Diffusivities from Dynamic Adsorption Data

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Early studies of diffusion in catalyst pellets employed steady state methods (Kallenbach and Wicke, 1941; Johnson and Stewart, 1965; Wakao and Smith, 1962) so that adsorption and desorption rates on pore walls were in equilibrium. Under such conditions interpretation of diffusion data was unaffected by adsorption, except for the possibility of surface diffusion. Recently a variety of dynamic methods have been used: weight change of adsorbent (Eberly, 1969; Kondis and Dranoff, 1971), concentration (or pressure) change in the fluid phase (Satterfield and Margretts, 1971), analysis of breakthrough curves (Antonson and Dranoff, 1967, 1969a, 1969b; Kawazoe and Fukuda, 1965; Mitani and Hamai, 1970), and analysis of chromatographic peaks (Eberly, 1969). It is not uncommon to evaluate diffusivities from such dynamic data by using a single, effective diffusivity. For bidisperse pellets (molecular sieves, for example) this interpretation can lead to unreal results, even when adsorption is taken into account. When the effective diffusivity so obtained is unduly large, the increase has often been attributed to surface diffusion. However, this is not necessarily so.

The difficulty in using a single diffusivity for bidisperse pellets is due to the fact that:

1. Significant adsorption occurs only on the micropores (pores within the particles of which the pellet is composed) because the surface area in the macropores is small,
2. The effective path length for diffusion is much less than the pellet radius when adsorption occurs.

The nature and magnitude of the errors in diffusivity can be easily demonstrated by employing models of bidisperse porous pellets. The procedure will be illustrated here by using the random pore model to show the effect of micro-pore adsorption and by employing the diffusion resistances of micro and macropores to show the path-length effect.

The influence of adsorption on the diffusive flux can be evaluated by considering a slab of porous pellet which is exposed to a diffusing component at $t = 0$. Suppose that the concentration of this component is low so that Fick's law expresses the diffusive flux. In the absence of adsorption, conservation of mass requires that

$$\epsilon \frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} \tag{1}$$

where D_e is the effective diffusivity. For an adsorbing substance the mass balance becomes

$$\epsilon \frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} - \rho \frac{\partial n}{\partial t} \tag{2}$$

Suppose that the adsorption-desorption process is fast with respect to diffusion so that equilibrium exists. For low concentrations the equilibrium relation between adsorbed and fluid concentrations is linear,

$$n = K\,C \tag{3}$$

Then the adsorbed concentration can be eliminated from Equation (2), giving

$$\epsilon \frac{\partial C}{\partial t} = \left[\frac{D_e}{1 + \frac{K\rho}{\epsilon}} \right] \frac{\partial^2 C}{\partial x^2} \tag{4}$$

Comparison of Equations (1) and (4) shows that the apparent diffusive flux, when equilibrium adsorption occurs, is

$$N = - \left[\frac{D_e}{1 + \frac{K\rho}{\epsilon}} \right] \frac{dC}{dx} \tag{5}$$

APPLICATION OF RANDOM PORE MODEL

This is an idealistic model which assumes series and parallel diffusion through macro and micropores. It is used here for illustrative purposes. In the model (Wakao and Smith, 1962) the flux through a bidisperse pellet is formulated as the sum of the fluxes through macropores, micropores, and a series combination of macro and micropores, weighted according to probabilities which are functions of macro and micro porosities (ϵ_M, ϵ_μ). The latter two contributions may be combined so that the total flux can be expressed as follows (Rao and Smith, 1963)

$$N_T = \epsilon_M^2 \text{ (flux through macropores)} + \frac{\epsilon_\mu^2 (1 + 3\,\epsilon_M)}{1 - \epsilon_M} \text{ (combined micropore and series flux)} \tag{6}$$

Since adsorption in the macropores is negligible with re-

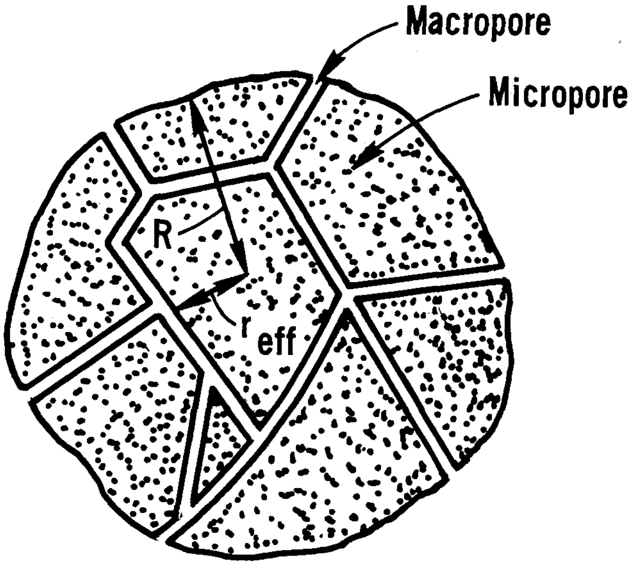

Fig. 1. Model of bidisperse spherical pellet.

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spect to that on the micropores, Equation (5) directly is applicable for the micropore flux while the macropore flux is given by Equation (5) with $(K\rho/\epsilon) = 0$. Hence Equation (6) becomes

$$N_T = -\epsilon_M^2 D_M \frac{dC}{dx} - \frac{\epsilon_\mu^2(1+3\epsilon_M)}{1-\epsilon_M}\left[\frac{D_\mu}{1+\frac{K\rho_{p\mu}}{\epsilon_\mu}}\right]\frac{dC}{dx} \qquad (7)$$

If dynamic adsorption data are interpreted in terms of a single, effective diffusivity, the flux is given by Equation (5) with the porosity replaced by the total value $\epsilon_M + \epsilon_\mu$. Equating the two expressions for N_T gives

$$N_T = -\frac{D_{eo}}{1+\frac{K\rho_p}{\epsilon_M+\epsilon_\mu}}\frac{dC}{dx} = \left[-\epsilon_M^2 D_M - \frac{\epsilon_\mu^2(1+3\epsilon_M)}{1-\epsilon_M}\,\frac{D_\mu}{1+\frac{K\rho_{p\mu}}{\epsilon_\mu}}\right]\frac{dC}{dx} \qquad (8)$$

or

$$D_{eo} = \left(1+\frac{\rho_p K}{\epsilon_M+\epsilon_\mu}\right)\epsilon_M^2 D_M + \frac{\epsilon_\mu^2(1+3\epsilon_M)}{1-\epsilon_M}\left[\frac{1+\frac{K\rho_p}{\epsilon_M+\epsilon_\mu}}{1+\frac{K\rho_{p\mu}}{\epsilon_\mu}}\right]D_\mu \qquad (9)$$

Application of this expression to the usual case where $D_M >> D_\mu$ shows that the observed diffusivity D_{eo} can be much greater than D_M. Often the adsorption capacity K is large enough that the first term reduces to the form

$$\frac{\rho_p K}{\epsilon_M+\epsilon_\mu}\epsilon_M^2 D_M \approx (\rho_p K \epsilon_M) D_M \qquad (10)$$

For example, for the chemisorption of hydrogen on a bidisperse catalyst of Ni on Kieselguhr at 25°C, K is about 11 cm^3/g (Padberg and Smith, 1968). With $\rho_p = 1.73$ g/cm^3 and $\epsilon_M = 0.20$ (Padberg and Smith, 1968), $D_{eo} = 3.9\ D_M$. Using the parallel pore model this result corresponds to an unrealistically low tortuosity factor of

$$\delta = \frac{\epsilon_M D_M}{D_e} = \frac{\epsilon_M}{3.9} \approx 0.05$$

EFFECTIVE PATH LENGTH IN BIDISPERSE PELLETS

Consider a spherical pellet with the simple macro and micropore system described in Figure 1. Suppose a dynamic adsorption experiment is carried out in which the pellet (initially free of adsorbable component) is immersed at $t = 0$ in surroundings where the concentration of adsorbable component is C_o. The time required for equalization of the concentration in the macropores will be of the order of R^2/D_M, while that for the micropores will be of the order of $K\rho_{p\mu}\, r^2_{\text{eff}}/D_\mu$. Here r_{eff} is the effective path length for diffusion within the microporous particle, as shown in Figure 1. Interpreted in terms of a single effective diffusivity, the observed equalization time would be related to D_{eo} by the equation

$$(t)_{\text{obs}} \sim K\rho_p \frac{R^2}{D_{eo}} \qquad (11)$$

In many cases the diffusion resistance in the macropores is negligibly small, so that

$$\frac{K\rho_{p\mu}\, r^2_{\text{eff}}}{D_\mu} >> \frac{R^2}{D_M} \qquad (12)$$

Then

$$(t_{\text{obs}}) = t_\mu = K\rho_{p\mu}\frac{r^2_{\text{eff}}}{D_\mu} \qquad (13)$$

Using Equation (11) for $(t)_{\text{obs}}$,

$$D_{eo} = \frac{R^2}{r^2_{\text{eff}}}\left(\frac{\rho_p}{\rho_{p\mu}}\right) D_\mu \qquad (14)$$

Since $R >> r_{\text{eff}}$, D_{eo} could be much larger than the correct value of the micropore diffusivity. In the case of molecular sieves, $D_M >> D_\mu$. Then dynamic experiments, interpreted in terms of a single diffusivity, would lead to a D_{eo} between the correct values for D_M and D_μ.

When Equation (12) is satisfied, as for molecular sieves, reasonable results for D_μ will be obtained when R is replaced by the crystal radius (radius of microporous particle) in Equation (11). This procedure has been used by Antonson and Dranoff (1969b) and Kondis and Dranoff (1971). Alternately, when separate mass conservation equations for macro and micropores are written (Ruckenstein et al., 1971; Sargent and Whitford, 1971) correct values of the diffusivities are possible. In addition, Ruckenstein et al. (1971) have developed a model for dynamic adsorption in a bidisperse pellet which may be used to obtain both micro and macropore diffusivities from experimental data.

DISCUSSION

The purpose of this note is to show that careful interpretation of dynamic adsorption experiments is necessary in bidisperse pellets in order to extract proper values for macro and micropore diffusivities. Effects of pellet shape and deviations from a linear isotherm may be much less than errors introduced by interpreting the data in terms of a single, effective diffusivity. Most reliable results will be obtained when diffusion in macro and micropores is treated separately with an adequate pore model. The random-pore model has been used to develop Equation (9) and, hence, to illustrate the problem, but similar conclusions would result from other models (Johnson and Stewart, 1965; Ruckenstein et al., 1971). Finally, it should be noted that design of cycling adsorption beds should not be based upon diffusivities estimated from steady state data or predicted from models which have not been modified to account for dynamic adsorption. The same restriction applies to breakthrough curves.

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NOTATION

C = concentration of adsorbate in fluid in pores, g-mole/cm^3
D_{eo} = single, effective diffusivity obtained from experimental data (observed diffusivity), cm^2/s
D_M = diffusivity in macropores, cm^2/s
D_μ = diffusivity in micropores, cm^2/s

K = adsorption equilibrium constant, cm^3/g
N = diffusive flux, g-mole/(cm^2)(s)
N_T = total diffusive flux in bidisperse pellet, g-mole/(cm^2)(s)
n = concentration of adsorbate on surface, g-mole/g
R = pellet radius, cm
r_{eff} = effective radius for micropore diffusion in bidisperse pellet, cm
t = time, s
t_{obs} = observed time for equalization of concentration gradient in pellet, s; t_M, t_μ = equalization times for macro and micropores, respectively
x = coordinate in the direction of diffusion, cm

Greek Letters

δ = tortuosity factor
ϵ = porosity; ϵ_M and ϵ_μ denote void fractions in macro and micropores, respectively
ρ_p = density of bidisperse pellet, g/cm^3
$\rho_{p\mu}$ = density of microporous particle in pellet, g/cm^3

LITERATURE CITED

Antonson, C. R., and J. S. Dranoff, "The Kinetics of Ethane Adsorption on Molecular Sieves," *Chem. Eng. Progr. Symp. Ser. No. 74*, 61 (1967).

———., "Nonlinear Equilibrium and Particle Shape Effects in Intraparticle, Diffusion-Controlled Adsorption," *ibid.*, No. 96, 20 (1969).

———., "Adsorption of Ethane on Type 4A and 5A Molecular Sieve Particles," *ibid.* 27.

Eberly, P. E., "Adsorption of Normal Paraffins in Erionite and 5A Molecular Sieves," *Ind. Eng. Chem. Product Research Develop.*, 8, 140 (1969).

———., "Diffusion Studies in Zeolites and Related Solids by Gas Chromatographic Techniques," *Ind. Eng. Chem. Fundamentals*, 8, 25 (1969).

Kallenbach, R., and E. Wicke, "Die Oberflaechen diffusion von Kohlendioxyde in Aktiven Kohler," *Kolloid-Z*, 97, 135 (1941).

Johnson, M. F. L., and W. E. Stewart, "Pore Structure and Gaseous Diffusion in Solid Catalysts," *J. Catalysis*, **4**, 248 (1965).

Kawazoe, K., and Y. Fukuda, "Studies on Solvent Recovery by Activated Carbon," *Kagaku Kogaku*, **29**, 374 (1965).

Kondis, E. F. and J. S. Dranoff, "Kinetics of Isothermal Sorption of Ethane on 4A Molecular Sieve Pellet," *Ind. Eng. Chem. Process Design Develop.*, **10**, 109 (1971).

Mitani, M., and S. Hami, "Research on Gaseous Diffusion Phenomena in Various Porous Catalysts—Measurement of Effective Diffusion Coefficient by Frontal Chromatography," *Kagaku Kogaku*, **34**, 1087 (1970).

Padberg, G., and J. M. Smith, "Chemisorption Rates by Chromatography," *J. Catalysis*, **12**, 172 (1968).

Rao, M. Raja, and J. M. Smith, "Diffusion Resistances in Alumina and Silica Catalysts," *AIChE J.*, **9**, 485 (1963).

Ruckenstein, E., A. S. Vaidyanathan, and G. R. Youngquist, "Sorption by Solids with Bidisperse Pore Structures," *Chem. Eng. Sci.*, **26**, 1305 (1971).

Sargent, R. W. H., and C. J. Whitford, "Diffusion of Carbon Dioxide in Type 5A Molecular Sieve," *Molecular Sieves Zeolites II*, Am. Chem. Soc. (1971).

Satterfield, C. N., and W. G. Margretts, "Diffusion in Sodium Mordenite," *AIChE J.*, **17**, 295 (1971).

Wakao, N., and J. M. Smith, "Diffusion in Catalyst Pellets," *Chem. Eng. Sci.*, **17**, 825 (1962).

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Description of Meniscus Profiles in Free Coating II—Analytical Expressions

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The authors are interested in describing the location of curved interfacial boundaries arising in dynamic menisci and in describing the profiles in terms of meniscus thickness h—as a function of laboratory position x (Lee and Tallmadge, 1972a). In a recent study, profile data were obtained for the case of free coating on a flat sheet over a range of speeds and bath depths (Lee and Tallmadge, 1972b). The purpose of this note is to describe the previously obtained profiles with analytical expressions for $h(x)$ and to present quantitatively the influence of speed and bath depth on the analytical parameters.

For free coating, we take x as the distance above the bath surface and note that the meniscus thickness decreases asymptotically up to a constant thickness h_0. Using $\lambda \equiv x/h_0$ and $L \equiv h/h_0$, the meniscus profile becomes $L(\lambda)$, where the thickness L decreases from a large value at the bath surface ($\lambda = 0$) to L of 1 at a large height λ. Some typical data are shown in Figure 1; the bath depths in Figure 1 are about 30 h_0 so that these data are called deep bath profiles. The coating speed U_w is given in terms of the nondimensional capillary number Ca which equals $U_w\ (\mu/\sigma)$. Figure 1 shows that meniscus profiles have two linear regions on this semilog plot, with a division near L of 2 to 3. The data can therefore be described by a linear analytical expression for each region of upper and lower meniscus. Exponential forms of these two expressions are

$$\text{Upper:} \quad (L < 2) \qquad L = 1 + B_1 \exp\ (-\lambda/M_1) \tag{1}$$

$$\text{Lower:} \quad (L > 2) \qquad L = 1 + B_2 \exp\ (-\lambda/M_2) \tag{2}$$

The M values represent the slopes in Figure 1 and the B values represent intercepts with the horizontal axis.

In repeatability tests using the same photographs, it was found that slopes did not vary appreciably, so that slopes do not appear to be sensitive to the experimental

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