τ = shear stress, N/m^2
τ_w = wall shear stress, N/m^2

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Linear Driving Force Approximations for Diffusion Controlled Adsorption in Molecular Sieve Columns

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For systems in which the rate of mass transfer is controlled by intraparticle diffusion, theoretical prediction of the breakthrough curve for a packed bed adsorption column from the simultaneous solution of the differential fluid phase mass balance and the relevant diffusion equation requires considerable computational effort. This has led to the use of simple linear driving force expressions as an approximate representation of the mass transfer rate in diffusion controlled systems:

$$\frac{\partial \bar{\bar{q}}}{\partial t} = k_s a(q^* - \bar{\bar{q}}) \qquad (1)$$

When the diffusivity is independent of concentration, it has been shown (Glueckauf, 1955) that Equation (1) with $k_s \approx 15\ D_e/R^2$ provides a good approximation for many boundary conditions. However, this approximation is not valid for adsorbents such as molecular sieves in which the diffusivity is strongly concentration dependent, and the purpose of this note is to develop the equivalent expressions for such systems.

For an isothermal plug flow system with equilibrium governed by a Langmuir isotherm and the mass transfer rate controlled by external fluid film resistance, the breakthrough curve for a step change in feed concentration at time zero is given by the solution of the following set of equations:

$$v\frac{\partial c}{\partial z} + \frac{\partial c}{\partial t} + \left(\frac{1-\epsilon}{\epsilon}\right)\frac{\partial \bar{\bar{q}}}{\partial t} = 0 \qquad (2)$$

$$\frac{\partial \bar{\bar{q}}}{\partial t} = k_f a(c - c^*) \qquad (3)$$

$$\frac{\bar{\bar{q}}}{q_s} = \frac{bc^*}{1 + bc^*} \qquad (4)$$

Adsorption:

$$\bar{\bar{q}}(z, z/v) = 0; \quad c(z, z/v) = 0; \quad c(0, t) = c_0 \qquad (5)$$

Desorption:

$$\bar{\bar{q}}(z, z/v) = q_0; \quad c(z, z/v) = 0; \quad c(0, t) = 0 \qquad (6)$$

Numerical solutions have been given by Zwiebel et al. (1972) and, for the equivalent problem with a Freundlich isotherm, by Kyte (1973). The corresponding solid film linear driving force representation for intraparticle diffusion control is obtained by replacing Equation (3) by Equation 1 and Equation (4) by

$$\frac{q^*}{q_s} = \frac{bc}{1 + bc} \qquad (7)$$

For adsorption under constant pattern conditions (adsorption front moving with uniform velocity), Equation (2) reduces simply to

$$\phi = c/c_0 = \bar{\bar{q}}/q_0 \qquad (8)$$

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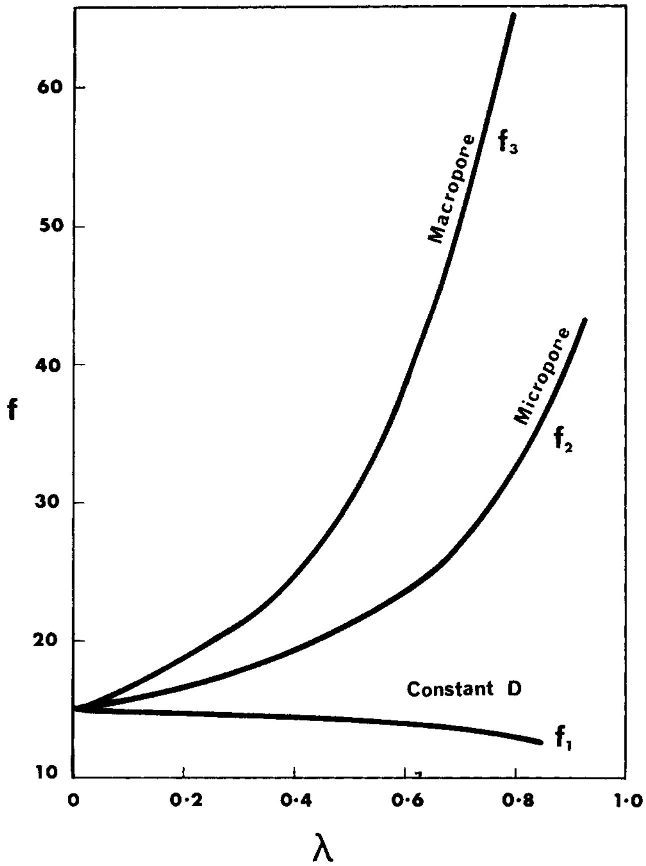

Fig. 1. Variation of factors in Equations (11) to (13) with λ.

and the rate equations may be integrated directly to give Fluid film:

$$\tau_{f2} - \tau_{f1} = k_f a (t_2 - t_1)\,\frac{c_0}{q_0}$$

$$= \frac{1}{\lambda}\ln\left[\frac{\phi_2(1-\phi_1)}{\phi_1(1-\phi_2)}\right] + \ln\left(\frac{1-\phi_2}{1-\phi_1}\right) \qquad (9)$$

as obtained by Michaels (1952) and Solid film:

$$\tau_{s2} - \tau_{s1} = k_s a (t_2 - t_1)$$

$$= \frac{1}{\lambda}\ln\left[\frac{\phi_2(1-\phi_1)}{\phi_1(1-\phi_2)}\right] + \ln\left(\frac{\phi_1}{\phi_2}\right) \qquad (10)$$

Although the curves given by Equations (9) and (10) have somewhat different shapes, the time difference between any two symmetric values of ϕ_1 and ϕ_2 (that is, $\phi_1 = 1 - \phi_2$) will be the same for both expressions. The equivalent values of k_s (or $k_f c_0/q_0$) may be obtained by matching the dimensionless time difference previously calculated (Garg and Ruthven, 1973a) from the asymptotic constant pattern solution of the diffusion equation with the dimensionless time difference calculated from Equation (9) or (10), for specified values of ϕ_1 and ϕ_2. Since the difference in the shapes of the curves is not very great, the actual values chosen for ϕ_1 and ϕ_2 (0.05 and 0.95) have little effect on the resulting factors. The results of such calculations are shown in Figure 1 in terms of factors f_1, f_2, and f_3 defined as follows:

Micropore diffusion; $D_z = D_* =$ constant:

$$k_s = f_1 D_*/r_z^2 \qquad (11)$$

Micropore diffusion; $D_z = D_*\,\partial \ln c/\partial \ln q$:

$$k_s = f_2 D_*/r_z^2 \qquad (12)$$

Macropore diffusion; $D_e = \dfrac{\epsilon_p D_p}{w(1-\epsilon_p) b q_s}$:

$$k_s = f_3 D_e/R_p^2 \qquad (13)$$

For the constant diffusivity case, f_1 is almost independent of the degree of nonlinearity of the isotherm (λ) and the range of values agrees well with the values given by Glueckauf (1955). For systems in which the diffusivity is concentration dependent, however, the factor f is very sensitive to λ and it is clear that Glueckauf's expression holds only as $\lambda \to 0$.

A comparison between the shapes of the asymptotic dimensionless breakthrough curves, calculated from the solutions of the appropriate diffusion equations for micropore and macropore control and the curves calculated from the linear driving force approximations [Equations (9) and (10)] is shown in Figure 2 for $\lambda = 0.67$. The dimensionless time scales have been matched using the values of f given in Figure 1 and, to facilitate comparison, time is measured relative to the midpoint. The curve for micropore control is well represented by the solid film linear driving force approximation over the entire range. For macropore control neither the fluid film nor the solid film model gives quite such a good representation, but in the initial region the fluid film model gives slightly the better fit.

To estimate the minimum column length required to establish constant pattern behavior it is necessary to solve the full problem defined by Equations (2) to (6) or (1), (2), and (5) to (7). These solutions were obtained by standard finite difference methods similar to those described in our earlier analysis of the diffusion problem (Garg and Ruthven, 1973b). The dimensionless column lengths required for the dimensionless time for 5 to 95% breakthrough to approach within 10% of the value corresponding to the asymptotic constant pattern limit [Equations (9) and (10)] are summarized in Table 1. It is apparent that the dimensionless column length required to establish a constant pattern front decreases with increasing nonlinearity of the isotherm (λ).

In Figure 3 breakthrough curves calculated from the linear driving force solid film model, with the factors given in Figure 1, are compared with the curves previously obtained from the general numerical solution of the diffusion equations (Garg and Ruthven, 1973b,c). The dimensionless time, denoted by T, is defined as $k_s a(t -$

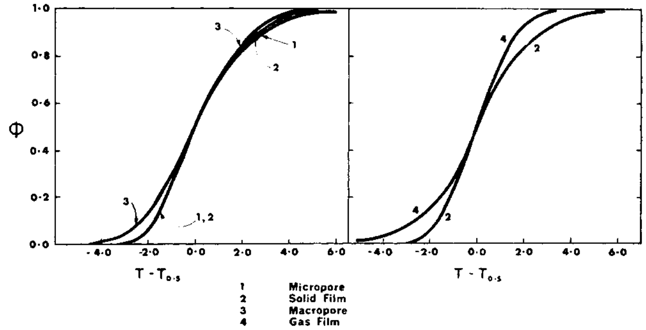

Fig. 2a. Comparison of the asymptotic adsorption breakthrough curves for solid film (2) and diffusion models (1—micropore diffusion model, 3—macropore diffusion model) for $\lambda = 0.67$.

Fig. 2b. Comparison of the asymptotic adsorption breakthrough curves for solid film (2) and fluid film model (4) for $\lambda = 0.67$.

TABLE 1. APPROACH OF ADSORPTION BREAKTHROUGH CURVES TO ASYMPTOTIC CONSTANT PATTERN LIMIT

λ	0.167	0.286	0.445	0.667	0.8
$X_f = \dfrac{k_f a z}{m' v}$	>50	>20	18	10	5
$X_s = \dfrac{b q_s k_s a z}{m' v}$	≈200	≈50	20	13	7.5

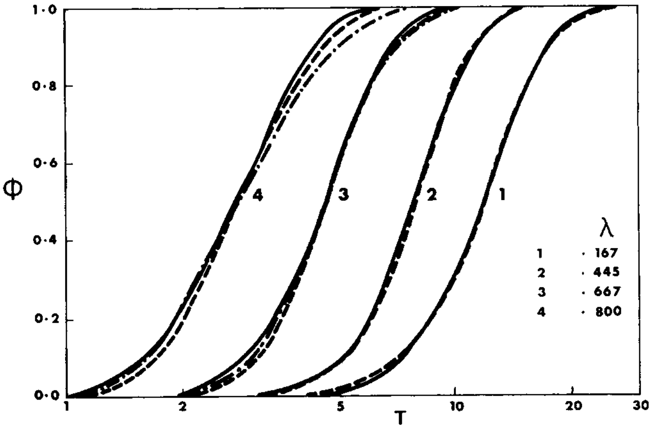

Fig. 3. Comparison of the adsorption breakthrough curves for solid film model (- - -) with those for micropore diffusion (— · — · —) and macropore diffusion (———) models at $X_s = 15$. Parameter λ.

$z/v)$ for the solid film solution, $f_2(D_*/r_z^2)\ (t - z/v)$ for the micropore solution, and $f_3(D_e/R_p^2)\ (t - z/v)$ for the macropore solution. It is evident that except at the highest values of λ the simplified solid film model provides a good representation even in the developing region before the constant pattern limit is reached.

The principal advantage of the linear driving force approximation is that it provides a simple method of comparing the relative importance of external film and internal diffusional resistances. Furthermore, for systems in which both external and internal resistances are significant, one may obtain an approximate estimate of the breakthrough curves using an overall solid film coefficient calculated from the law of additive resistances:

$$\frac{1}{k_0} = \frac{1}{k_s} + \frac{1}{k_f}\,\frac{q_0}{c_0} \tag{14}$$

An a priori estimate of k_s may be obtained from knowledge of basic diffusivity data together with the factors given in Figure 1 while k_f may be estimated from established mass transfer correlations (for example, Petrovic and Thodos, 1968).

This analysis is restricted to the adsorption curves for systems with favorable equilibrium isotherms. The corresponding desorption curves for such systems tend, in a long column, to the proportionate pattern limit in which the form of the concentrations front is governed entirely by equilibrium consideration and the kinetics of sorption are unimportant.

NOTATION

a = surface area to volume ratio of adsorbent pellets
b = Langmuir equilibrium constant
c = sorbate concentration in fluid phase
c_0 = sorbate concentration at column inlet
c^* = fluid phase concentration in equilibrium with $\bar{\bar{q}}$
D_z = micropore diffusivity
D_* = limiting micropore diffusivity at zero sorbate concentration
D_p = macropore diffusivity (based on pore sectional area)
D_e = effective diffusivity
f_1, f_2, f_3 = factors as defined in Equations (11) to (13)
k_s = solid film mass transfer coefficient
k_f = external fluid film mass transfer coefficient
k_0 = overall film mass transfer coefficient
m' = ratio of bed void space to adsorbent volume = $\epsilon/(1 - \epsilon)$
$\underline{q}$ = sorbate concentration
$\bar{\bar{q}}$ = average sorbate concentration in a pellet
q^* = sorbate concentration in equilibrium with fluid phase concentration, c
q_s = saturation sorbate concentration in Langmuir equation
q_0 = sorbate concentration in equilibrium with fluid phase concentration c_0
r_z = radius of molecular sieve crystal
R = radius of spherical particle
R_p = radius of molecular sieve pellet
t = time
v = linear fluid velocity
w = volume fraction of zeolite crystals to total solid material in a pellet
X_f = dimensionless distance for fluid film model, $k_f\, az/m'v$
X_s = dimensionless distance for solid film model, $k_s\, az\, bq_s/m'v$
z = distance measured from bed inlet
T = appropriate value of dimensionless time τ

Greek Letters

ϵ = void fraction of bed
ϵ_p = void fraction of pellet
ϕ_1 and ϕ_2 = dimensionless fluid phase concentrations (c/c_0)
λ = $q_0/q_s = bc_0(1 + bc_0)^{-1}$
τ_{f1}, τ_{f2} = dimensionless times for external fluid film control corresponding respectively to ϕ_1 and ϕ_2
τ_{s1}, τ_{s2} = dimensionless times for solid film control corresponding respectively to ϕ_1 and ϕ_2

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