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Mass Transfer in Cylindrical Couette Flow

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Abstract

Theoretical equations for mass transfer to a section of the inner cylinder for laminar cylindrical couette flow are presented. The effects of curvature, the non-linear velocity profile, and the elliptic nature of the convective diffusion equation are included to extend the result of a previous treatment by Gabe and Robinson. The equations indicate that the correction to the result of Gabe and Robinson is dominated by elliptic effects for short electrodes and by curvature and velocity profile effects as the electrode comprises a larger proportion of the inner cylinder circumference.

Introduction

Gabe and Robinson[1] have recently described mass transfer to a small section of the inner cylinder for laminar cylindrical Couette flow. As presented, however, their results are applicable only in the limit of infinite Schmidt number, and errors due to the finite, though large, Schmidt numbers of electrolytic solutions are the result of three effects not considered in their analysis. These are: (1) the elliptic nature of the diffusion layer at the leading and trailing edge regions of the mass transfer area, (2) the curvature of the electrode surface, and (3) the non-linear nature of the velocity profile. In this paper, a method used by Newman[3,4] to extend the Lévêque solution[8] to the Graetz problem accounting for these effects is employed to extend the results of Gabe and Robinson.

Mathematical Formulation

The appropriate form of the equation of convective diffusion[5] is:

$$\frac{\partial c}{\partial t} + \frac{v'_\theta}{r}\frac{\partial c}{\partial \theta'} = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 c}{\partial \theta'^2}\right] \qquad (1)$$

with boundary conditions:

(1) At $t = 0$; $c = c_\infty$

(2) At $t > 0$, $r = \kappa R$, $-L/\kappa R + \Omega t < \theta' \leq \Omega t$

(3) $t > 0$, $r = \kappa R$, $\Omega t < \theta' \leq \Omega t + 2\pi - \frac{L}{\kappa R}$; $\frac{\partial c}{\partial r} = 0$

(4) $t > 0,\ r = R;\ \frac{\partial c}{\partial r} = \text{constant}$

Boundary condition 4 being necessary to insure constant inventory of the electroactive species in the cell.

For the inner cylinder rotating with angular velocity Ω,

$$v'_\theta = \frac{\kappa^2 R}{1-\kappa^2}\left(\frac{R}{r} - \frac{r}{R}\right) \quad . \tag{2}$$

In order to transform to a steady state problem, the substitution

$$\theta = \theta' - \Omega t$$

is used. We must now assume that a steady state approximation is a reasonable simplification. That is, that the presence of the transfer area does not disturb the overall concentration, c_∞, except in the regions close to, or downstream from, the transfer surface. This corresponds to the usual boundary condition used in diffusion layer analyses: that the concentration outside the diffusion layer is equal to the bulk concentration. In other words, we assume that at no time does the electrode rotate into a region where the concentration has been disturbed by the previous presence of the electrode. In terms of the boundary-layer coördinates

$$y = r - \kappa R \ , \quad x = -\kappa R\theta \quad ,$$

Equation 1 then becomes

$$v_x \frac{\partial c}{\partial x} = D\left[\frac{\partial^2 c}{\partial y^2} + \frac{1}{y+\kappa R}\frac{\partial c}{\partial y} + \frac{\kappa^2 R^2}{(y+\kappa R)^2}\frac{\partial^2 c}{\partial x^2}\right] \qquad . \qquad (3)$$

With boundary conditions

(1) $y = 0, \quad 0 \leq x \leq L \; ; \quad c = c_o$

(2) $y = 0, \quad L < x < 2\pi \; ; \quad \frac{\partial c}{\partial y} = 0$

(3) $y \to \infty \; ; \quad c \to c_\infty$

where $v_x = -\frac{\kappa R}{r}(v_\theta' - r\Omega)$.

v_x may be expressed as a power series in y:

$$v_x = \beta y\left(1 - \gamma \frac{y}{\kappa R} + \delta \frac{y^2}{\kappa^2 R^2} + \ldots.\right) \qquad (4)$$

where: $\beta = \left.\frac{\partial v_x}{\partial r}\right|_{r=\kappa R} = \frac{2\Omega}{1-\kappa^2}$

$$\gamma = -\frac{\kappa R}{2!\beta}\left.\frac{\partial^2 v_x}{\partial r^2}\right|_{r=\kappa R} = \frac{3}{2}$$

$$\delta = \frac{\kappa^2 R^2}{3!\beta}\left.\frac{\partial^3 v_x}{\partial r^3}\right|_{r=\kappa R} = 2 \qquad .$$

It is now appropriate to introduce dimensionless variables. In order to show clearly the method of extension of the Lévêque solution, and follow more closely the development by Gabe and Robinson,[1] the Lévêque similarity variable will be used. The dimensionless variables are

$$\eta = y(\beta/90x)^{1/3} \quad , \; Z = (9Dx/\beta\kappa^3R^3)^{1/3}, \quad \Theta = \frac{c-c_o}{c_\infty-c_o} \quad .$$

Equation (3) thus becomes

$$3\eta(1-\gamma\eta Z + \delta\eta^2Z^2 + \ldots)(Z\frac{\partial\Theta}{\partial Z} - \eta\frac{\partial\Theta}{\partial\eta}) =$$

$$\frac{\partial^2\Theta}{\partial\eta^2} + \frac{Z}{1+\eta Z}\frac{\partial\Theta}{\partial\eta} + (\frac{D}{3\beta L^2})^{2/3}\frac{(x/L)^{-4/3}}{(1+\eta Z)^2} \cdot$$

$$\left[\eta^2\frac{\partial\Theta}{\partial\eta^2} + 4\eta\frac{\partial\Theta}{\partial\eta} - 2\eta Z\frac{\partial^2\Theta}{\partial\eta\partial Z} + Z^2\frac{\partial^2\Theta}{\partial Z^2} - 2Z\frac{\partial\Theta}{\partial Z}\right] \quad . \tag{5}$$

The last term corresponds to longitudinal diffusion and is negligible (due to the factor $(D/3\beta L^2)^{2/3}$, a small parameter for systems of interest) everywhere except in a small region near $x = 0$. A change of variables $x_2 = L - x$ would demonstrate that this term must also be retained in a small region near $x_2 = 0$, thus conforming to the familiar concept of small elliptic regions at the beginning and end of a diffusion layer of parabolic nature.[3,4] The contribution of the elliptic regions to the total mass transfer will be treated later.

In the limit as $D \to 0$, equation 5 reduces to

$$\frac{\partial^2\Theta}{\partial\eta^2} + 3\eta^2\frac{\partial\Theta}{\partial\eta} = 0 \tag{6}$$

to which the Lévêque solution[8] applies. This is also the equation upon which Gabe and Robinson based their analysis. The extension of the solution for a small, but non-zero, diffusion coefficient is effected by considering

$$\Theta(\eta,Z) = \sum_{n=0}^{\infty} Z^n \, \Theta_n(\eta)$$

to be a solution of equation 5 without the longitudinal diffusion term. This yields equations for like orders in Z:

$$\Theta_0'' + 3\eta^2\Theta_0' = 0 \qquad (7)$$

$$\Theta_1'' + 3\eta^2\Theta_1' - 3\eta\Theta_1 = (3\gamma\eta^3 - 1)\Theta_0' \qquad (8)$$

$$\Theta_2'' + 3\eta^2\Theta_2' - 6\eta\Theta_2 =$$

$$(3\gamma\eta^3 - 1)\Theta_1' - 3\gamma\eta^2\Theta_1 - (3\delta\eta^4 + \eta)\Theta_0' \qquad (9)$$

with boundary conditions

$$\Theta_0(0) = 0 \quad ; \quad \Theta_0(\eta \to \infty) \to 1$$

$$\Theta_1(0) = \Theta_2(0) = 0 \quad ; \quad \Theta_1(\eta \to \infty) = \Theta_2(\eta \to \infty) \to 0$$

leading to solutions

$$\Theta_0 = \frac{1}{\Gamma(4/3)} \int_0^\eta e^{-x^3} dx \tag{10}$$

$$\Theta_1 = \frac{\eta}{5\Gamma(4/3)} \int_\eta^\infty e^{-x^3} dx - \frac{3\eta^2}{10\Gamma(4/3)} e^{-\eta^3} \tag{11}$$

$$\Theta_2 = - \frac{\eta^2}{10\Gamma(4/3)} \int_\eta^\infty e^{-x^3} dx - (0.135\ \eta^6 - \frac{17}{70}\eta^3 - \frac{1}{210}) \frac{e^{-\eta^3}}{\Gamma(4/3)}$$

$$- \frac{1}{630} \frac{\Gamma(5/3)}{[\Gamma(4/3)]^3} \int_0^1 \frac{x^{1/3}}{(1-x)^{2/3}} e^{-\eta^3/(1-x)} dx \tag{12}$$

so that $\Theta_0'(0) = 1/\Gamma(4/3) = 1.119847$, $\Theta_1'(0) = 0.2$,

$$\theta_2'(0) = \frac{1}{140\Gamma(4/3)} \left[\frac{\Gamma(5/3)}{\Gamma(4/3)}\right]^2 = 0.0081748 .$$

Now the elliptic regions will be treated. Substituting $Y_2 = y\sqrt{\beta/2D}$, $X_2 = x\sqrt{\beta/2D}$, and the power series expansion for v_x into equation (3) and considering $\varepsilon = \sqrt{2D/\beta\kappa^2 R^2}$ to be a small parameter yields:

$$2Y_2[1 - \varepsilon\gamma Y_2 + \varepsilon^2\delta Y_2^2 - O(\varepsilon^3)]\frac{\partial\Theta}{\partial X_2} = \frac{\partial^2\Theta}{\partial X_2^2} + \frac{\partial^2\Theta}{\partial Y^2}$$

$$- \varepsilon Y_2[2 - 3\varepsilon Y_2 + 4\varepsilon^2 Y_2^2 + 4\varepsilon^2 Y_2^2 - \ldots]\frac{\partial^2\Theta}{\partial X_2^2} + \frac{\varepsilon}{1+\varepsilon Y_2} \frac{\partial\Theta}{\partial Y_2} . \tag{13}$$

Newman[3] has solved this equation in the limit as $\varepsilon \to 0$ with boundary conditions appropriate to this system:

(1) $Y_2 = 0$, $X_2 \geq 0$; $\theta = 0$

(2) $Y_2 = 0$, $X_2 < 0$; $\frac{\partial\Theta}{\partial Y_2} = 0$

(3) $Y_2 \to \infty$ $\Theta \to 1$

(4) $X_2 \to \infty$, $\Theta \to 1$

(5) $\frac{\partial^2\Theta}{\partial X_2^2}$ Becomes negligible as $X \to \infty$.

The results of the numerical solution of this equation will be included in the correlation for total mass transfer.

For the elliptic region at the trailing edge of the electrode, we substitute

$Y_3 = Y_2$, $X_3 = (x-L)\sqrt{\beta/2D}$, and

$\overline{\Theta} = \Theta\Gamma(4/3)(9/2)^{1/3}(\beta L^2/2D)^{1/6}$

with the resulting equation (as $\varepsilon \to 0$)

$$2Y_3 \frac{\partial\overline{\Theta}}{\partial X_3} = \frac{\partial^2\overline{\Theta}}{\partial X_3^2} + \frac{\partial^2\overline{\Theta}}{\partial Y_3^2} \tag{14}$$

and boundary conditions

1) $Y_3 = 0$, $X_3 \leq 0$; $\overline{\Theta} = 0$

2) $Y_3 = 0$, $X_3 > 0$; $\frac{\partial\overline{\Theta}}{\partial Y_3} = 0$

3) $Y_3 \to \infty$ and $X_3 \to -\infty$; $\overline{\Theta} \to Y_3$

4) $X_3 \to \infty$; $\frac{\partial^2\overline{\Theta}}{\partial X_3^2}$ becomes negligible.

The third boundary condition reflects the matching of the elliptic region with the upstream diffusion layer. This problem has been solved numerically by Smyrl and Newman.[7]

The equation governing the mass transfer rate to the surface may now be derived in terms of the Nusselt number, $Nu = JL/D(c_\infty - c_0)$

$$J = D \int_0^L \left.\frac{\partial c}{\partial r}\right|_{r=\kappa R} dx = D(c_\infty - c_0) \int_0^L \left(\frac{\beta}{9Dx}\right)^{1/3} \left.\frac{\partial \Theta}{\partial \eta}\right|_{\eta=0} dx \quad .$$

$$\text{Thus } Nu = JL/D(c_\infty - c_0) = \frac{0.3288}{(\beta L^2/2D)^{1/6}} + \frac{B}{(\beta L^2/2D)^{1/6}}$$

$$- \frac{0.15746}{(\beta L^2/2D)^{1/3}} + \frac{6^{1/3}}{2} (\beta L^2/2D) \, [\Theta_0'(0) + \frac{2}{3}\Theta_1'(0) \, (9DL/\beta\kappa^3 R^3)^{1/3}$$

$$+ \frac{\Theta_2'(0)}{2} (9DL/\beta\kappa^3 R^3)^{2/3} + \ldots] \quad . \tag{15}$$

The first three terms are due to contributions of the elliptic regions. B is approximately equal to 0.3.[4] The last term includes contributions due to the diffusion layer, including the effect of curvature and the second and third normal velocity derivatives at the inner cylinder surface. The final result is:

$$Nu = 1.0174\, Pe^{1/3} \left\{ 1 + 0.1966\left(\frac{1}{\kappa R}\right) Pe^{-1/3} + 0.618 Pe^{-1/2} \right.$$

$$\left. + \left[0.009949 \left(\frac{L}{\kappa R}\right)^2 - 0.1548\right] Pe^{-2/3} + \ldots \right\} \tag{16}$$

where $Pe = \beta L^2/2D$ is the Péclet number.

Discussion

The first term, of order $Pe^{1/3}$, is identical to that obtained by Gabe and Robinson.[1] The second term in equation (16), of order unity, is similar to a correction term given by Kimla and Štrafelda.[2] It should be pointed out that Gabe and Robinson erroneously criticized Kimla and Štrafelda for using an incorrect velocity profile in their analysis. In fact, Gabe and Robinson erred in this respect, and to interpret correctly their results, one must substitute the proper first derivative of velocity at the inner cylinder for the one suggested by those authors.

As an indication of the importance of higher order terms in equation 16, the following example, roughly corresponding to an experimental system studied by Kimla and Štrafelda, is examined:

$$\kappa = 0.28 \ , \ R = 2.5 \text{ cm}, \ \Omega = 0.05 \text{ sec}^{-1} \ , \ D = 10^{-5} \text{ cm}^2/\text{sec} \ ,$$

and $L = 0.2$ cm

From this, $\beta = 0.108507 \text{ sec}^{-1}$ and Pe = 434.03. The correction to the Lévêque solution totals approximately 3.5% with most of this (2.8%) resulting from the effect of the elliptic regions. It is to be expected that for a greater electrode length, L, the correction due to curvature would become dominant. In fact for $L = \kappa R$ (the inner cylinder radius), the corrections total only 2.5%, but over half is now due to the diffusion layer. This correction factor is plotted in Figure 1 at several values of $L/\kappa R$ as the ratio of the Nusselt number given by equation 16 to that given by the Lévêque solution versus the Péclet number.

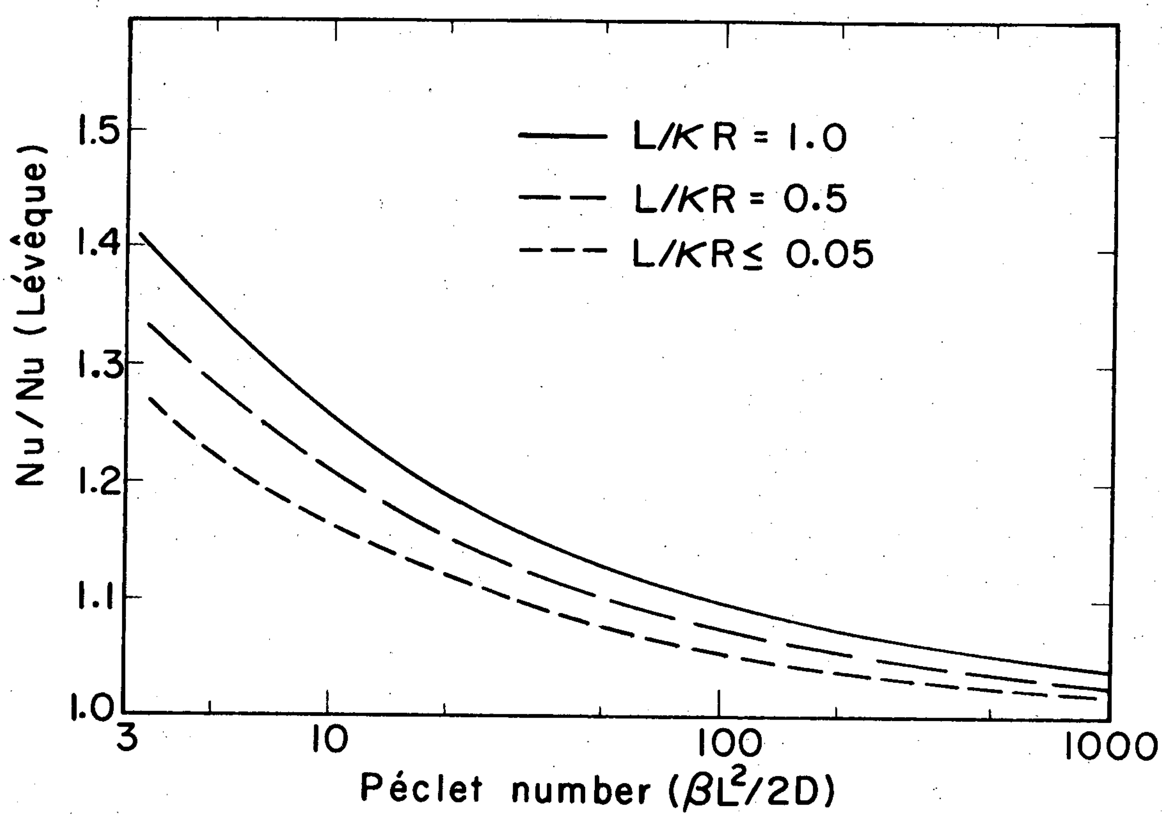

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Fig. 1. Correction to Lévêque solution.

Although this system has prompted little experimental investigation,[2] it seems to hold some promise as a compact and convenient means for studies in which flow channels have been used previously.[6]

Acknowledgments

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Nomenclature

c	concentration of diffusing species (g/cm^3)
D	diffusion coefficient (cm^2/sec)
r	radial distance (cm)
t	time (sec)
v	fluid velocity (cm/sec)
x,y	boundary layer coördinates (cm)
J	mass transfer rate per unit length of electrode (gm/cm sec)
L	length of mass transfer surface (cm)
Pe	Péclet number
R	radius of outer cylinder (cm)
X,Y	stretched dimensionless cartesian coordinates in elliptic regions
Z	dimensionless distance along electrode
β	first velocity derivative at inner cylinder (sec^{-1})
γ,δ	modified second and third velocity derivatives at inner cylinder
ε	perturbation parameter
η	Lévêque similarity variable
κ	ratio of inner to outer cylinder diameters
θ	cylindrical angle coordinate (radian)
Θ	dimensionless concentration variable
Ω	angular velocity of rotation of inner cylinder (sec^{-1})

References

(1) Gabe, D. R., and Robinson, D. J., Electrochimica Acta, 17, 1121 (1972).

(2) Kimla, A., and Štrafelda, F., Coll. Czech. Chem. Comm., 32, 56 (1967).

(3) Newman, J., J. Heat Trans., 91, 177 (1969).

(4) Newman, J., Allen J. Bard, ed., Electroanalytical Chemistry, 6 (New York: Marcel Dekker, Inc., 1973).

(5) Levich, V., Physicochemical Hydrodynamics (Englewood Cliffs, J. J.: Prentice-Hall, Inc., 1962), p. 65.

(6) Tobias, C., and Hickman, R., Z. Physik. Chem., 229, 145 (1965).

(7) Smyrl, W., and Newman, J., J. Electrochem. Soc., 118, 1079 (1971).

(8) Lévêque, M., Les Lois de la Transmission de Chaleur par Convection, Annales des Mines, Memoires, ser. 12, 13, 201 (1928).

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