studies. The electrodes in the flow model were inaccessible to any convenient optical method for area measurement, and in some instances machining had altered the circular shape and smoothness of the electrode's surface. Optical methods would not reveal possible contaminants or films that could build up on the surfaces with time, thus changing their conductance properties. Impedance measurements seemed impractical since the numerous electrodes were distributed in several branch sites in the flow model each with a different location relative to the counter electrode which would alter the impedance readings.

This polarographic technique is a quick, convenient method for electrode area measurements involving simple circuitry. Area measurements are independent of the geometry of the fluid test system for sufficiently fast ramp rates so that the peak current is achieved before the zone of concentration depletion reaches toward the opposite walls of the test channel. For our system, it had the added advantage that the unknown area measurements could be made *in situ* with the identical test solution being used for the shear rate or mass transfer studies. Randles (1948) lists numerous other electrolyte systems for which the voltage sweep polarographic method is applicable. The method was originally intended as a means of measuring the concentration of electroactive species by polarography, but lends itself easily to electrode area calculations.

NOTATION

A = electrode surface area
B = constant in electrochemical shear rate equation (Lutz, 1977, Eq. 12)
C_o = bulk concentration of electroactive species
D = diameter of circular electrode
D_o = diffusivity of electroactive species
F = Faraday's constant
i = current in shear rate or mass transfer Eq. 1 or 2
i_p = peak current in voltage sweep polaragraphic method
k = mass transfer coefficient
K = constant in Eq. 3 (Meites, 1965)
n = number of electrons exchange per molecule
s = shear rate
v = voltage sweep rate

LITERATURE CITED

Bard, A. J., "Effect of Electrode Configuration and Transition Time in Solid Electrode Chronopotentiometry," *Anal. Chem.*, **33**, 11 (1961).

Bergel, D. H., R. M. Nerem, and C. J. Schwartz, "Fluid Dynamic Aspects of Arterial Disease," *Atherosclerosis*, **23**, 253 (1976).

Fortuna, G., and T. J. Hanratty, "Frequency Response of the Boundary Layer on Wall Transfer Probes," *Int. J. Heat and Mass Transfer*, **14**, 1499 (1971).

Lingane, P. J., "Chronopotentiometry and Chronoamperometry with Unshielded Planar Electrodes," *Anal. Chem.*, **36**, 1723 (1964).

Lutz, R. J., J. N. Cannon, K. B. Bischoff, R. L. Dedrick, R. K. Stiles, and D. L. Fry, "Wall Shear Stress Distribution in a Model Canine Artery During Steady Flow," *Circulation Research*, **41**, 391 (1977).

Meites, L., *Polarographic Techniques*, 2nd ed., John Wiley and Sons, New York (1965).

Mizushina, T., "The electrochemical method in transport phenomena," *Advances in Heat Transfer*, T. F. Irvin and J. P. Hartnett, eds., New York, Academy Press, p. 87 (1971).

Nerem, R. M., and J. F. Cornhill, "The Role of Fluid Mechanics in Atherogenesis, "*J. Biomech. Eng.*, **102**, 181 (1980).

Randles, J. E. B., "A Cathode Ray Polarograph, Part II: The Current-Voltage Curves," *Trans. Faraday Soc.*, **44**, 327 (1948).

Sawyer, D. T., and J. L. Roberts, *Experimental Electrochemistry for Chemists*, John Wiley and Son, New York (1974).

Yoganathan, A. P., W. H. Corcoran, and E. C. Harrison, "Wall Shear Stress Measurements in the Near Vicinity of Prosthetic Aortic Heart Valves," *J. of Bioeng.*, **2**, 369 (1978).

Manuscript received May 18, 1981; revision received September 14, and accepted October 9, 1981.

Numerical Calculation of Effectiveness Factors for the Michaelis-Menten Type Kinetics with High Thiele Moduli

HO NAM CHANG

Department of Chemical Engineering
Korea Advanced Institute of Science and Technology
Seoul 131, Korea

It is common chemical engineering practice to employ effectiveness factors in determining whether the chemical or biochemical reactions in solid-supported catalysts are limited by pore and/or film diffusion. The results of calculated effectiveness factors for various chemical reactions and the asymptotic expressions thereof are well documented by Aris (1975).

Recently, there have been extensive investigations on immobilized enzymes and microbial cells, which permit the reuse of a number of expensive enzymes and thus reduce the production cost of several biochemical processes (Mosbach, 1976). In order to understand the efficacies of these immobilized enzymes and cells compared with those of free ones, there have been growing interests among chemical and biochemical engineers in evaluating effectiveness factors for immobilized enzymes and cells in solid supports (Moo-Young and Kobayashi, 1972; Lee and Tsao, 1974; Ramachandran, 1975).

Unlike most of chemical reactions, enzymic reaction is an isothermal one and is represented mostly by the Michaelis-Menten equation. This simple looking boundary value problem has not been solved analytically yet. Therefore, generally we resort to numerical methods for the solution of the problem. However, in the case of high Thiele moduli it is not uncommon to experience numerical

---

difficulties associated with the stiff concentration gradient near the catalyst surface.

It is the purpose of this study to suggest a convenient way of calculating effectiveness factors especially for high Thiele Moduli when we adopt the finite difference scheme as the method of the solution.

GOVERNING EQUATIONS

An enzymic reaction in a solid support is written in a dimensionless form as follows:

$$\frac{1}{x^{s-1}}\frac{d}{dx}x^{s-1}\frac{dy}{dx} = r(y,x) \tag{1}$$

B.C.

$$x = 1 \quad \frac{dy}{dx} = \mathrm{Sh}(1-y) \tag{2}$$

$$x = 0 \quad \frac{dy}{dx} = 0 \tag{3}$$

where $r(y,x)$ represents the rate of reaction of the substrate per unit volume of the support. In order to account for external and pore diffusion effects, the Robin boundary conditions are selected in this problem whereas the Dirichlet conditions are usually chosen by others (Moo Young and Kobayashi, 1972; Lee and Tsao, 1975). The exponent s of x refers to the shape factor, of which values are 3 for a sphere, 2 for a cylinder, and 1 for a slab geometry. The rate expression $r(y,x)$ can be Michaelis-Menten, substrate or product inhibition kinetics, and is generally given by (Moo-Young and Kobayashi, 1972):

$$r(y,x) = \phi^2 \frac{y}{\beta_1 + y + \beta_2 y^2} \tag{4}$$

where ϕ is the Thiele modulus which can range from very small values ($\phi \ll 1$) to very large ones ($\phi \gg 1$).

It can be easily seen that Eq. 1 is reduced to first order kinetics when y, $\beta_2 y^2$ are much smaller than β_1. In this case, Eq. 1 becomes linear and their solutions for different s are well known.

The effectiveness factor η for an immobilized enzyme in a solid support is given by

$$\eta = \frac{s(\beta_1 + 1 + \beta_2)}{\phi^2} \left.\frac{dy}{dx}\right|_{x=1} \tag{5}$$

Therefore knowing dy/dx at $x = 1$ is enough to calculate the effectiveness factor at a steady state.

METHOD OF SOLUTION

The numerical solution of Eq. 1 to 3 is usually obtained by integrating Eq. 1 starting from $x = 0$ to $x = 1$. Owing to the nonlinear nature of this boundary value problem, the value of y is assumed at $x = 0$, and it is checked whether y and dy/dx ($= y'$) at $x = 1$ satisfy Eq. 2. If Eq. 2 is not satisfied, a new improved approximation for y is made at $x = 0$. This shooting procedure is repeated until the desired accuracy for y and y' is obtained. Fink et al. (1973) transformed this boundary value problem to an initial value problem using Na and Na's technique. However, in either case a trial-and-error method is unavoidable for given values of dimensionless parameters.

For high Thiele moduli with small β_1 values, numerical difficulties arise if an integration at $x = 0$ is performed as usual. That is, the value of y at $x = 0$ becomes very small and goes easily beyond the numerical limitation of digital computers because of a steep gradient. If this is the case, the numerical solution becomes very difficult or fails.

In order to cope with this difficulty, we utilize the first-order analytical solution of the problem for $0 \leq x \leq \zeta$ where y, $\beta_2 y^2$ are negligibly small compared with β_1. Accordingly, we start the numerical integration of Eq. 1 from $x = \zeta$ to $x = 1$ with the assumed $y(\zeta)$ and the corresponding derivative $y'(\zeta)$ obtained from the analytical solution given in Table 1. Irrespective of geometries, the ratio of $y'(\zeta)/y(\zeta)$ approaches asymptotically to ϕ' for high ϕ' (Aris, 1975). A proper shooting procedure is necessary for the desired accuracy of the solution. Naturally we do not need to calculate the analytical solution from $x = 0$ to $x = \zeta$ for the purpose of calculating effectiveness factors.

RESULTS AND DISCUSSION

We have chosen a system whose Thiele modulus is high enough to cause numerical difficulties at the center of a catalyst particle. Even though the definition of Thiele modulus varies from publication to publication, that of immobilized catalyst on porous glass beads as high as 300 has been reported (Tai and Greenfield, 1981). Table 2 shows the result of the calculated effectiveness factors using the present proposed scheme. In this example, the determining factor for the steepness of the equation is not the Thiele modulus alone but the modified modulus defined by

$$\phi' = \phi/\sqrt{\beta} \tag{6}$$

In this first case where ϕ' equals 1,000, the calculation y,y' is not possible even at $x = 0.8$ since their values are beyond the limit of the commercially available minicomputer (HP 3000). The case would be even worse at $x = 0$ where the boundary condition for y' is exactly specified. The solutions obtained by the present method are consistent with each other as long as the assumptions are valid. That is, the values of y and y' at $x = 0.90$, and 0.95 are entirely negligible compared with β_1 of which value is 0.01. However, the value of y at $x = 0.99$ is .109172D-02 which amounts to 10.9% of β_1, which is not completely negligible. Even in this case, the ef-

TABLE 1. ANALYTICAL SOLUTIONS FOR EQS. 1 TO 3 IN THE CASE OF FIRST-ORDER KINETICS ($y,\beta_2 y^2 \ll \beta_1$)

Function / Geometry	$y(x)$	$y'(x)$	$\frac{y'(x)}{y(x)}$
Sphere (s = 3)	$c\left[\frac{1}{x}\sinh(\phi' x)\right]$	$c\left[-\frac{1}{x^2}\sinh(\phi' x) + \frac{\phi'}{x}\cosh(\phi' x)\right]$	$-\frac{1}{x} + \phi' \coth(\phi' x)$
Cylinder (s = 2)	$c[I_o(\phi' x)]$	$c[\phi' I_1(\phi' x)]$	$\frac{\phi' I_1(\phi' x)}{I_0(\phi' x)}$
Slab (s = 1)	$c[\sinh(\phi' x)]$	$c[\phi' \cosh(\phi' x)]$	$\phi' \coth(\phi' x)$

c = a constant, $\phi' = \frac{\phi}{\sqrt{\beta_1}}$

TABLE 2. CALCULATED EFFECTIVENESS FACTORS USING THE PRESENT SCHEME ($s = 3$)

Parameters $X(\zeta)$		I	II	III
		$\phi = 100$	$\phi = 100$	$\phi = 100$
		$\beta_1 = 0.01$	$\beta_1 = 0.10$	$\beta_1 = 1.00$
		$\beta_2 = 0.00$	$\beta_2 = 0.00$	$\beta_2 = 0.00$
		Sh = 100	Sh = 100	Sh = 100
0.8	$y(0.8)$	*	0.390099D − 27	0.165371D − 08
	$y'(0.8)$	*	0.122872D − 24	0.163304D − 06
	$y(1.0)$	*	0.360049D + 00	0.540247D + 00
	$y'(1.0)$	*	0.639951D + 02	0.459754D + 02
	η	*	0.211184D − 01	0.275852D − 01
0.9	$y(0.9)$	0.104202D − 41	0.187578D − 13	0.323760D − 04
	$y'(0.9)$	0.104086D − 38	0.591090D − 11	0.320163D − 02
	$y(1.0)$	0.289210D + 00	0.360049D + 00	0.540247D + 00
	$y'(1.0)$	0.710790D + 02	0.639951D + 02	0.459753D + 02
	η	0.215369D − 01	0.211184D − 01	0.275852D − 01
0.95	$y(0.95)$	0.511490D − 20	0.130702D − 06	0.454164D − 02
	$y'(0.95)$	0.510952D − 17	0.411939D − 04	0.449384D + 00
	$y(1.0)$	0.2892100 + 00	0.360049D + 00	0.540247D + 00
	$y'(1.0)$	0.710790D + 02	0.639951D + 02	0.459753D + 02
	η	0.2153690 − 01	0.211184D − 01	0.275852D − 01
0.99	$y(0.99)$	0.109172D − 02	0.327623D − 01	0.213622D + 00
	$y'(0.99)$	0.109061D + 01	0.103273D + 02	0.211464D + 02
	$y(1.0)$	0.289208D + 00	0.359395D + 00	0.536846D + 00
	$y'(1.0)$	0.710792D + 02	0.640605D + 02	0.463154D + 02
	η	0.215370D − 01	0.211400D − 01	0.277893D − 01

* = beyond the limit of HP 3000 minicomputer.

fectiveness factor differs from the two previous ones only by a minute amount.

Considering the cases of II and III at $x = 0.99$, the values of y are 32.7%, 21.3% of β_1 respectively, but the effectiveness factors are in error only by 0.10%, and 0.74%. Thus, the selection of the starting point ζ depends on the required accuracy for the effectiveness factor η. A considerably accurate solution can be obtained if we choose ζ such that ζ may be equal to $[1 - (10/\phi')]$. This method should be applicable to the solutions of Monod and Langmuir-Hinshelwood (isothermal case) kinetics, since they are mathematically the same.

As a conclusion this technique will prove useful in obtaining the effectiveness factor for catalyst particles of high Thiele modulus with the Michaelis-Menton type kinetics even when normal numerical scheme fails and consequently in saving much of the computing time.

NOTATION

$r(y,x)$ = reaction kinetics describing the reaction by enzyme solid support
s = shape factor, 3 for a sphere, 2 for a cylinder and 1 for a slab geometry
Sh = Sherwood number
x = distance variable measured from the surface to the inside of the particle
y,y' = dependent variable and its derivative along x

Greek Letters

β_1,β_2 = constants for Michaelis-Menten, or inhibition kinetics
η = effectiveness factor
ϕ = Thiele modulus
ϕ' = modified Thiele modulus

LITERATURE CITED

Aris, R., *The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts*, **I, II**, Clarendon Press, Oxford (1975).

Fink, D. J., T.Y. Na, and J. S. Schultz, "Effectiveness Factor Calculations for Immobilized Enzyme Catalysts," *Biotechnol. Bioeng.*, **15**, 879 (1973).

Lee, Y. Y., and G. T. Tsao, "Mass Transfer Characteristics of Immobilized Enzymes," *J. Food Sci.*, **39**, 667 (1974).

Mosbach, K., *Methods in Enzymology Vol. XLIV*, *Immobilized Enzymes*, Academic Press, New York (1976).

Moo-Young, M., and T. Kobayashi, "Effectiveness Factors for Immobilized-Enzyme Reactions," *Can. J. Chem. Eng.*, **50**, 162 (1972).

Ramachandran, P. A., "Solution of Immobilized Enzyme Problems by Collocation Methods," *Biotechnol. Bioeng.*, **17**, 211 (1975).

Tai, N. M., and P. F. Greenfield, "Determination of the Inherent Deactivation Characteristics for the Parallel Poisoning of Immobilized Catalase," *Biotechnol. Bioeng.*, **23**, 805 (1981).

Manuscript received August 4, 1980; revision received September 22 and accepted October 9, 1981.