The Effect of Rotational Masking on Optimum Pore Size

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Introduction

The increasing importance of bioprocessing technology, as well as that of the catalytic processing of heavy petroleum residua and coal-derived liquids, has led numerous groups to investigate the diffusion of large molecules in the fine pores of various support media. The results of these investigations demonstrate that the diffusion of such macromolecules in liquids within finely porous materials is reduced when the solute molecular size is comparable to that of the pore size (Satterfield et al., 1973).

The effective diffusivity within the porous media is typically expressed in terms of its bulk value by the following relationship:

$$D_e = \frac{\epsilon_p D_b}{\tau} K_r \tag{1}$$

K_r represents the fractional decrease in the solute diffusivity within the pore as the solute size approaches that of the pore. Various expressions have been developed for K_r (Renkin, 1954; Satterfield et al., 1973; Colton et al., 1975; Prasher and Ma, 1977; Prasher et al., 1978; Chantong and Massoth, 1983).

For a given immobilized enzyme or catalyst pellet of constant porosity and constant activity per unit surface area of support, there exists an optimum pore size that maximizes the reaction rate. This optimum pore size is a result of two opposing effects. Increasing the pore size decreases the reaction rate, since the surface area is decreased, and increases the diffusion rate.

Determination of an optimum pore size for the hydrodesulfurization of petroleum feedstocks was presented by Ruckenstein and Tsai (1981). Their results for petroleum residua indicate an optimum pore size on the order of twice the molecular diameter. A further analysis of optimal pore size was recently presented by Do (1984). In this study, the effect of the bulk concentration on the optimum pore size was examined by relating the pore surface concentration to the bulk concentration by a nonlinear partition expression developed by Glandt (1981). The results indicate that the nonlinear partition coefficient reduces the optimal pore size.

In determining the optimal pore size, previous investigations accounted for the reduction in bulk diffusivity using an expression for K_r. It was assumed that the intrinsic rate of the reaction was not affected by the ratio of molecular diameter to support pore diameter. Webster (1983a, b), in an examination of the restricted diffusion of substrate in porous immobilized enzymes, introduced the concept of rotational masking. This additional limitation on the observed reaction rate was proposed to be the result of two factors. The first is that many reactions are highy specific, requiring that the reactant bind at the active site in the correct stereospecific configuration. The second factor is that the rotational mobility of the reactant when its molecular diameter is comparable to that of the pore size will be reduced relative to its rotational freedom in free solution. Therefore, it is to be expected that not only the effective diffusivity of the solute, but its intrinsic reaction rate, will be decreased when the solute molecular size is comparable to that of the pore. This has important implications not only in determining the optimal pore size, but also in the interpretation of kinetic data wherein intraparticle gradients can be neglected; the intrinsic rate constants that are determined will be a function of pore size.

In this note a simple functional dependence of the rate constant on relative pore size is introduced into the mass balance equation for a spherical catalyst pellet. The effect of various degrees of rotational masking on optimal pore size is presented.

Mathematical Model

The mass balance for the reactant in the spherical catalyst pellet, assuming first-order kinetics, is:

$$D_e \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c}{\partial r} \right) - \rho_p S_g k'' c = 0 \tag{2}$$

With restricted diffusion, D_e is given by Eq. 1 and in this analysis K_r is given by the expression proposed by Renkin (1954).

$$K_r = 1 - 2.104\lambda + 2.09\lambda^3 - .95\lambda^5 \qquad (3)$$

where λ is the ratio of solute size to pore size.

The dependence of k'' on λ can be simply expressed as

$$k'' = k_0'' e^{-\alpha\lambda} \qquad (4)$$

The constant α represents the degree of rotational masking. This expression for the dependence of k'' on λ is not without some justification. First it would be expected that k'' would decrease continuously with increasing λ. Second, assuming k_0'' is given by an Arrhenius-type expression, then it is reasonable to assume that the activation energy for the reaction would increase due to the decreased rotational mobility of the reactant as λ increases. If the activation energy dependence on λ is linear, then Eq. 4 results.

The boundary conditions include the usual symmetry condition at the pellet center

$$r = 0 \quad \frac{dc}{dr} = 0 \qquad (5)$$

and the pellet surface concentration is related to the bulk concentration using the expression developed by Glandt (1981), but neglecting the higher order terms in bulk concentration

$$r = R \quad c(R) = c_b K_o \qquad (6)$$

where $K_o = (1 - \lambda)^2$.

By introducing the following dimensionless variables

$$y = c/K_o c_b, \; x = r/R, \quad \phi_o^2 = \frac{2R^2 k_o'' \tau}{D_b a} \qquad (7)$$

it follows that the solution to Eq. 2 for the nondimensional reaction rate is

$$\Omega = K_r(\lambda)(1 - \lambda)^2 \left[\phi_o \sqrt{\frac{\lambda}{g(\lambda)}} \coth\left(\phi_o \sqrt{\frac{\lambda}{g(\lambda)}} \right) - 1 \right] \qquad (8)$$

Equation 8 is similar to Eq. 18 of Do (1984) with the exception that here $g(\lambda)$ includes both diffusional and rotational masking effects and is defined as

$$g(\lambda) = K_r(\lambda)/e^{-\alpha\lambda} \qquad (9)$$

Results and Conclusions

Using Eq. 8, Figure 1 illustrates the dependence of the dimensionless optimum pore size, λ_{opt}, on ϕ_o, with the rotational masking constant α as a parameter.

As expected, it is found that the effect of rotational masking on the optimum pore size is more pronounced in the reaction-controlled regime than in the diffusion-controlled regime. As shown in Figure 1, rotational masking can have a significant effect on optimal pore size. For $\phi_o = 1$ and $\alpha = 4$, the optimum pore size is nearly twice that with no rotational masking, whereas at $\phi_o = 100$, the optimum pore size with the same degree of rotational masking is nearly 60% greater. Even for moderate degrees of rotational masking, $\alpha = 1$, there is a 19% increase in pore size for $\phi_o = 1$. For the $\phi_o = 1$ and $\alpha = 4$ case, the rate constant at λ_{opt} has been reduced by about 48%, whereas for $\phi_o = 1$ and $\alpha = 1$, the rate constant at λ_{opt} was reduced by about 23%. Thus, only moderate reductions in the intrinsic rate are needed to affect the optimal pore size.

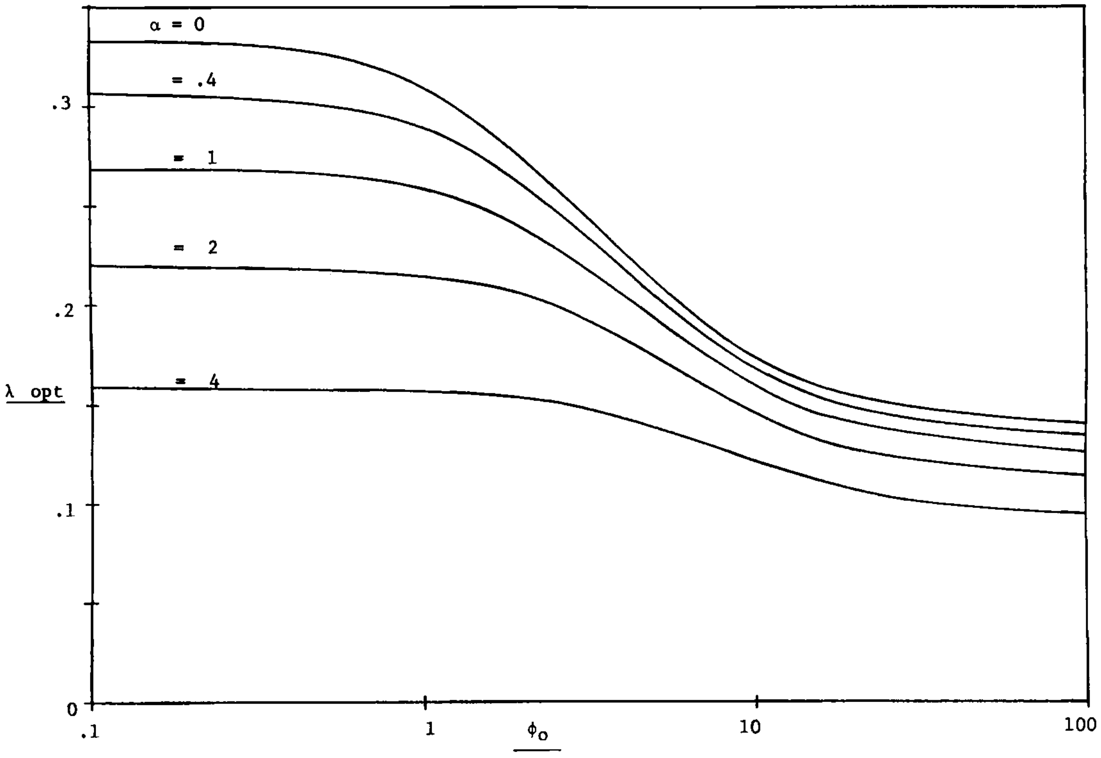

Figure 1. Effect of rotational masking on optimum pore size.

Although the form chosen for the dependence of k'' on λ is simplified the results indicate that rotational masking should be considered in those cases where restricted diffusion is known to occur. Failure to include this effect could significantly decrease the performance of an optimally designed catalyst. Experimental studies of rotational masking are needed to further understand the mechanism of the effect and to determine the functional dependence of the intrinsic rate constant on pore size.

Notation

a = reactant molecular radius
c = intraparticle concentration
c_b = bulk concentration
D_b = bulk diffusivity
D_e = effective diffusivity
g = function, Eq. 9
k'' = surface reaction constant
k''_o = surface reaction constant at $\lambda \ll 1$
K_r = drag coefficient
K_o = linear partition coefficient
r = radial coordinate
r_p = pore radius
S_g = interior surface area per unit mass
x = nondimensional radial coordinate
y = nondimensional intraparticle concentration

Greek letters

α = rotational masking constant
ϵ_p = pellet porosity
λ = ratio of reactant molecular size to pore size
ρ_p = pellet density
τ = tortuosity factor
ϕ_o = Thiele modulus, Eq. 7
Ω = nondimensional reaction rate, $[4\pi R^2 D_e (dc/dr)|_R]/[(4\pi R\epsilon_p D_b c_b)/\tau]$

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