Intraparticle Adsorbate Concentration Profile for Linear Driving Force Model

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The linear driving force (LDF) model of gas sorption kinetics, originally proposed by Glueckauf (1955), is frequently used in the mathematical simulations of adsorptive process designs (Gemmingen, 1993; Hartzog and Sircar, 1995) because of its simplicity. For the case of isothermal adsorption (constant system temperature, T) of a pure gas into a single adsorbent particle, the model yields

$$\frac{d\bar{c}(t)}{dt} = k[\bar{c}^* - \bar{c}(t)] \tag{1}$$

where $\bar{c}(t)$ is the average concentration (moles/cm^3 of particle) of the adsorbate within the adsorbent particle at time t. $\bar{c}^*$ is the concentration of the adsorbate in the particle in equilibrium with the instantaneous gas-phase pressure (P) at time t. k is the mass-transfer coefficient for the adsorbate at P and T or $\bar{c}(t)$ and T.

Although the LDF model deals with the average concentrations of the adsorbate within the adsorbent particle, several authors have demonstrated that Eq. 1 is compatible with different adsorbate concentration profiles within the particle (Liaw et al., 1979; Do and Rice, 1995). The parabolic concentration profile (Liaw et al., 1979) is the best known

$$c(r,t) = a(t) + b(t) \cdot r^2 \tag{2}$$

where $c(r,t)$ is the local adsorbate concentration at radius r and time t within a spherical adsorbent particle of radius R. The variables $a(t)$ and $b(t)$ are functions of time only. The local adsorbate concentration within the particle at the surface ($r = R$) is c_R, which is in equilibrium with the superincumbent gas phase at pressure P and temperature T. c_R is a constant for a constant gas-pressure uptake experiment. For this case, the first boundary condition for Eq. 2 is

$$c_R = a(t) + b(t) \cdot R^2 \tag{3}$$

The other boundary condition arises from the concentration symmetry at the center ($r = 0$) of the adsorbent particle

$$\left[\frac{\delta c(r,t)}{\delta r}\right]_{r=0} = 0 \tag{4}$$

Equation 2 satisfies Eq. 4. The average adsorbate concentration within the particle at time t is given by

$$\bar{c}(t) = \frac{3}{R^3}\int_0^R r^2 c(r,t) \cdot dr \tag{5}$$

Equations 2–5 can be combined to get Eq. 1, which demonstrates that the parabolic adsorbate concentration profile is compatible with the LDF model.

Furthermore, Liaw et al. (1979) demonstrated that a relationship between k and the Fickian diffusivity (D) can be obtained by equating the isothermal and isobaric rate of uptake of a pure gas by the spherical adsorbent

$$\frac{d\bar{c}(t)}{dt} = k[c_R - \bar{c}(t)] = \frac{3D}{R}\left[\left\{\frac{\delta c(r,t)}{\delta r}\right\}_t\right]_{r=R} \tag{6}$$

Equations 1–6 can be simultaneously solved to obtain

$$k = \frac{15D}{R^2} \tag{7}$$

Equation 7 is the well-known relationship between k and D, which was also derived by Glueckauf (1955) by comparing the mathematical solutions of chromatographic effluent curves using the LDF and the Fickian diffusion models.

The purpose of this note is to demonstrate that a very general adsorbate concentration profile within the spherical adsorbent particle can satisfy the LDF model (Eq. 1). It is assumed that

$$c(r,t) = a(t) + b(t) \cdot F(r) \tag{8}$$

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where $F(r)$ is any monotonic and continuous function of r in the domain of $0 \le r \le R$, which satisfies the boundary condition 4

$$\left.\frac{dF(r)}{dr}\right|_{r=0} = 0 \tag{9}$$

For a constant pressure uptake experiment, Eqs. 5, 6, and 8 can be combined to obtain

$$c(r,t) = c_R - b(t) \cdot F_R[1 - F(r)/F_R] \tag{10}$$

$$b(t) = \frac{(c_R - \bar{c}_o)}{[F_R - G_R]} \cdot e^{-kt} \tag{11}$$

$$k = \frac{3D}{R} \cdot \frac{H_R}{[F_R - G_R]} \tag{12}$$

where F_R is the value of function $F(r)$ at $r = R$, and $\bar{c}_o$ is the initial $(t = 0)$ equilibrium adsorbate loading of the particle. The variables G_R and H_R are given by

$$G_R = \frac{3}{R^3}\int_0^R r^2 \cdot F(r)\,dr \tag{13}$$

$$H_R = \left.\frac{dF(r)}{dr}\right|_{r=R} \tag{14}$$

Thus, Eq. 10, under the constraint of Eq. 9, provides a very general adsorbate concentration profile within a spherical adsorbent particle, which satisfies the overall LDF model equation. However, the adsorbate concentration profile at small values of t will be unrealistic $[c(r,t) < \bar{c}^o]$, because Eq. 8 cannot describe the step function concentration profile that was imposed on the particle at $t = 0$ for a constant pressure experiment. The function $b(t)$ is given by Eq. 11. The corresponding general relationship between k and D is given by Eq. 12. It shows that the proportionality constant between k and (D/R^2) is not limited to 15 as generally accepted. The value of this constant depends on the nature of the function $F(r)$.

For the special case where $F(r)$ is given by $(r)^p$ $(p \ge 2)$, one can demonstrate using Eqs. 10–14 that

$$b(t) = \frac{3+p}{p} \cdot \frac{c_R}{(R)^p} e^{-kt} \tag{15}$$

$$k = \frac{3(3+p)D}{R^2} \tag{16}$$

Equation 16 reduces to Eq. 7 when $p = 2$, as required. It also shows that the proportionality constant between k and (D/R^2) depends on the choice of the parameter p for this special case.

The intraparticle adsorbate concentration profile for the above described special case may be written as

$$c(r,t) = c_R - [c_R - \bar{c}(t)]\left[\frac{(3+p)}{p}\right]\left[1 - \left(\frac{r}{R}\right)^p\right] \tag{17}$$

Recently, Li and Yang (1999) proposed that the function $F(r) = (r)^p$ is compatible with the LDF model. However, they obtained a different intraparticle concentration profile (Eq. 11 of Li and Yang (1999)) than Eq. 17 due to an algebraic error. This leads to the erroneous conclusion that $p = 2$ and 5 are the only two acceptable indices for the function $F(r) = (r)^p$. The results of our work show that any value of $p(\ge 2)$ is acceptable and the relationship between k and D is given by Eq. 16.

Conclusions

The LDF model is compatible with any adsorbate concentration profile within a spherical adsorbent particle provided that the form of the profile is functionally given by Eq. 8 and that the constraint given by Eq. 9 is satisfied. Consequently, a very general relationship between the LDF mass-transfer coefficient (k) and the Fickian diffusivity (D) can be derived. Equations 12–14 show that this relationship depends on the nature of the function $F(r)$ in Eq. 8. It follows that the generally accepted relationship $(k = 15D/R^2)$, which is obtained for the special case of $[F(r) = r^2]$, is not the only permissible relationship.

The flexibility of the intraparticle adsorbate concentration profile for the LDF model strengthens the argument for its use in process design. More importantly, the general relationship between k and D (Eq. 12) removes the conventional restriction imposed on the relationship between these two variables $[k = 15D/R^2]$. This justifies the use of the LDF model even when the conventional relationship is found to be inadequate.

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