

Unsteady State Effectiveness Factor for Immobilized-Enzyme Reaction

By

Kenji HASHIMOTO*, Shuji ADACHI** and Masaru YOKOYAMA***

(Received June 29, 1985)

Abstract

The unsteady state concentration profiles of substrate in immobilized-enzyme particles were calculated numerically for the Michaelis-Menten kinetics. The analytical solution of the profile was also derived when the reaction was approximated to be of the first-order. The integration of the profile gives an unsteady state effectiveness factor. The unsteady state effectiveness factor was obtained under various conditions. The critical time at which a pseudo-steady state approximately holds, was presented graphically as a function of the steady state effectiveness factor for various $\nu_0(=K_m/C_{A0})$ values. The charts indicate that the pseudo-steady state is achieved within 10-20s under usual operating conditions.

1. Introduction

An isothermal batch reactor is conveniently used to study the kinetics of an immobilized-enzyme reaction. The reaction catalyzed by the immobilized enzyme is heterogeneous. For heterogeneous reactions, the transient diffusional phenomena sometimes complicate the interpretation of the data taken from such a batch reactor.

The purpose of this paper is to discuss the unsteady state effectiveness factor in the heterogeneous reactor involving immobilized-enzyme particles. Here, we consider two cases where an enzyme reaction is represented by the Michaelis-Menten kinetics, and is approximated to be of the first-order. The discussion will give the critical time at which the pseudo-steady state approximately holds.

Some investigators have reported on the unsteady state effectiveness factor in a batch reactor where a first-order reaction proceeds. Villadsen and Stewart¹⁾ considered the unsteady state effectiveness factor in a batch reactor with an infinite volume of reactant. Lewis and Paynter²⁾ discussed the unsteady state effectiveness factor for a finite volume of reactant. A typical rate expression of enzyme reaction is the Michaelis-Menten form, which is applicable for many enzyme reactions. This

* Department of Chemical Engineering.

** Present address: Niihama National College of Technology, Niihama.

*** Present address: Matsushita Denko Co. Ltd., Kadoma.

expression is approximated to be of the first-order only when the substrate concentration is much lower than the Michaelis constant. There is no paper which deals with the unsteady state effectiveness factor for the Michaelis-Menten kinetics. We calculate the transient concentration profiles within a spherical immobilized-enzyme particle, and then integrate the profiles to give the unsteady state effectiveness factor for the kinetics.

There is some discussion^{3,4)} about the steady state effectiveness factor for immobilized-enzyme reactions. Some investigators^{5,6)} have presented approximate correlations between the steady state effectiveness factor and the general modulus proposed by Bischoff⁷⁾. These papers assumed implicitly that the pseudo-steady state is achieved immediately. However, no verification is given for this assumption. We will show that the implicit assumption is appropriate under usual operating conditions.

2. Problem Formulation

The Michaelis-Menten kinetics is considered for an immobilized-enzyme catalyzed reaction. The immobilized-enzyme particles with the interior void fraction, ϵ , which contains a diluent, are immersed into a volume, V_0 , of reactant. For simplicity, the following assumptions are made: i) the reaction proceeds under an isothermal condition, ii) the enzyme is homogeneously distributed within the particles, and iii) the effect of film diffusion of substrate on the reaction rate can be ignored.

The problem can be stated by the following partial differential equation and its associated boundary conditions.

$$\frac{\partial y^*}{\partial \theta} = \left(\frac{\partial^2 y^*}{\partial \xi^2} + \frac{2}{\xi} \cdot \frac{\partial y^*}{\partial \xi} \right) - 9\phi^2 \nu_0 \cdot \frac{y^*}{y^* + \nu_0} \quad (1)$$

$$\text{at } \xi=1, \theta > 0, \partial y / \partial \theta = -\alpha (\partial y^* / \partial \xi) \quad (2)$$

$$\text{at } \xi=0, \theta > 0, \partial y^* / \partial \xi = 0 \quad (3)$$

$$\text{at } \xi=1, \theta=0, y^*=1 \quad (4)$$

$$\text{at } 0 \leq \xi < 1, \theta=0, y^*=0 \quad (5)$$

where the dimensionless variables and parameters are defined by

$$y^* = C_A^* / C_{A0} \quad (6a)$$

$$y = C_A / C_{A0} \quad (6b)$$

$$\theta = D_{eA} t / (\epsilon R^2) \quad (6c)$$

$$\xi = r / R \quad (6d)$$

$$\phi = (R/3) \{V_{\max} / (K_m \cdot D_{eA})\}^{1/2} \quad (6e)$$

$$\nu_0 = K_m / C_{A0} \quad (6f)$$

$$\alpha = 3W\epsilon / (V_0 \rho_p) \quad (6g)$$

Since it is not easy to solve analytically the above basic equations, they were numerically solved.

When the substrate concentration is much less than K_m , that is, $y^* \ll \nu_0$, the

reaction term in Eq. (1) can be approximated to be of the first-order.

$$9\phi^2\nu_0 \cdot y^*/(y^* + \nu_0) \simeq 9\phi^2 y^* \quad (7)$$

In such a case, the following analytical solution of Eq. (1) can be obtained:

$$y^* = \frac{2\alpha k_i'^2 \exp\{-(9\phi^2 - k_i'^2)\theta\}}{k_i'^2(2 + \alpha) - (9\phi^2 - k_i'^2)(9\phi^2 - k_i'^2 + \alpha)} \cdot \frac{1}{\xi} \cdot \frac{\sinh(k_i'\xi)}{\sinh(k_i')} \\ + \sum_{n=1}^{\infty} \frac{2\alpha k_n^2 \exp\{-9(\phi^2 + k_n^2)\theta\}}{\alpha k_n^2(2 + \alpha) + (9\phi^2 + k_n^2)(9\phi^2 + k_n^2 + \alpha)} \cdot \frac{1}{\xi} \cdot \frac{\sin(k_n\xi)}{\sin(k_n)} \quad (8)$$

where k_i' and k_n , respectively, are the positive roots of the following two transcendental equations.

$$\tanh(k_i') = \alpha k_i' / (9\phi^2 - k_i'^2 + \alpha) \quad (9)$$

$$\tan(k_n) = \alpha k_n / (9\phi^2 + k_n^2 + \alpha) \quad (10)$$

The dimensionless concentration of substrate at the surface of immobilized-enzyme particles can be obtained by setting $\xi=1$ at Eq. (8). Towler and Rice⁸ derived an equation similar to Eq. (8) for an isothermal continuous stirred tank reactor with a first-order reaction. Their solution is, however, applicable only in a case where the mean residence time is less than $1/k$ (k : rate constant). Such a condition is unpractical. Our solution does not have such an unrealistic limitation.

Lewis and Paynter² have defined the effectiveness factor in a batch reactor as follows:

$$E_{t\theta} = \frac{\int_0^1 (4\pi\xi^2) \{y^*/(y^* + \nu_0)\} d\xi}{(4\pi/3) \{y/(y + \nu_0)\}} \quad (11)$$

or

$$\eta_0 = \frac{1}{3\phi^2} \cdot \frac{(\partial y^*/\partial \xi)|_{\xi=1}/V}{\{\nu_0[y/(y + \nu_0)]\}/V_0} \quad (12)$$

where V and V_0 are related by Eq. (13).

$$V = V_0 + \varepsilon V_c \quad (13)$$

The effectiveness factor defined by Eq. (11), $E_{t\theta}$, is different from that defined by Eq. (12), η_0 . There is the following relation between them.

$$E_{t\theta} = (V/V_0)\eta_0 \\ = \{1 + \varepsilon(V_c/V_0)\}\eta_0 \quad (14)$$

In this work, the effectiveness factor defined by Eq. (11), $E_{t\theta}$, is discussed. In a case where the first-order reaction can be used approximately because of a low substrate concentration, the unsteady state effectiveness factor is easily calculated from Eq. (8). On the other hand, Eq. (1) is solved numerically by the Crank-Nicolson method. The integration of the resulting concentration profile in the particle by Simpson's method gives the unsteady state effectiveness factor, $E_{t\theta}$.

3. Computed Results

The steady state effectiveness factor $E_{t\infty}$ can be obtained by designating the

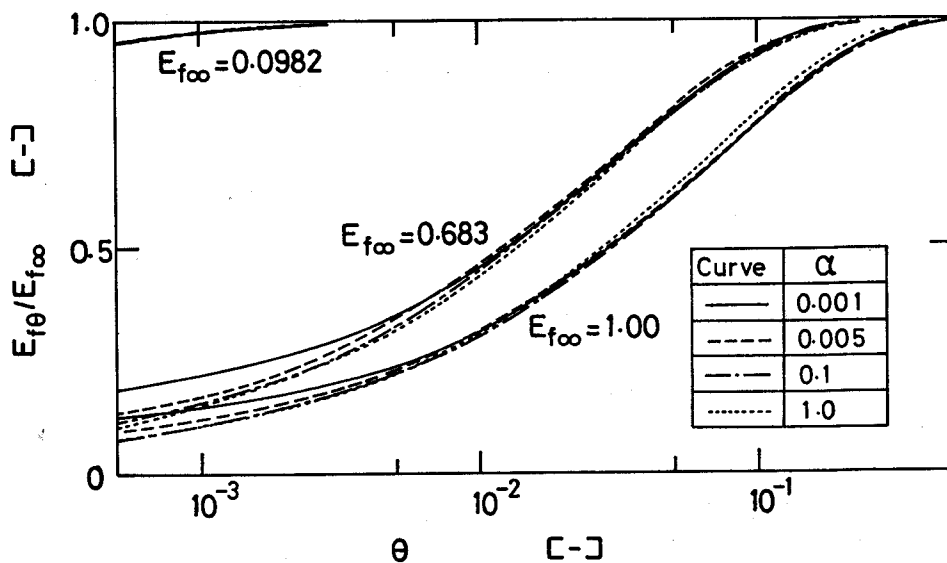


Fig. 1. Transient change of $E_{t\theta}/E_{t\infty}$ values for various $E_{t\infty}$ and α values when an enzymatic reaction can be approximated to be first-order.

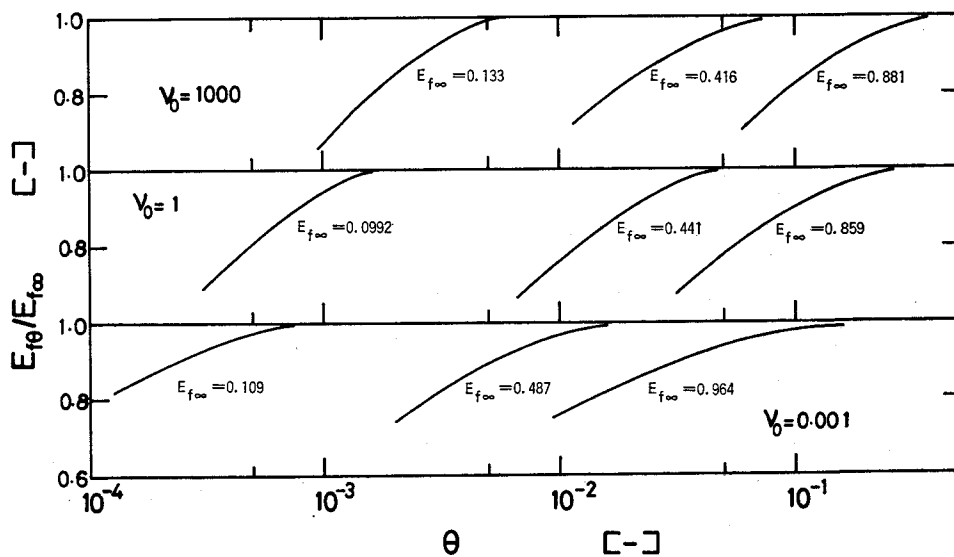


Fig. 2. Relation between $E_{t\theta}/E_{t\infty}$ and θ for Michaelis-Menten kinetics.

left-hand side of Eq. (1) to be zero. First, we considered the first-order reaction. Figure 1 shows the transient changes of $E_{t\theta}/E_{t\infty}$ values for various values of $E_{t\infty}$ and α . As shown in Fig. 1, the effect of the parameter α on $E_{t\theta}/E_{t\infty}$ is negligible. Figure 2 illustrates the relation between $E_{t\theta}/E_{t\infty}$ and θ for the Michaelis-Menten

kinetics under various ν_0 values. In Fig. 2, the α value is fixed at 0.1. When the value of $E_{t0}/E_{t\infty}$ reaches 0.98, we consider conveniently a pseudo-steady state to be achieved. The critical time necessary to achieve the pseudo-steady state is represented by θ_c . Figure 3 illustrates the relation between θ_c and $E_{t\infty}$ using ν_0 as a parameter. When $\nu_0 = \infty$, the reaction is of the first-order. On the other hand, the case where ν_0 value is equal to 0.001 corresponds to the case where the Michaelis-Menten equation is approximated to the zeroth-order reaction.

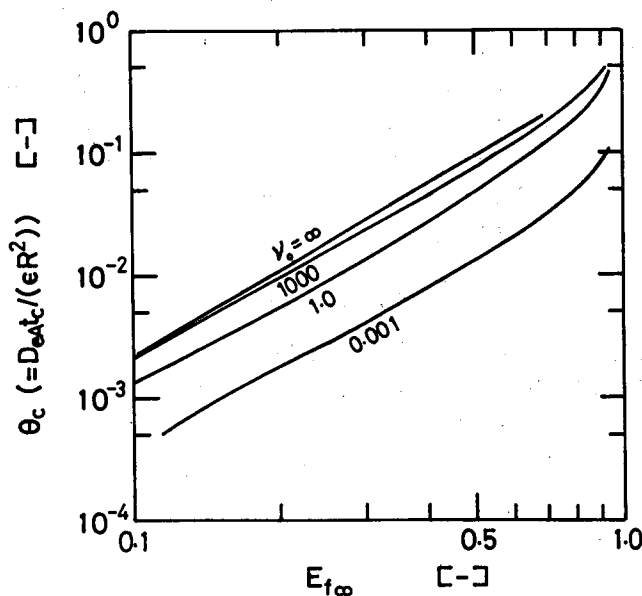


Fig. 3. Charts for estimating an actual time necessary to achieve the pseudo-steady state approximation.

The critical time θ_c is a function of $E_{t\infty}$, ϕ , ν_0 and α values. However, the effect of α value on the θ_c value is negligibly small. The effect of ϕ on θ_c is included in $E_{t\infty}$ because $E_{t\infty}$ is a function of ϕ . From Fig. 3, an actual time taken to achieve the pseudo-steady state after the start of reaction in the batch reactor is calculated under typical conditions. The pseudo-steady state is achieved within 10 ~ 20 s under the conditions that $E_{t\infty} = 0.8$, $\epsilon = 0.5$, $R = 0.025$ cm, and that the D_{0A} value is in the order of 10^{-6} cm²/s. With a decrease of the $E_{t\infty}$ value the θ_c value becomes smaller, that is, the pseudo-steady state is achieved faster. This result shows that the pseudo-steady state is achieved in a relatively short time in the batch reactor involving immobilized-enzyme particles, excepting extreme operating conditions. In conclusion, the steady state effectiveness factor can be used through the course of reaction.

4. Conclusion

The unsteady state effectiveness factor for immobilized enzyme reaction represented by the Michaelis-Menten kinetics was discussed. The transient concentration profiles of substrate within immobilized-enzyme particles were obtained by solving numerically the system transport equations. In the case where the reaction was approximated to be of the first-order, an analytical solution of the transient profile with generality was presented. Integration of the resulting profile gave the unsteady state effectiveness factor, $E_{t\theta}$. The $E_{t\theta}$ value was insensitive to the parameter α , which means the ratio of the volume of interior void of particle to that of bulk solution. The time necessary to achieve the pseudo-steady state was illustrated as a function of the steady state effectiveness factor $E_{t\infty}$ for various $\nu_0 (=K_m/C_{A0})$ values. Our discussion showed that the pseudo-steady state is achieved within 10~20 s under usual operating conditions.

Nomenclature

C_A : concentration of substrate in bulk solution	(mol/cm ³)
C_A^* : concentration of substrate at stationary phase	(mol/cm ³)
D_{oA} : effective diffusivity of substrate	(cm ² /s)
$E_{t\theta}$: unsteady state effectiveness factor defined by Eq. (11)	(—)
$E_{t\infty}$: steady state effectiveness factor	(—)
K_m : Michaelis constant	(mol/cm ³)
R : radius of the bead	(cm)
r : radial distance	(cm)
t : time	(s)
V_c : volume of stationary phase	(cm ³)
V_{max} : maximum reaction rate	(mol/cm ³ ·s)
V_0 : volume of the reactant	(cm ³)
W : weight	(g)
$y = C_A/C_{A0}$	(—)
$y^* = C_A^*/C_{A0}$	(—)
$\alpha = 3W\varepsilon/(V_0\rho_p)$	(—)
ε : interior void fraction	(—)
η_0 : unsteady state effectiveness factor defined by Eq. (12)	(—)
$\theta = D_{oA}t/(\varepsilon R^2)$	(—)
$\xi = r/R$	(—)
$\nu_0 = K_m/C_{A0}$	(—)
ρ_p : apparent density	(g/cm ³)

$$\phi = (R/3) \{V_{\max}/(K_m \cdot D_{eA})\}^{1/2} \quad (—)$$

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