LECTURES 13-17: Immobilized Enzymes

Problem 1

Determine the effect of diffusion (in percent) on the reaction rate constant for a first order reaction

for an immobilized enzyme of radius r=1nm, rate constant $k=3\times10^{-8}$ $mol^{-1}\ s^{-1}$

$D_{eff} = 6.5\times10^{-7}\ cm^2/sec$

Solution : $k = 5 \times 10^{-13}\ cm^3/mol.sec$

$$\text{Observed reaction rate coefficient, } k_{obs} = \frac{4\pi r D_{eff}\, k}{4\pi r D_{eff} + k}$$

Coefficient of diffusion = Intrinsic reaction rate – observed reaction rate

$$= k_D - k_{obs}$$

$$= \left(\frac{k}{4\pi r D_{eff} + k}\right) k_D$$

So calculating $\left(\frac{k}{4\pi r D_{eff} + k}\right)$ we get,

Effect of diffusion will be 38%

Problem 2

Calculate the effectiveness parameter η for the following structures which contains enzymes immobilized within them. The volumetric rate for the enzymatic reaction is assumed to be first order with a rate constant of 3.5 s^{-1} .

a)slab
b)cylinder
c)sphere

Note that $\phi^2 = \frac{K_m L^2}{D_{eff}}$ and $L = L_{slab} = R_c/2 = R_s/3$

Solution:

For slab:

Diffusion –Reaction equation for symmetrical geometry is given as

$$D_{eff}\nabla^2 C = -R_v \quad (7.1)$$

where

D_{eff} – effective diffusion

$R_v = K_v C$

BCs: at x=0 $\frac{dc}{dx} = 0$

at x=0 $C = K_{av} C_0$

Nondimensionalization :

Consider $\hat{x} = \frac{x}{L}$ and $\theta = \frac{C}{K_{av} C_0}$

Using non-dimensional quantities (7.1) becomes

$$\frac{d^2 C}{d\hat{x}^2} = \frac{K_v L^2}{D_{eff}} C \tag{7.2}$$

or

$$\frac{d^2 \theta}{d\hat{x}^2} = \phi^2 \theta \tag{7.3}$$

where $\phi^2 = \frac{K_m L^2}{D_{eff}}$

Solving eqn. (7.3), we get

$$\theta = \frac{\text{Cosh}\left(\varphi \hat{x}\right)}{\text{Cosh }\varphi} \tag{7.4}$$

Reaction rate over a volume V is

$$\overline{\text{Rv}} = \frac{1}{V}\int_V R_v dV \tag{7.5}$$

Substituting for R_v we get

$$\overline{\text{Rv}} = \frac{K K_{av} C_0}{\text{Cosh}(\phi)}\int_0^L \text{Cosh}\left(\phi \hat{x}\right) d\hat{x} \tag{7.6}$$

$$\overline{\text{Rv}} = \frac{K'\text{Sinh}\phi}{\phi\text{Cosh}\phi} \tag{7.7}$$

Solving and putting the limits, we get

$$\overline{\text{Rv}} = \frac{K'\tanh\phi}{\phi} \tag{7.8}$$

Effectiveness factor,

$$\eta = \frac{\overline{Rv}}{Rv\left(C_0\right)}$$

Therefore

$$\eta = \frac{\tanh\varphi}{\varphi}$$

For sphere:

Governing eqn.:

$$\frac{D_{eff}}{r^2}\frac{d}{dr}\left(r^2\frac{dC}{dr}\right) = K_{\mathrm{v}}C \tag{7.9}$$

$$\text{B.Cs}: \quad r{=}0 \qquad \frac{dC}{dr} = 0$$

$$r{=}\mathrm{R_m} \qquad C{=}\mathrm{K_{av}}C_0$$

Assuming dimensionless quantities

$$\xi = \frac{r}{R_m} \quad \text{and} \quad C = \frac{f}{\xi}$$

Inserting dimensionless quantities in eqn.(7.9) and after manipulations, we get

$$\frac{1}{\xi^2}\frac{d}{d\xi}\left(\xi^2 \frac{dC}{d\xi}\right) = \phi^2 C \qquad (7.10)$$

B.Cs :

$$\text{at } \xi = 0 \quad \frac{dC}{d\xi} = 0$$

$$\xi = 1 \quad \mathrm{C = K_{av} C_0}$$

$$\& \ \phi^2 = \frac{K_{av} R_m{}^2}{D_{eff}}$$

Solving eqn. (7.10), we get

$$\frac{d^2 f}{d\xi^2} = \phi^2 f \tag{7.11}$$

Using B.Cs, we get

$$f = \frac{K_{\text{av}} C_0}{\sinh(\phi)} \sinh(\phi\xi) \tag{7.12}$$

Thus

$$C = \frac{K_{\text{av}} C_0}{\xi} \frac{\sinh(\phi\xi)}{\sinh(\phi)} \tag{7.13}$$

Effectiveness factor is given by

$$\eta = \frac{\int_0^R C r^2 dr}{K_{\text{av}} C_0 \int_0^R r^2 dr} \tag{7.14}$$

Solving eqn. (7.14)

Numerator :

$$\int_0^R Cr^2 dr = \frac{K_{\text{av}} C_0 R_m{}^3}{\phi}\left(\frac{1}{\tanh\phi} - \frac{1}{\phi}\right)$$

Denominator:

$$K_{\text{av}} C_0 \int_0^R r^2 dr = \frac{K_{\text{av}} C_0 R_m{}^3}{3}$$

Therefore

$$\eta = \frac{3}{\phi}\left(\frac{1}{\tanh\phi} - \frac{1}{\phi}\right) \qquad (7.15)$$