The Relative Contribution of Pore Volume Diffusion and Surface Diffusion to Mass Transfer in Capillaries and Porous Media

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There are two pathways of diffusion in a porous medium: diffusion in the volume of the fluid (gas or liquid) filling the pores and surface diffusion in the adsorption layer on the pore walls (Damköhler, 1935). If one observes that the diffusional flux in such a porous medium is greater than would be expected for diffusion in the pore volume alone, then one can conclude that both mechanisms contribute to the observed effective diffusivity (Barrer, 1967). It is not possible, however, to derive from this observation a coefficient of surface diffusion (D_S) that depends only on the mobility of the diffusing substance in the adsorbed layer and would thus be independent of the geometry of the pore space.

Consider a capillary of radius r and length L, filled with a fluid that contains a dilute solution of a solute (concentration c), the concentration difference $c_1 - c_2$ between the openings of the capillary being constant (Figure 1). If the solute is either not adsorbed or strictly immobile while adsorbed on the pore wall, then we would observe the diffusive flux $\dot{n}_F$ at steady state

$$\dot{n}_F = D_F \cdot r^2 \pi \cdot \frac{c_1 - c_2}{L} \tag{1}$$

where D_F is the diffusivity of the solute in the fluid. If the observed flux $\dot{n}$ is greater than $\dot{n}_F$ according to Eq. 1, then one has to conclude that surface diffusion of solute adsorbed on the pore wall is taking place and contributes to the observed flux $\dot{n}$. For surface diffusion, we have

$$\overrightarrow{\left(\frac{\dot{n}}{l}\right)} = - D_S \cdot \overrightarrow{\text{grad}}\; c_S \tag{2}$$

where $\overrightarrow{(\dot{n}/l)}$ is the flux normal to length l (in mol·m^{-1}·s^{-1}) in a two-dimensional layer of adsorbed particles due to a gradient of surface concentration c_S (c_S in mol/m^2), D_S being the coefficient of surface diffusion. If both diffusion in the fluid and surface diffusion contribute to the flux of solute through the capillary, then we have at steady state

$$\dot{n} = -r^2\pi \cdot D_F \cdot \frac{dc}{dx} - 2r\pi \cdot D_S \cdot \frac{dc_S}{dx} = \text{const.} \tag{3}$$

with

$$c = c_1 \text{ at } x = 0$$
$$c = c_2 \text{ at } x = L$$

It is not possible to obtain D_S from the observed flux $\dot{n}$, even if pore radius r and the diffusivity D_F in the fluid are known, as long as the gradients dc/dx and dc_S/dx cannot be evaluated separately.

The concentration c in the fluid and the surface concentration c_S on the pore wall must follow the pattern shown schematically in Figure 1 if an exchange of solute between fluid and adsorbed layer takes place along the pore and if the solute is mobile in either state. At both ends of the capillary ($x = 0,L$) there will be no contribution from surface diffusion and dc_S/dx must vanish there, since the solute can enter and leave the system only through the fluid. The fraction of the observed flux, which is due to surface diffusion, must be zero at the ends of the capillary and will reach a maximum at $x = L/2$.

In order to evaluate D_S from the observed flux $\dot{n}$, we must first obtain dc/dx and dc_S/dx at some position $0 < X < L$ through the local material balances at steady state. For the present discussion it is sufficient to consider the simple case where c_S at equilibrium is linear in the concentration c of the solute in the fluid

$$(c_S)\,\text{eq} = K \cdot c \tag{4}$$

We have, then, at steady state for the fluid

$$D_F \cdot \frac{d^2c}{dx^2} - \frac{2}{r \cdot \tau_{\text{ad}}} \cdot (Kc - c_S) = 0 \tag{5}$$

with boundary conditions

$$c = c_1 \text{ at } x = 0$$
$$c = c_2 \text{ at } x = L$$

and for the adsorbed layer

$$D_S \cdot \frac{d^2c_S}{dx^2} + \frac{1}{\tau_{\text{ad}}} \cdot (Kc - c_S) = 0 \tag{6}$$

with boundary condition

$$\frac{dc_S}{dx} = 0 \text{ for } x = 0,L$$

τ_{ad} is the relaxation time for the establishment of local equilibrium between fluid and adsorbed layer. τ_{ad} will depend on the rate constant of desorption and on the time constant r^2/D_F of radial

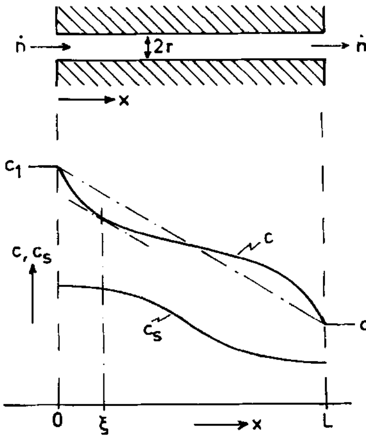

Figure 1. Distribution of concentration c in fluid and of surface concentration c_S along a capillary in the case of simultaneous diffusion in fluid and surface migration at steady state.

diffusion in the fluid, since mass transfer between the fluid and the pore wall involves diffusion in the fluid. If τ_{ad} were known, one could obtain dc_S/dx and dc/dx from Eqs. 3, 5, and 6 and then evaluate D_S from the observed flux $\dot{n}$. Without knowledge of the kinetics of exchange between fluid and adsorbed layer—which means without knowledge of τ_{ad}—one cannot obtain D_S from the observed flux $\dot{n}$. Assuming that adsorption equilibrium is established everywhere and that the kinetics of exchange between fluid and adsorbed layer is immaterial cannot solve the problem. For the assumption of local equilibrium between fluid and adsorption layer

$$c_S = Kc$$

implies

$$\frac{d^2c_S}{dx^2} = \frac{d^2c}{dx^2} = 0$$

which would then follow from Eqs. 5 and 6. Local equilibrium would thus require that the gradients dc/dx and dc_S/dx and also the diffusive fluxes in the fluid as well as in the adsorbed layer must be constant along the length of the capillary. This condition can only be approximated in the trivial case where the diffusive flux in the adsorbed layer is negligible compared to the diffusive flux in the fluid.

Relating the observed excess $\dot{n}_S$ of the diffusive flux $\dot{n}$ (above the flux $\dot{n}_F$ expected for diffusion in the fluid alone)

$$\dot{n}_S = \dot{n} - \dot{n}_F \tag{7}$$

to the maximum difference in surface concentration over the length of the capillary [which would be $K(c_1 - c_2)$] as a driving force and to the circumference $2r\pi$ of the capillary, one may define an apparent surface diffusivity D_S' in an operational way:

$$\dot{n}_S = D_S' \cdot 2r\pi \cdot \frac{K(c_1 - c_2)}{L} \tag{8}$$

The coefficient D_S' in Eq. 8 is not identical with the coefficient of surface diffusion D_S as defined in Eq. 2, which depends only on the mobility of the adsorbate in the adsorbed layer. From Eqs. 1, 3, and 7 we have for any position $x = \xi$ along the capillary $(0 < \xi < L)$:

$$\dot{n}_S = r^2\pi \cdot D_F \cdot \left[-\left(\frac{dc}{dx}\right)_\xi - \frac{c_1 - c_2}{L}\right] - 2r\pi \cdot D_S \cdot \left(\frac{dc_S}{dx}\right)_\xi \tag{9}$$

Choosing ξ such that $dc/dx = (c_2 - c_1)/L$ (see Figure 1), the first term on the righthand side of Eq. 9 will be zero; we have then

$$\dot{n}_S = -2r\pi D_S \left(\frac{dc_S}{dx}\right)_\xi \tag{10}$$

and therefore from Eq. 8

$$\frac{D_S'}{D_S} = \frac{L}{K(c_2 - c_1)} \cdot \left(\frac{dc_S}{dx}\right)_\xi \tag{11}$$

The gradient $(dc_S/dx)_\xi$ of the surface concentration at $x = \xi$ will depend interalia on the rate coefficient of desorption and on the ratio r/L, that is, on the geometry of the system. The apparent surface diffusivity D_S' can be smaller or greater than D_S; it will depend not only on the mobility of the adsorbate in the adsorbed layer but also on the kinetics of adsorption/desorption and on the geometric configuration of the system.

The difficulties with respect to the evaluation of surface diffusivities D_S from observed rates of diffusion in a single capillary will necessarily also be encountered in the case of a real porous medium with an irregularly shaped pore space, where we have a few additional complications. Surface migration will then more or less bridge the resistances of narrows in the fluid network. It is not possible to predict quantitatively the effect of a given surface diffusivity D_S on the total flux in an irregular pore structure, since the kinetics of exchange between adsorbed layer and fluid must again depend on the geometry of the pore structure, which is generally unknown. Consequently, D_S cannot be evaluated from an observed incremental flux $\dot{n}_S$, which is due to the occurrence of surface diffusion in the porous medium.

Several authors (e.g., Komiyama and Smith, 1974a; Neretnieks, 1976; and Satterfield et al., 1973) have related such incremental fluxes $\dot{n}_S$ observed in porous media to the gradient of equilibrium surface concentration as driving force and thus obtained apparent (effective) coefficients of surface diffusion D_S', analogous to D_S' as defined by Eq. 8 for a capillary. These coefficients depend on the morphology of the porous medium, which determines the relative importance of different pathways of diffusion in the presence and in the absence of surface migration. Komiyama and Smith (1974b) have acknowledged this influence by introducing a tortuosity factor for surface transport, which cannot be determined experimentally, however. Moreover "surface tortuosity" and "pore volume tortuosity" must be both substrate-specific and interdependent as soon as an exchange of material between the adsorbed layer and the fluid is possible, so that surface diffusion and diffusion in the fluid are no longer independent parallel processes.

R. Aris (1983) has shown recently that the apparent diffusivity in a porous medium will depend interalia on the finite rates of adsorption and desorption, if surface diffusion contributes to transport. The paper by Aris appeared while the present note was under review.

NOTATION

c = concentration in fluid, mol·m^{-3}
c_S = concentration on surface, mol·m^{-2}
D_F = diffusivity in fluid, m^2·s^{-1}
D_S = diffusivity in surface, m^2·s^{-1}
D_S' = apparent surface diffusivity (Eq. 8), m^2·s^{-1}
K = equilibrium constant (Eq. 4), m^{-1}
l = length, m
L = length of capillary, m
$\dot{n}$ = observed diffusive flux, mol·s^{-1}
$\dot{n}_F$ = diffusive flux expected in the absence of surface migration, mol·s^{-1}
$\dot{n}_S$ = increment of diffusive flux due to surface migration, mol·s^{-1}
t = time, s
r = capillary radius, m
x = length coordinate, m
τ_{ad} = relaxation time, s
ξ = position on x axis, m

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