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A Method for the Study of Interphase Mass Transfer at Very Low Reynolds Numbers in Packed Beds

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The purpose of this note is to discuss a methodology for studying interphase mass transfer in packed beds at very low Reynolds numbers ($< 10^{-3}$). Reynolds numbers in this region usually occur in fluid-solid systems consisting of very small particles. Such systems are often referred to as porous media rather than packed beds. Another type of porous media or packed bed is a soil. It has been demonstrated by Novak (1976) that a Reynolds number of 10^{-3} would likely be an upper bound for gravity flow through soils. And so mass transfer at very low Reynolds numbers may be of importance in endeavors such as agricultural production and mineral extraction.

Very little data on interphase mass transfer exist in the very low Reynolds number region. However, a fair amount of experimental and theoretical work has been carried out in the low Reynolds number region (10^{-3} to 50). The major characteristic of that work has been the scatter in experimental data, the disagreement over the limiting value (if any) of the Sherwood number, and the lack of agreement on the form of the Sherwood number correlation. These characteristics have been discussed in an earlier paper (Novak, 1976).

The effect of solute diffusion has been incorporated into mass transfer models for nonadsorbable solutes (Miyauchi et al., 1976) and for adsorbable solutes (Shah et al., 1975; Novak et al., 1975) at low and very low Reynolds numbers. The model discussed below provides the foundation of a methodology for studying interphase mass transfer in packed beds at very low Reynolds numbers.

THEORY

When we deal with adsorbable solutes, the ideal system for studying the fluid film mass transfer phenomenon would consist of strictly nonporous solid particles which could reversibly adsorb a solute. Since porous solids may also be of interest, a model will be presented for the general case where the resistance to mass transfer occurs in both the fluid and the solid phases.

Two formulations are possible, depending on which driving force is used. The following solute material balances and the equilibrium relationships are given in dimensionless form with variables defined in the notation section:

Liquid phase driving force model (LPDF)

$$\frac{\partial Y}{\partial \tau} = \frac{1}{Pe}\frac{\partial^2 Y}{\partial \xi^2} - \frac{\partial Y}{\partial \xi} - \frac{St_L}{\epsilon}(Y - Y^*) \qquad (1)$$

$$\frac{\partial X}{\partial \tau} = \frac{St_L}{N}\left(\frac{\rho_L}{\rho_p(1-\epsilon)}\right)(Y - Y^*) \qquad (2)$$

$$Y^* = \frac{X}{1 + A(1 - X)} \qquad (3)$$

Solid phase driving force model (SPDF)

$$\frac{\partial Y}{\partial \tau} = \frac{1}{Pe}\frac{\partial^2 Y}{\partial \xi^2} - \frac{\partial Y}{\partial \xi} - \frac{St_s}{\epsilon}\left(\frac{\rho_p}{\rho_L}\right)N(X^* - X) \qquad (4)$$

$$\frac{\partial X}{\partial \tau} = \frac{St_s}{1-\epsilon}(X^* - X) \qquad (5)$$

$$X^* = \frac{(1 + A)Y}{1 + AY} \qquad (6)$$

Deviations from ideal plug flow are incorporated in the Peclet number term. At very low Reynolds numbers, the Peclet number would also be low ($Pe < 1$) for both gases and liquids. In this situation, the Peclet number would largely represent the effect of hindered solute diffusion in the fluid phase. This fact has been demonstrated by flow experiments using tracers (Miyauchi and Kikuchi, 1975).

The equilibrium relationships represented in Equations (3) and (6) are dimensionless forms of the Langmuir adsorption isotherm. For solutes that are very weakly adsorbed and/or present in very dilute concentrations, the dimensionless variable A would approach zero. This would result in a linear equilibrium relationship.

The Stanton numbers contain the overall mass transfer coefficients. By analogy with the two-film theory which has been applied to fluid-fluid interfacial mass transfer, the overall mass transfer coefficients can be related to the individual film coefficients.

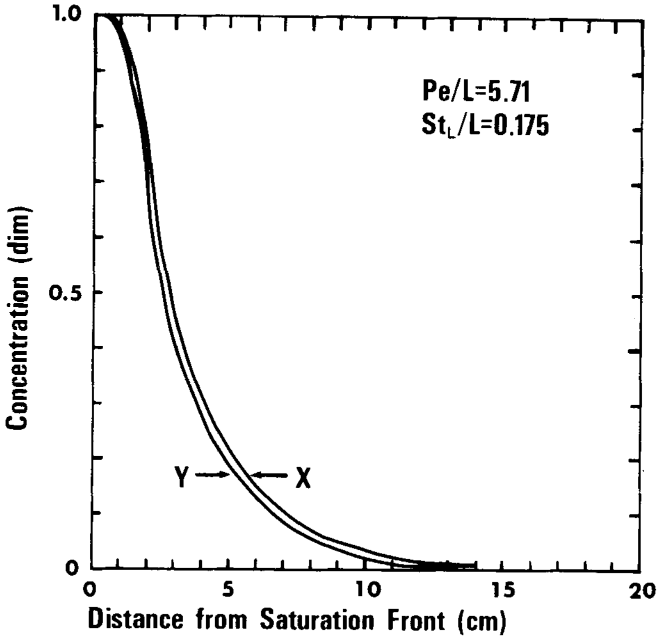

Fig. 1. Shock layer profile.

TABLE 1. LEGEND FOR FIGURES 1 AND 2

Adsorbent—spinks sand
Adsorbate—orthophosphate ion
Langmuir constants[*] $K = 1.20$
$b = 68.4$ p.p.m. of orthophosphate—P
Porosity—0.35
Particle density—2.65 g/cm^3
Pore velocity—571 cm/day
Effective diffusivity[†]—100 cm^2/day
Overall volumetric interphase[†]
mass transfer coefficient—100 day^{-1}
Boundary conditions $C_o = 10$ p.p.m. of orthophosphate—P
$M_o = 0.63$ p.p.m. of orthophosphate—P

[*] Novak, L. T., Unpublished data.
[†] Varied to generate Figure 2.

METHODOLOGY

Consider an experiment in which all solutes are absent from a column packed with an adsorbent. At an instant in time, the entrance fluid phase solute concentration changes from zero to C_o and remains constant thereafter. It is well known that a saturation front moves down the column and has a certain thickness which, in general, varies with time since the start of the experiment. Figure 1 illustrates the saturation front profile for an isothermal, one solute system. Figure 1 was obtained by integration of Equations (1) to (3) for the adsorption problem specified in Table 1. The values of the variables in Table 1 which were not determined experimentally represent reasonable values.

Dimensional analysis of the LPDF and SPDF models would indicate that the saturation front thickness ($\delta\xi^*$) would be a function of several dimensionless variables:

$$\delta\xi^* = f(\xi, \tau, St, Pe, \epsilon, \rho_p/\rho_L, A, N) \qquad (7)$$

This result implies that the mass transfer coefficient could be determined from an adsorption experiment providing that the last five dimensionless variables are known from independent experiments. This result presents one with a considerable computational effort. Fortunately, for certain solute-adsorbent systems, a much simpler relationship exists.

The LPDF model was used by Shah et al. (1975) to describe experimental results on the movement of orthophosphate in a soil. Numerical solutions to Equations (1) to (3) showed that the shape of the adsorption front approached a constant pattern after a period of time (Shah et al., 1975; Novak et al., 1975). This constant pattern has been referred to as a shock layer by Rhee and Amundson (1972). A time criterion for the development of a shock layer has not yet been developed. As a result, this can only be determined now by experiment or by integration of Equations (1) to (3) or (4) to (6).

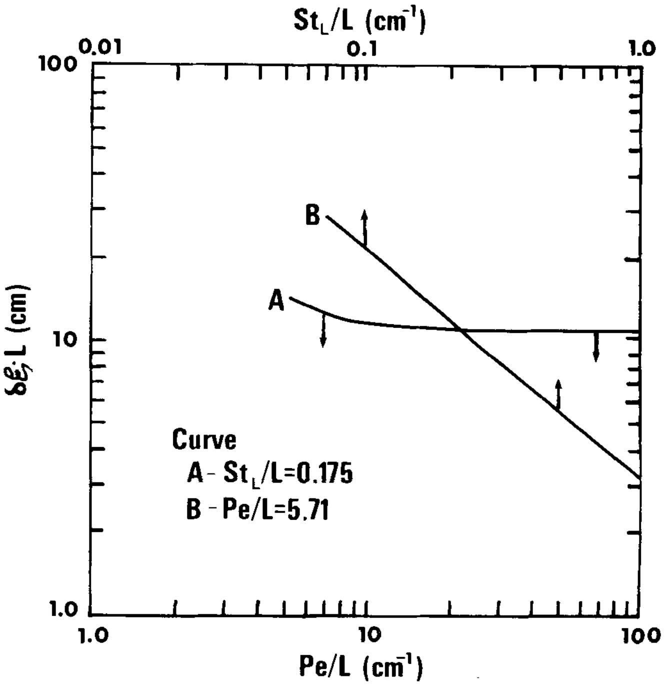

Fig. 2. Shock layer variation with Peclet and Stanton numbers.

A mathematical and numerical analysis of the SPDF model resulted in the finding that a shock layer also exists for the adsorption problem when a favorable equilibrium relationship exists (Rhee and Amundson, 1972). The Langmuir adsorption isotherm is one such favorable equilibrium relationship. Care must be exercised when the concept of a solid film mass transfer coefficient is used to describe a pore diffusion phenomenon. From the results of Garg and Ruthven (1975), it can be seen that the SPDF model is probably applicable for $M_o/b < 2/3$.

The major advantage of solute-adsorbent systems which result in shock layers is that Equation (7) can be simplified to

$$\delta\xi = g(St, Pe, \epsilon, \rho_p/\rho_L, A, N) \qquad (8)$$

The first two dimensionless variables account for the effects of interphase mass transfer and axial dispersion of solute. The remaining variables account for the bed packing characteristic, the equilibrium characteristics of the solute-adsorbent system, and the boundary condition for the adsorption experiment.

Rhee and Amundson (1972) have developed a relationship for the shock layer thickness using the SPDF model. Their Equation (28) reduces to the following form for a given solute-adsorbent system and given initial and feed conditions:

$$\delta\xi = \frac{C_1}{Pe} + \frac{C_2}{St_s} \qquad (9)$$

From dimensional analysis it also appears that a mass transfer correlation would likely involve the Sherwood number, Peclet number (Pe'), and possibly a packing factor. This point can be reinforced by the work of Kunii and Suzuki (1967) and others, as discussed in a previous paper

(Novak, 1976). It should be emphasized that mass transfer at a given very low Reynolds number could result in much different Sherwood numbers depending on whether the fluid was a gas or liquid. This would likely be the result of the different values of the respective Peclet numbers.

In order to investigate the relationship between $\delta\xi$, Pe, and St_L for the LPDF model, Equations (1) to (3) were solved numerically by using the Crank-Nicholson implicit method. Numerical convergence was based on the liquid phase concentration and an overall material balance criterion.

Results of the numerical computations are illustrated in Figures 1 and 2. Figure 1 is a shock layer profile for the problem defined in Table 1. The shock layer thickness ($\delta\xi$) can be determined from this profile by the procedure defined by Rhee and Amundson (1972). Figure 2 was developed by using the information in Table 1 and varying the effective diffusivity (D) and overall mass transfer coefficient (K_L). The values chosen for D and K_L are thought to be within a reasonable range expected for soils based on the work by Shah et al. (1975) and Kirda et al. (1973). Curve A in Figure 2 can be seen to be consistent with Equation (9) over the range studied. However, curve B has a slope of -0.84 in contrast to a slope of -1.0 as predicted by Equation (9) for the SPDF model. Based on the information presented here, it appears that the LPDF model may not result in the same Peclet and Stanton number dependency as the SPDF model for strongly nonlinear problems (A relatively large). However, it should be recalled that the Stanton numbers for the LPDF and SPDF models are different, and a simple linear relationship between the Stanton numbers only exists for linear isotherms. Under these conditions, a shock layer does not exist.

The overall mass transfer coefficient (K_L) could be determined by the following procedure. First, the adsorbent-adsorbate system would need to be characterized by measurements of K, b, M_o, a, ϵ, ρ_p, and ρ_L. For a given V_p, one would need to determine D. This would likely be done indirectly by determining the tortuosity factor for the bed by use of an inert tracer. Then, for a given adsorbate inlet concentration, one could experimentally determine the shock layer thickness ($\delta\xi$). This information would be used to generate curve B (Figure 2) for the particular adsorption problem, and K_L could then be calculated from the St_L corresponding to the experimental $\delta\xi$.

NOTATION

A = Langmuir equilibrium characteristic = KC_o
a = fluid-solid interfacial area per volume of porous media (or packed bed)
b = Langmuir adsorption maximum
C = fluid phase concentration
C_1, C_2 = constants
D = effective diffusivity
$\mathfrak{D}$ = ordinary diffusion coefficient
K = Langmuir equilibrium constant
K_L, K_s = overall interphase mass transfer coefficients
L = characteristic length
M = solid phase concentration
N = Langmuir adsorption characteristic = $K(b - M_o)$
Pe = Peclet number = V_pL/D
Pe' = Peclet number = $V_pL/\mathfrak{D}$
St_L = Stanton number = K_LaL/V_p
St_s = Stanton number = K_saL/V_p
t = time
V_p = pore velocity
X = dimensionless solid phase concentration = M/M_o
Y = dimensionless fluid phase concentration = C/C_o
z = distance from bed inlet

Greek Letters

ρ = density
ϵ = porosity
τ = dimensionless time = tV_p/L
ξ = dimensionless distance = z/L
$\delta\xi^*$ = dimensionless saturation front thickness
$\delta\xi$ = dimensionless shock layer thickness

Subscripts

o = inlet condition
p = particle
L = liquid phase
s = solid phase

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A Modified Crystallizer Design for Specialized Applications

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The utility requirements of evaporative vacuum crystallizers may be reduced substantially (sometimes by as much as 90%) by a simple design modification discussed in this paper.

A schematic diagram of the conventional evaporative crystallizers is shown in Figure 1 *a*. A warm, saturated solution is fed to a lagged closed vessel that is maintained under vacuum. The solution cools adiabatically to the boil-