Mass Transfer to the Inner Wall of an Annulus with Non-Newtonian Fluids

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Several works, confirming the Leveque equation applied to mass transfer under streamline flow conditions in annuli, have been reported in the literature. Ross and Wragg (1965, 1968), for instance, obtained mass transfer data in an annular flow cell using the electrochemical method for the deposition of copper from acidified solutions of cupric sulfate, varying the electrode length and the annulus radius ratio. Xifra and Böhm (1975), working with the ferro-ferricyanide-sodium hydroxide system and various electrode lengths, also found very close coincidence between experiment and theoretical prediction. Both electrochemical systems used are Newtonian fluids.

The aim of the present work is to adapt the Leveque solution for the case of mass transfer from a flowing fluid to the core of an annulus in fully developed streamline flow, the liquid exhibiting non-Newtonian behavior, and to test the relationship experimentally.

The fluid mechanical phenomenon for axial Non-Newtonian annular flow has been studied by Fredrickson and Bird (1958) who solved numerically the equation of motion for the power law model.

THEORY

Following the procedure outlined by Leveque, the integration of the convective diffusion equation yields, for the mean mass transfer coefficient between surface and fluid

$$k = 0.807\, D \left(\frac{\beta}{DL} \right)^{1/3} \tag{1}$$

For the inner wall of an annulus

$$\beta = \left. \frac{dU}{dr} \right|_{r=aR}$$

which, for the case of Newtonian fluids in laminar flow, becomes

$$\beta = \frac{8U_m}{de}\, \phi(a) \tag{2}$$

with

$$\phi(a) = \frac{1-a}{a} \cdot \frac{\left(0.5 - \dfrac{a^2}{1-a^2} \ln \dfrac{1}{a} \right)}{\left(\dfrac{1+a^2}{1-a^2} \ln \dfrac{1}{a} - 1 \right)} \tag{3}$$

Equation (1), written in dimensionless terms, becomes

$$Sh = 1.614 \left[Re \cdot Sc \cdot \frac{de}{L}\, \phi(a) \right]^{1/3} \tag{4}$$

which was verified by the authors mentioned before.

The equation of motion integrated over an annular region and for purely viscous fluids reads

$$\tau_{rz} = \frac{\Delta P}{2} \cdot \left[r - \frac{\lambda(a,n) \cdot R)^2}{r} \right] \tag{5}$$

Now, for a fluid following the power law model

$$\tau_{rz} = -K \cdot \left| \frac{dU}{dr} \right|^{n-1} \cdot \left. \frac{dU}{dr} \right|_{r=aR} \tag{6}$$

which may be combined with Equation (5) to give

$$\beta = \left(\frac{\Delta P}{2K} \right)^{1/n} \cdot \left(\frac{\lambda(a,n) \cdot R)^2}{aR} - aR \right)^{1/n} \tag{7}$$

$(\Delta P/2K)^{1/n}$ may be obtained from the equations

$$Q = \pi R^3 \left(\frac{\Delta P \cdot R}{2K} \right)^{1/n} \Omega(a,n) = \pi R^2 (1-a^2) U_m \tag{8}$$

derived by Frederickson and Bird for the flow of power law fluids and may be replaced in Equation (7) to yield

$$\beta = \frac{(1-a^2)\, a^{1/n} \left[\left(\dfrac{\lambda(a,n)}{a} \right)^2 - 1 \right]^{1/n} U_m}{R\Omega(a,n)}$$

or, as is customary in this field

$$\beta = \frac{8U_m}{de}\, \Gamma(a,n) \tag{9}$$

with

$$\Gamma_{(a,n)} = \frac{(1-a^2)\, a^{1/n} \left[\left[\dfrac{\gamma(a,n)}{a} \right]^2 - 1 \right]^{1/n} (1-a)}{4\Omega(a,n)} \tag{10}$$

The values of $\lambda(a, n)$ and $\Omega(a, n)$, were obtained numerically by Fredrickson and Bird and are tabulated elsewhere.

Substituting Equation (9) into Equation (1), we get

$$k = 0.807\, D \left[\frac{8U_m}{de} \cdot \frac{\Gamma(a,n)}{D \cdot L} \right]^{1/3} \tag{11}$$

If we express this result in dimensionless form, the following relationship is derived:

$$Sh = 1.614 \left[Re_n Sc_n \frac{de}{L}\, \Gamma(a,n) \right]^{1/3} \tag{12}$$

Here Re_n and Sc_n are the Reynolds and Schmidt numbers, respectively, modified for power law fluids.

EXPERIMENTAL

Mass transfer coefficients were determined by the electrochemical method, measuring limiting currents for different electrolyte flow rates.

The equipment and details of the test section are given in Figure 1. The unit consists of a lucite column of annular section with a reservoir on its upper part. This storage tank, where the electrolyte is maintained at constant temperature of 20°C by means of a thermostat, has a cross section forty times greater than the annulus. The flow rate is adjusted by means of a valve located at the lower part of the column. The inner lucite tube contains the test section composed of two nickel electrodes, on which the mass transfer process takes place.

At least twenty equivalent diameters were allowed as entrance length and ten equivalent diameters as exit length.

The annulus radius ratio was varied by using two different

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Table 1. Electrolyte Properties at 20°C and Values of $\Gamma(a, n)$

Solution	ρ $(g \cdot cm^{-3})$	K $(dyne \cdot s^n \cdot cm^{-2})$	n	$D \times 10^6$ $(cm^2 \cdot s^{-1})$	$a = 0.68$ $\Gamma(a, n)$	$a = 0.30$ $\Gamma(a, n)$
A	1.075	0.01549	1	5.00	1.611	1.959
B	1.022	0.01076	1	6.65	1.611	1.959
C_1	1.025	0.755	0.88	6.33	1.695	2.082
C_2	1.030	4.25	0.86	5.82	1.711	2.113
C_3	1.036	21.36	0.77	5.41	1.796	—

outer columns 2.35 and 5.20 cm in internal diameter respectively.

Five different electrolytes were circulated through the system; solutions *A* and *B*, presenting Newtonian behavior, were aqueous solutions having equal concentrations 10^{-2} M of potassium ferro and ferricyanide, containing 2 M sodium hydroxide the first and 0.1 M sodium hydrogen carbonate —0.1 M sodium carbonate the second, as indifferent electrolyte. (Solution *A* was used to test the arrangement of equipment.)

The other three solutions (C_1, C_2, and C_3) had the same composition of solution *B*, but carboxymethylcellulose was added in concentrations of 1, 2, and 3% by weight, respectively, yielding non-newtonian fluids.

The characteristics of the solutions were obtained as described by Tonini et al. and are given in Table 1, as well as the values of the function $\Gamma(a, n)$ calculated for each solution and the two diameter ratios used.

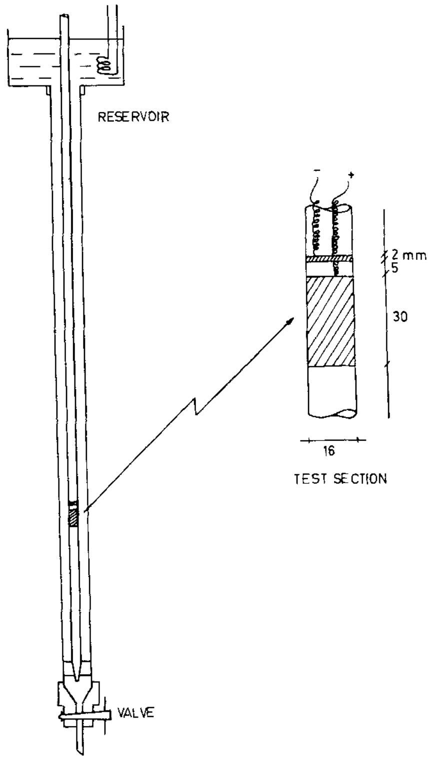

Fig. 1. Experimental equipment.

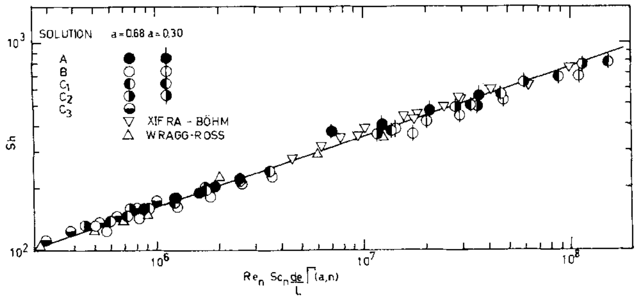

Fig. 2. Correlation of mass transfer rates to the inner wall of annuli for Newtonian and Non-Newtonian fluid flow.

Based on the related theory, the experimental results were correlated in terms of *Sh* vs. $[Re_n \cdot Sc_n\, de/L\; \Gamma(a, n)]$ as shown in Figure 2 together with Equation (12). Also included were the data of Xifra and Böhm who worked with an annulus radius ratio of 0.25, electrode lengths varying between 3.2 and 11.2 mm, and the system $K_4\,Fe(CN)_6 - K_3\,Fe(CN)_6\; 10^{-2}$ M., HONa 0.5 M at 25°C; and the experimental results of Ross and Wragg (1968) obtained for $a = 0.5$, seven electrode lengths ranging from 0.5 to 152.4 mm, and solutions of SO_4Cu in SO_4H_2 1.5 M.

CONCLUSIONS

As can be readily observed from Figure 2, the experimental data covering the following ranges of involved parameters

$$110 < Sh < 800$$

$$1.4 \times 10^{-2} < Re_n < 1\,940$$

$$1\,583 < Sc_n < 3 \times 10^6$$

$$2.9 \times 10^5 < \left[Re_n \cdot Sc_n \frac{de}{L} \Gamma(a, n) \right] < 1.2 \times 10^8$$

indicate a close coincidence with the proposed correlation. This means that mass transfer in non-Newtonian fluids following the power law model is well represented by the simplified Leveque solution suitably modified and can be predicted by the relationship

$$Sh = 1.614 \left[Re_n \cdot Sc_n \cdot \frac{de}{L} \Gamma(a, n) \right]^{1/3}$$

The agreement between this expression and the experimental data obtained with Newtonian fluids also indicates that the dimensionless function $\Gamma(a, n)$ tends to $\phi(a)$ when n approaches 1.

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NOTATION

a = radius ratio, r_i/R
D = diffusivity, cm^2/s
de = equivalent diameter, cm
k = mass transfer coefficient, cm/s
K = power law constant, $dyne \cdot s^n/cm^2$
L = electrode length, cm
n = flow index, dimensionless
ΔP = pressure drop per unit length, $dyne/cm^3$
Q = volumetric flow rate, cm^3/s
r = radius, cm
r_i = inner radius of annulus, cm
R = radius of outer cylinder of annulus, cm
Re_n = Reynolds number for power law model, $de^n \cdot \rho \cdot U_m^{2-n}/8^{n-1} \cdot K \cdot (3n + 1)^n/(4n)^n$

Sc_n = Schmidt number for power law model, $K \cdot [(3n + 1)/4n]^n (8U_m/de)^{n-1}/D \cdot \rho$
Sh = Sherwood number $k \cdot de/D$
U = velocity, cm/s
U_m = mean velocity, cm/s

Greek Letters

ρ = density, g/cm^3
β = velocity gradient at the wall, s^{-1}
$\Omega(a, n)$ = dimensionless flow rate
$\lambda(a, n)$ = dimensionless radius for maximum velocity, r/R
$\Gamma(a, n)$ = function defined in Equation (10), dimensionless
τ_{rz} = local shear stress, dyne/cm^2
$\phi(a)$ = function defined in Equation (3), dimensionless

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Comments on Sufficiency Conditions for Constrained Extrema

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This journal has devoted space (Law and Fariss, 1971; Reklaitis, 1972) to the analysis of equality constrained optimization problems of the type

Extremize $f(\mathbf{x})$

subject to,

$$g_j(\mathbf{x}) = 0, \quad j = 1, 2, \ldots, m \tag{1}$$

The solution usually consists of two parts. In part one, the critical points are located, while in part two, the critical points are classified. Classification involves identifying the critical points as corresponding to either a maximum, a minimum, or a saddle. In nonexceptional cases, the critical points may be located by using either constrained derivatives or Lagrange multipliers. The remainder of this note will be directed to some of the computational aspects involved in the classification of critical points. In particular, for both the constrained derivative and the Lagrange multiplier approaches, methods will be presented for the computation of $\mathbf{H}_c$, which is the constrained Hessian matrix. This matrix is useful since if $\mathbf{H}_c$ is negative (positive) definite, the critical point being tested will correspond to a maximum (minimum). Also, a method for implementing Hancock's test will be presented.

CONSTRAINED DERIVATIVES

The $\mathbf{G}$ matrix is of rank r. By proper choice of the indexes of the x_α, $\alpha = 1, 2, \ldots, n$, and the $g_j(\mathbf{x})$, $j = 1, 2, \ldots, m$, the leading $(r \times r)$ portion of $\mathbf{G}$ may be made nonsingular. This submatrix of $\mathbf{G}$ is called $\mathbf{J}$, while the $(r \times n - r)$ matrix in the north-east corner of $\mathbf{G}$ is called $\mathbf{C}$. The first r components of $\mathbf{x}$ are designated as state variables, while the remaining $(n - r)$ components of $\mathbf{x}$ are called decision variables. From the chain rule

$$\mathbf{J}\, d\mathbf{s} + \mathbf{C}\, d\mathbf{d} = 0 \tag{2}$$

Since $\mathbf{J}$ has an inverse it follows that

$$d\mathbf{s} = -\mathbf{P}\, d\mathbf{d} \tag{3}$$

as well as

$$d\mathbf{x} = \begin{bmatrix} -\mathbf{P} \\ \mathbf{I} \end{bmatrix} (d\mathbf{d}) \tag{4}$$

Wilde and Beightler (1967) show that first-order constrained derivatives may be computed from

$$\frac{\delta(\cdot)}{\delta d_a} = \frac{\partial(\cdot)}{\partial d_a} - P_{ia} \frac{\partial(\cdot)}{\partial s_i} \tag{5}$$

where the summation convention has been used. Second-order constrained derivatives of f are given by

$$\frac{\delta^2 f}{\delta d_a \delta d_b} = \left[\frac{\partial}{\partial d_a} - P_{ia} \frac{\partial}{\partial s_i} \right] \left[\frac{\partial f}{\partial d_b} - P_{jb} \frac{\partial f}{\partial s_j} \right] \tag{6}$$

Further manipulation yields

$$\frac{\delta^2 f}{\delta d_a \delta d_b} = P_{ia} \frac{\partial^2 f}{\partial s_i \partial s_j} P_{jb} - P_{ia} \frac{\partial^2 f}{\partial s_i \partial d_b} - \frac{\partial^2 f}{\partial d_a \partial s_j} P_{jb} + \frac{\partial^2 f}{\partial d_a \partial d_b} - \left[\frac{\delta P_{jb}}{\delta d_a} \right] \left[\frac{\partial f}{\partial s_j} \right] \tag{7}$$

The matrix equivalent of Equation (7) is

$$\mathbf{H}_c = [-\mathbf{P}^T, \mathbf{I}]\, \mathbf{H} \begin{bmatrix} -\mathbf{P} \\ \mathbf{I} \end{bmatrix} + \mathbf{T} \tag{8}$$

where the first four terms on the right side of Equation (7) correspond to the first term on the right side of Equation (8), and

$$\mathbf{T} = - \left\| \left[\frac{\delta P_{jb}}{\delta d_a} \right] \left[\frac{\partial f}{\partial s_j} \right] \right\| \tag{9}$$

Owing to the occurrence of a triply indexed quantity in the definition of $\mathbf{T}$, further matrix reduction of Equation (9) is impossible. It may be shown, however, that the b^{th}

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