Restricted Diffusion through Pores with Periodic Constrictions

D. M. Smith
Department of Chemical & Nuclear
Engineering
University of New Mexico
Albuquerque, NM 87131

Introduction

The effective diffusivity of a solute in a porous solid is related to the solute diffusivity in bulk solution and the solid's porosity by:

$$D_e = \epsilon D_o/\tau \tag{1}$$

The value of the tortuosity, τ, is a function of the pore size distribution, pore shape, pore connectivity, and degree of pore constrictions. When the effective molecular size of the solute is not negligible with respect to the pore dimensions, the actual effective diffusivity will be less than values calculated using Eq. 1. This phenomenon is referred to as restricted diffusion or hindered diffusion. The reduction in D_e is the result of steric exclusion effects and increased hydrodynamic drag on the molecule. For restricted diffusion, the effective diffusivity is (Satterfield et al., 1973):

$$D_e = \epsilon D_o K_p(\lambda) K_r(\lambda)/\tau \tag{2}$$

The equilibrium partition coefficient, K_p, and the hydrodynamic drag coefficient, K_r, are both functions of λ, the ratio of molecular size to pore size. In contrast, the tortuosity factor, τ, has always been taken to be independent of λ. In this work, the question of tortuosity changes with varying λ as a result of nonuniformities in the pore cross section is addressed. In addition, methods of defining and measuring the characteristic pore size are assessed in order to minimize pore constriction effects.

Background

The magnitude of K_p and K_r is determined by assuming that pores are uniform, nonintersecting cylinders. K_p for solid spherical molecules in a cylindrical pore with no pore wall-molecule interactions has been given by Ferry (1936) as

$$K_p = (1 - \lambda)^2 \tag{3}$$

The effect of viscous drag on the solute transport rate is determined by calculating the local Stokes friction coefficient as a function of position and taking the spatial average. For small λ, Brenner and Gaydos (1977) have shown

$$K_r = (1 + 9/8\lambda \ln(\lambda) - 1.54\lambda)/(1 - \lambda)^2 \tag{4}$$

For larger values of λ ($\lambda < 0.5$), Pappenheimer et al. (1951) assumed that the local Stokes coefficient is equal to the centerline value and is calculated:

$$K_r = 1 - 2.104\lambda + 2.089\lambda^3 - 0.948\lambda^5 \tag{5}$$

Paine and Scherr (1975) presented K_r values in tabular form for $\lambda < 0.9$ by employing the centerline assumption.

In general, experimental studies of restricted diffusion may be grouped into two areas. For studies using track-etched membranes, τ is equal to 1 and the question of τ changing with λ is moot. Work conducted using nonideal porous media does not show satisfactory agreement with theory (Eqs. 2–5). This discrepancy may be the result of assuming a constant tortuosity factor.

Although the effect of pore constrictions on restricted diffusion has not been previously addressed, several investigators have analyzed the effect of pore constrictions in the bulk diffusion and Knudsen diffusion regimes. Petersen (1958) modeled a constricted pore as a series of hyperbolas of revolution about the pore axis. The reduction of D_e in a single pore due to constrictions was obtained via an analytical solution to obtain δ, the convergence factor, as a function of β, the ratio of maximum pore cross-sectional area to minimum cross-sectional area. The convergence factor, δ, is the ratio of the diffusivity in the constricted pore to that in an equivalent uniform cylindrical pore. A β value of 1 corresponds to a uniform pore and δ will equal 1. As the value of β increases, the pore becomes more constricted. Michaels (1959) analyzed bulk diffusion in a model pore comprised of capillaries of two diameters connected in series. Findings similar to those of Petersen were obtained at the expense of introducing a second parameter related to the relative lengths of the capillaries. Haynes and Brown (1971) use the capillary-in-series model to assess pressure effects on the constriction factor in both the bulk and Knudsen diffusion regimes. Recently, Smith (1985) has used Monte Carlo techniques to simulate Knudsen transport in constricted pores using the hyperbola of revolution pore model. Both Haynes and Brown and Smith point out that for Knudsen diffusion (or for any transport process where the transport coefficient is a function of pore size), how one defines the characteristic pore radius will affect the magnitude of δ, and hence τ.

Calculation Scheme

In order to estimate the effects of pore constrictions on restricted diffusion, we analyze transport in a single pore comprised of unit cells containing a large capillary (radius = R_1, length = L_1) and a small capillary (radius = R_2, length = L_2) connected in series. This pore model is identical to the capillary-in-series model used by Michaels and by Haynes and Brown.

For steady state transport in a single unit cell, the total molar flow rate through the large capillary is given by:

$$Q = D_1 \pi R_1^2 (C_{12} - C_1)/L_1 \tag{6}$$

and Q for the small capillary is:

$$Q = D_2 \pi R_2^2 (C_2 - C_{12})/L_2 \tag{7}$$

Equations 6 and 7 may be combined to solve for the concentration at the junction between the small and large capillaries:

$$C_{12} = C_2 - QL_2/(D_2 \pi R_2^2) \tag{8}$$

Combining Eqs. 6 and 8, and defining L as the dimensionless pore length ratio (L_1/L_2) and β as the dimensionless pore area ratio (R_1^2/R_2^2), the molar flow rate is:

$$Q = \frac{D_1 \pi R_1^2 (C_2 - C_1)}{L_1 (1 + \beta D_1/(LD_2))} \tag{9}$$

At this point, the question of the proper characteristic radius must be addressed. From a practical viewpoint, the characteristic pore size may either be determined using mercury porosimetry/sorption isotherm analysis, which measures the size of the smallest constriction in a pore, or by taking twice the ratio of pore volume to surface area (Satterfield, 1970). Since an experimenter may use either approach, we determine δ as a function of λ for both techniques. Defining an equivalent pore as a uniform cylinder of the same length and volume as the constricted pore, the value of the convergence factor, δ, is given by:

$$\delta = \frac{D_1 \beta (1 + L)^2}{D_e (1 + L\beta)(L + \beta D_1/D_2)} \tag{10}$$

When Eq. 10 is used, the value of λ is the ratio of the solute size to the equivalent pore radius. The diffusivity in the equivalent uniform pore, D_e, is calculated via Eqs. 3–5. Diffusivities in the constricted pore, D_1 and D_2, are calculated using Eqs. 3–5 and:

$$\lambda_1 = \lambda \{(\beta L + 1)/[\beta(L + 1)]\}^{0.5} \tag{11}$$

$$\lambda_2 = \lambda [(\beta L + 1)/(L + 1)]^{0.5} \tag{12}$$

Thus, the convergence factor is a function of the pore length parameter, L, the pore area parameter, β, and the solute-pore radius parameter, λ. If the radius at the smallest constriction is selected as the characteristic pore size (i.e., using mercury porosimetry or sorption isotherm analysis), λ is defined as a/R_2. The volume of a pore of radius R_2 and length $L_1 + L_2$ is less than the constricted pore volume. Therefore, the convergence factor is calculated from the ratio of the transport rates in a constricted pore and an equal volume of pores of radius R_2. The convergence factor is:

$$\delta = \frac{D_1 \beta (1 + L)^2}{D_2 (1 + L\beta)(L + \beta D_1/D_2)} \tag{13}$$

and

$$\lambda_1 = \lambda/\beta^{0.5} \tag{14}$$

Results and Discussion

When the characteristic pore size is taken to be the radius of a pore with the same volume to surface area ratio as our constricted pore model, the variation in the convergence factor, δ, is calculated as a function of β using Eqs. 10–12. The results of these calculations for $L = 1$ and five λ values are presented in Figure 1. The δ-β relationship for $\lambda = 0$ is identical to that reported by Michaels (1959). As the value of λ is increased, a large deviation between the convergence factor at a given λ value and the factor for $\lambda = 0$ is observed. Since the tortuosity is a direct function of the convergence factor, this implies that the value of the tortuosity will be a strong function of λ. Even at a relatively small β value of 4, corresponding to a constriction one-half the diameter of the large portion of the pore, an order-of-magnitude variation in the tortuosity factor will occur as the molecule size increases from negligible size to one-half of the mean pore radius. Many experimental studies have covered this wide a range of λ while assuming constant tortuosity.

Figure 2 is an analogous plot to Figure 1 except that the characteristic pore size is that obtained using mercury porosimetry or sorption isotherm analysis (i.e., the minimum pore size, R_2). The value of the pore length parameter, L, is held at 1. For this mean pore radius definition, the variation of δ from the value of $\delta(\lambda = 0)$ for a particular β value is much less pronounced than for Figure 1. This implies that the variation in tortuosity with molecular size is less when the mean pore radius is determined via mercury porosimetry/sorption isotherm analysis. For β values greater than 10, the value of δ is essentially independent of the molecule-pore size ratio. However, for β between 1 and 10, the value of δ is a strong function of λ.

The use of the smallest pore radius as a characteristic pore size is more satisfactory than using twice the ratio of pore volume to surface area. Since the product $K_p K_r$ is a highly nonlinear function of λ, most mass transfer resistance is occurring in the constricted portion of the pore. The mean pore radius that best reflects the size of the constriction therefore results in the least variation of tortuosity with λ.

For the results presented in Figures 1 and 2, the pore length parameter, L, was maintained at a value of one. Figure 3 illustrates the effect of changing L on the β-δ relationship. As Fig-

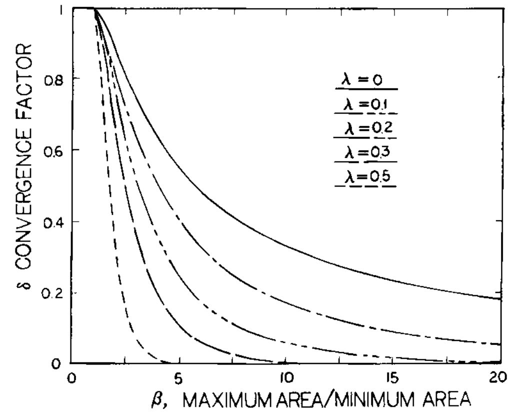

Figure 1. Variation of convergence factor.

Characteristic pore size = volume average pore radius. L (i.e., L_1/L_2) = 1.

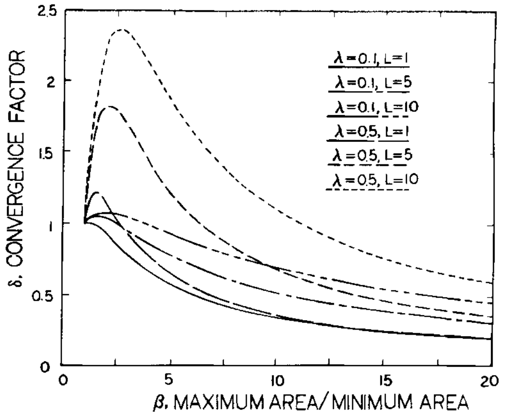

Figure 3. Effect of changing pore length parameter on variation of convergence factor with changing degree of pore restriction.

λ based on minimum pore radius.

ures 1 and 2 illustrate, the use of the minimum pore size as the characteristic pore radius is superior for minimizing the variation of δ and τ with λ. Therefore, all additional results will be reported using this definition. For $\lambda = 0.1$, the variation of δ with β is significantly affected by changing L from 1 to 10. For $\lambda = 0.5$, the effect of changing L on the relationship between δ and β is more pronounced. However, the coresponding calculations for $\delta(\lambda = 0)$ also changes with varying L. From a practical viewpoint, it is virtually impossible to determine β or L for a particular porous medium. However, a rough estimate of β may be obtained by comparing the pore radius measured with mercury porosimetry/sorption isotherm analysis to that obtained from twice the ratio of pore volume to surface area.

The principal intent of this note is to illustrate the variation of the tortuosity factor with changing molecule size. This is demonstrated in Figure 4, a plot of $\delta/\delta(\lambda = 0)$ vs. λ for various β and L values. It is common in restricted diffusion studies to extrapolate diffusion data to $\lambda = 0$ to find τ or to measure τ directly via the use of a relatively small molecule. The ratio $\delta/\delta(\lambda = 0)$ is a direct measure of the deviation of convergence factor and tortuosity with molecule-pore size ratio. For $L = 1$, the tortuosity will remain within $\simeq$20% of the $\lambda = 0$ value. For larger β values, the variation of the tortuosity with λ tends to zero. For $L = 5$, a much larger variation of $\delta/\delta(\lambda = 0)$ with λ is noted. We point out that significant changes in the tortuosity factor with λ are predicted for slightly constricted pores. A β value of 1.44 implies that radius of the large capillary is 1.2 times the size of the constriction.

Conclusions

By using a simplified model of a constricted pore, we have demonstrated that the convergence factor, and hence tortuosity, for restricted diffusion will change significantly as the ratio of molecule size to pore size changes. The variation of τ with λ may be minimized by defining the characteristic pore size as that determined via mercury porosimetry or adsorption isotherm analysis. The relationship between τ and λ is observed even for pores with slight constrictions. The magnitude of these constriction effects is a function of two pore parameters that cannot be directly measured. Therefore, the variation of tortuosity with

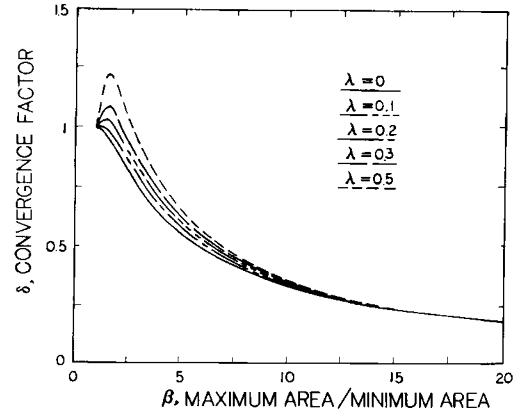

Figure 2. Variation of convergence factor.

Characteristic pore size = minimum pore radius. L (i.e., L_1/L_2) = 1

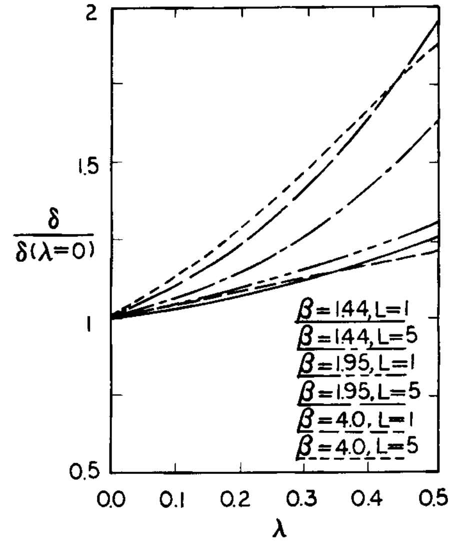

Figure 4. Effect of ratio of molecule size to pore size on the change in tortuosity.

λ based on minimum pore radius.

changing λ cannot be determined *a priori* for a particular porous medium. The fact that past studies assume a constant tortuosity may serve to explain the often-observed descrepancies between experiment and the steric exclusion-hydrodynamic drag theory of restricted diffusion.

Acknowledgment

The author gratefully acknowledges the financial support of the National Science Foundation Grant No. CPE-8419919.

Notation

a = molecule radius
C_1 = concentration at the large capillary inlet
C_2 = concentration at the small capillary outlet
C_{12} = concentration at the capillary junction
D_c = diffusion coefficient in a constricted pore
D_e = effective diffusivity
D_o = diffusion coefficient in bulk solution
K_p = equilibrium partition coefficient
K_r = hydrodynamic drag coefficient
L = pore length ratio, L_1/L_2
L_1 = length of large capillary
L_2 = length of small capillary
Q = total molar flow rate
R = pore radius
R_1 = pore radius of large capillary
R_2 = pore radius of small capillary

Greek letters

β = maximum pore cross-sectional area/minimum cross-sectional area
δ = convergence factor, D_c/D_o
ϵ = porosity
λ = a/characteristic pore radius
$\lambda_1 = a/R_1$
$\lambda_2 = a/R_2$
τ = tortuosity factor

Literature cited

Brenner, H., and L. J. Gaydos, "The Constrained Brownian Movement of Spherical Particles in Cylindrical Pores of Comparable Radius," *J. Colloid Interface Sci.*, **58**, 312 (1977).

Ferry, J. D., "Statistical Evaluation of Sieve Constants in Ultrafiltration," *J. Gen. Physiol.*, **20**, 95 (1936).

Haynes, H. W., and L. F. Brown, "Effect of Pressure on Predicted and Observed Diffusion Rates in Constricted Pores—A Theoretical Study," *AIChE J.*, **17**, 491 (1971).

Michaels, A. S., "Diffusion in a Pore of Irregular Cross Section—A Simplified Treatment," *AIChE J.*, **5**, 270 (1959).

Paine, P. L., and P. Scherr, "Drag Coefficients for the Movement of Rigid Spheres through Liquid-Filled Cylindrical Pores," *Biophysical J.*, **15**, 1,087 (1975).

Pappenheimer, J. R., E. M. Renkin, and L. M. Borrero, "Filtration, Diffusion, and Molecular Sieving through Peripheral Capillary Membranes. A Contribution to the Pore Theory of Capillary Permeability," *Am. J. Physiol.*, **167**, 13 (1951).

Petersen, E. E., "Diffusion in a Pore of Varying Cross Section," *AIChE J.*, **4**, 343 (1958).

Satterfield, C. N., *Mass Transfer in Heterogenous Catalysis*, MIT Press (1970).

Satterfield, C. N., C. K. Colton, and W. H. Pitcher, "Restricted Diffusion in Liquids within Fine Pores," *AIChE J.*, **19**, 628 (1973).

Smith, D. M., "Knudsen Diffusion in Constricted Pores: Monte Carlo Simulations," *AIChE J.*, **32**, 329 (1986).

Manuscript received Apr. 22, 1985, and revision received Oct. 15, 1985.