and consequently is not influenced by the flow rate of the fluids. The term $1/Sh_i$ in Eq. 18 is influenced by the flow rate of the inner fluid.

Equations 7 and 18 can be combined to give

$$\frac{1}{Sh_o} = \frac{1}{2Sh_w} + \frac{1}{A}(Pe)^{-1/3} \tag{19}$$

The Wilson plot of $1/Sh_o$ vs. $(Pe)^{-1/3}$ for the experimental results is shown in Figure 2. Apparently a good agreement between observed results and Eq. 19 is obtained. From the intercept on the $1/Sh_o$ axis the wall Sherwood number for the experimental system under consideration is obtained, $Sh_w = 6.35$. The slope of the plot determines a value of the constant $A = 2.18$.

In Figure 3 the Wilson plot relates theoretical courses of

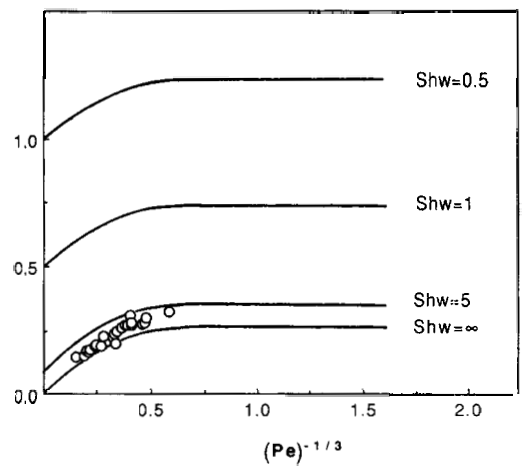


**Figure 3. Wilson plot of the theoretical overall local Sherwood numbers obtained according to the continuity mass conservation equation for wall Sherwood numbers of ∞, 5, 1, and 0.5.**

o: experimental results.

**Table 2. Influence of the Inner Fluid Flow Rate on Phenol Separation**

| $u$, cm/s | $L$, cm | $C$, g/L | $z^*$ | $C^*_{B\,EXP}$ |
|---|---|---|---|---|
| 0.615 | 45 | 0.409 | 0.811 | 0.082 |
| 1.130 | 45 | 1.153 | 0.442 | 0.231 |
| 1.231 | 48 | 1.071 | 0.432 | 0.214 |
| 1.257 | 45 | 1.175 | 0.397 | 0.235 |
| 1.768 | 45 | 1.832 | 0.282 | 0.367 |
| 1.796 | 45 | 1.787 | 0.278 | 0.357 |
| 1.834 | 45 | 2.076 | 0.272 | 0.415 |
| 2.050 | 45 | 2.032 | 0.243 | 0.406 |
| 2.172 | 45 | 2.138 | 0.230 | 0.428 |
| 2.541 | 45 | 2.349 | 0.196 | 0.470 |
| 3.144 | 45 | 2.500 | 0.159 | 0.450 |
| 3.275 | 48 | 2.581 | 0.163 | 0.516 |
| 3.556 | 45 | 2.682 | 0.140 | 0.536 |
| 3.583 | 48 | 2.679 | 0.149 | 0.536 |
| 5.665 | 45 | 3.397 | 0.0881 | 0.679 |
| 6.693 | 48 | 3.304 | 0.0795 | 0.661 |
| 8.270 | 45 | 3.681 | 0.0603 | 0.736 |
| 8.842 | 46 | 3.679 | 0.0577 | 0.736 |
| 11.500 | 45 | 3.909 | 0.0434 | 0.782 |
| 12.326 | 45 | 3.928 | 0.0405 | 0.786 |
| 14.701 | 45 | 4.103 | 0.0339 | 0.821 |
| 18.990 | 48 | 4.166 | 0.0280 | 0.833 |
| 33.992 | 45 | 4.518 | 0.0147 | 0.904 |
| 34.945 | 45 | 4.535 | 0.0143 | 0.907 |

the reciprocal of the overall permeability coefficient with $(Pe)^{-1/3}$, where the values of $Sh_o$ have been obtained according to Eq. 17 from the resolution of the continuity mass conservation equation and the related boundary conditions (Eqs. 8-11). The theoretical courses in Figure 3 have been derived for different values of the wall Sherwood number ranging from $Sh_w = 0.1$ to $Sh_w = \infty$. As it is shown in Figure 3, the linear dependency of $1/Sh_o$ with $(Pe)^{-1/3}$ is not valid for the full range of Peclet numbers. The experimental results of phenol separation listed in Table 2 are also plotted in Figure 3. Now a more realistic evolution of the overall Sherwood number with the Peclet number is obtained.

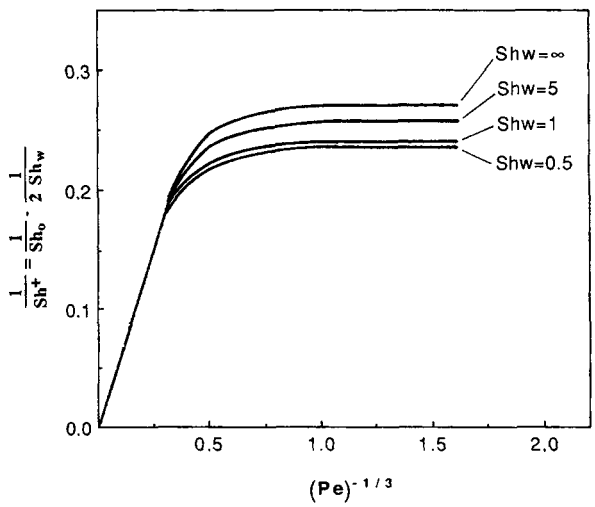


**Figure 4. Wilson plot of the theoretical modified Sherwood number ($Sh^+$) in the range of wall Sherwood numbers $0.1 < Sh_w < \infty$.**

A modified Sherwood number $Sh^+$, related to the mass transfer in the inner boundary layer can be defined as follows

$$\frac{1}{Sh^+} = \frac{1}{Sh_o} - \frac{1}{2Sh_w} \tag{20}$$

Figure 4 plots $1/Sh^+$ against $(Pe)^{-1/3}$ from the theoretical courses in Figure 3. Figure 4 indicates that for values of approximately $(Pe)^{-1/3} < 0.3$, corresponding to Peclet numbers over 40, the linearization of $1/Sh^+$ with $(Pe)^{-1/3}$ provides a reasonable estimation of the overall permeability coefficients in hollow fiber supported liquid membrane modules with a wall resistance to mass-transfer proportional to the solute concentration. The best fit in the range $40 < Pe < \infty$ is obtained according to the following expression

$$Sh^+_{\text{Local}} = 1.718 Pe^{1/3} \tag{21}$$

The application of Eq. 21 in the design of hollow fiber supported liquid membrane modules in operation conditions implying a Peclet number under 40 will involve an error in the estimation of the overall permeability coefficient. Prasad and Sirkar (1988) discussed the suitability of using correlations and considered the solutions given by Leveque and Sieder and Tate (Table 1) as a rough estimate of the actual conditions existing in the lumen side of the contractor. The authors attributed the differences in the theoretical and experimentally observed $Sh_o$ to the lack of validity of the boundary condition of constant wall concentration. However, as it is observed in Figure 3 the local overall Sherwood number converges rapidly for small values of $Pe$, reaching different converging values of $Sh_o$ as a function of the wall Sherwood number. For a $Sh_w = \infty$ an overall permeability coefficient $Sh_o = 3.66$ is obtained when $Pe$ is less than 1. This value coincides with that given by Skelland (1974; p. 165) for local overall Sherwood numbers in systems with uniform wall concentration.

Consequently the validity of the correlations in Table 1 is limited not only by the type of boundary condition at the fiber wall but also by the Peclet number. Taking into account Eq. 12, the diffusivity of the solute, the linear velocity of the inner fluid, and the length and diameter of the hollow fibers will determine the Peclet number of the system. The design will be conditioned by the interval of Peclet numbers in which the system under consideration is operated.

## Conclusions

The design of hollow fiber supported liquid membrane modules with a constant wall Sherwood number can be appropriately performed making use of the following correlation:

$$Sh^+_{\text{Local}} = 1.718 Pe^{1/3}$$

which is valid for the calculation of inner boundary layer coefficients for values of the Peclet number over 40. Under this conditions, the overall permeability coefficient for the system can be obtained from Eq. 19. The modified local Sherwood number $Sh^+_{\text{Local}}$ accounts for the influence of the flow rate of the inner fluid on the mass-transfer parameters. When $Pe < 40$, the linking of mass transfer in the inner fluid and across the immobilized liquid membrane does not allow to

employ the previous expression. In this case the design must be accomplished according to the continuity mass conservation equation and the related boundary conditions. The evaluation of the experimental results obtained in a wide range of Peclet numbers confirms the above analysis. The additional mathematical work required for the resolution of the continuity mass conservation equation allows a sounder understanding of the process of solute separation by hollow fiber supported liquid membranes.

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## Notation

$A$ = constant in Eq. 7
$C_A, C_A^b, C_A^i, C_A^o$ = solute concentration in the inner fluid, in the bulk phase, in the aqueous phase at the fiber inside wall, in the organic phase at the fiber inside wall, respectively, $g/L$
$(C_A)_{in}$ = initial solute concentration in the inner fluid, $g/L$
$C^*$ = dimensionless solute concentration in the inner fluid
$C_B^*$ = dimensionless mixing-cup concentration
$C_R, C_R^b, C_R^i, C_R^o$ = solute concentration in the stripping fluid, in the bulk phase, in the aqueous phase at the fiber outside wall, in the organic phase at the fiber outside wall, respectively, $g/L$
$C_w^*$ = dimensionless solute concentration at the wall
$D$ = diffusivity of the solute in the inner fluid phase, $cm^2/s$
$d, d_{lm}$ = inner and logarithmic mean diameters respectively of the hollow fiber, cm
$E_m$ = numerical constant
$H$ = equilibrium distribution coefficient of the solute between the organic and the aqueous phase
$k_i$ = inner boundary layer mass-transfer coefficient, cm/s
$k_m$ = membrane mass-transfer coefficient, cm/s
$L$ = length of the hollow fiber, cm
$P_m$ = membrane permeability coefficient, cm/s
$Pe$ = modified Peclet number, defined as $Pe = ReSc\,(d/L) = d^2u/DL$
$P_o$ = overall permeability coefficient, cm/s
$r$ = radial coordinate
$r^*$ = dimensionless radial coordinate
$Re$ = Reynolds number $Re = u\rho d/\mu$
$s$ = shape factor, $s = d_{lm}/d$
$Sc$ = Schmidt number, $Sc = \mu/D\rho$
$Sh$ = Sherwood number, $Sh = kd/D$
$Sh^+$ = modified inner boundary layer Sherwood number defined in Eq. 21
$Sh_i$ = inner boundary layer Sherwood number
$Sh_o$ = overall Sherwood number
$Sh_w$ = wall Sherwood number defined in Eq. 15
$u$ = average linear velocity of the inner fluid, cm/s
$z$ = axial coordinate
$z^*$ = dimensionless axial coordinate

### *Greek letters*

$\lambda_m$ = eigenvalue
$\mu$ = viscosity of the inner fluid (g/cm·s)
$\rho$ = density, $g/cm^3$

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