Linear Driving Force Formulas for Diffusion and Reaction in Porous Catalysts

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Since the classical work of Glueckauf (1955), the linear driving force (LDF) approximation has been used in the analysis of chromatography (Raghavan and Ruthven, 1985) and packed bed adsorbers (Morbidelli et al., 1982; Doong and Yang, 1987). The main advantage of the approximation is in its greatly simplified formulas for unsteady-state diffusion in porous particles. Instead of the partial differential equation

$$\frac{\partial C}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(Dr^2\frac{\partial C}{\partial r}\right) \tag{1}$$

the LDF approximation gives the following ordinary differential equations:

$$\frac{\partial \bar{C}}{dt} = \frac{15D}{R^2}(F - \bar{C}) \tag{2}$$

or

$$\frac{d\bar{C}}{dt} = \frac{\pi^2 D}{R^2}(F - \bar{C}) + \left(1 - \frac{\pi^2}{15}\right)\frac{dF}{dt} \tag{3}$$

where $\bar{C}$ is the volume-averaged fluid-phase concentration in the particle and $F(t)$ is an arbitrary time-varying surface concentration. To calculate the rate of mass exchange between the particle and its surroundings in a formal way, one has to solve Eq. 1 with appropriate initial and boundary conditions, and then determine $D(\partial C/\partial r)|_{r=R}$ as the mass exchange rate per outer surface unit of the particle. With the LDF approximation, one can directly determine the rate per unit volume of the particle by Eq. 2, or more accurately by Eq. 3. A comparison of the numerical predictions by Eq. 1 and those by Eq. 2 and Eq. 3 showed that Eq. 2 was fully adequate, while Eq. 3 was almost perfect (Glueckauf, 1955).

Exact solutions of Eq. 1 are available for a number of initial and boundary conditions. However, when Eq. 1 is coupled with the dynamics of an adsorber or a chromatographic column, the resulting set of equations may become too bulky to be solved analytically or even numerically. In such cases, the simplicity afforded by the LDF expressions allows the resulting problem to be mathematically more tractable.

It is worth noting that the LDF expressions, Eqs. 2 and 3, have been developed only for no-reaction cases. Further, as it is clear from Eqs. 1 through 3, the LDF expressions either do not distinguish between the adsorbed phase and the diffusing phase in the particles or consider the diffusing phase only. Adsorption is one of the primary phenomena in most processes involving porous particles, and except in very fine pore structures such as in zeolite crystals, the two phases are distinguishable. Thus Eqs. 2 and 3, in a strict sense, may have limited usefulness.

In this paper, LDF approximations which take into account reaction, adsorption, as well as unsteady-state diffusion, are developed. This work can be regarded as an extension of the work of Glueckauf (1955).

Theory

A mass balance equation for unsteady-state diffusion, adsorption, and a first-order reaction in a porous spherical catalyst particle is

$$\epsilon_p\frac{\partial C}{\partial t} = \epsilon_p\frac{1}{r^2}\frac{\partial}{\partial r}\left(Dr^2\frac{\partial C}{\partial r}\right) - (1 - \epsilon_p)\frac{\partial Q}{\partial t} - (1 - \epsilon_p)kC \tag{4}$$

We assume that the adsorption is in equilibrium and its isotherm is linear, i.e., $Q = KC$. We scale the problem by introducing

$$\tau = \frac{\epsilon_p D}{R^2[\epsilon_p + (1 - \epsilon_p)K]}t, \quad x = \frac{r}{R} \tag{5}$$

The problem becomes

$$\frac{\partial C}{\partial \tau} = \frac{1}{x^2}\frac{\partial}{\partial x}\left(x^2\frac{\partial C}{\partial x}\right) - \phi^2 C \tag{6}$$

The initial and boundary conditions are

I.C.:

$$C(x, 0) = 0 \tag{7}$$

B.Cs.:

$$C(1, \tau) = f(\tau) \tag{8}$$

$$\left.\frac{\partial C}{\partial x}\right|_{x=0} = 0 \tag{9}$$

Here $f(\tau)$ is an arbitrary time-varying surface concentration and ϕ is the Thiele modulus $(=R\sqrt{[(1-\epsilon_p)k]/(\epsilon_p D)})$. Following the method of solution illustrated in Ramkrishna and Amundson (1985), we obtain the exact solution of the problem:

$$C(x, t) = \frac{2}{x}\sum_{n=1}^{\infty}(-1)^{n+1} n\pi \sin n\pi x \, e^{-\lambda_n \tau}\int_0^{\tau} e^{\lambda_n \xi} f(\xi)\, d\xi \tag{10}$$

where

$$\lambda_n = \phi^2 + n^2\pi^2 \tag{11}$$

The volume-averaged fluid-phase concentration in the catalyst is

$$\overline{C}(\tau) = 3\int_0^1 C(x, \tau)x^2\, dx = 6\sum_{n=1}^{\infty} e^{-\lambda_n \tau}\int_0^{\tau} e^{\lambda_n \xi} f(\xi)\, d\xi \tag{12}$$

Integrating by parts successively, we expand the integral in Eq. 12:

$$\begin{aligned}\int_0^{\tau} e^{\lambda_n \xi} f(\xi)\, d\xi &= \frac{e^{\lambda_n \tau}}{\lambda_n} f(\tau) - \frac{1}{\lambda_n} f(0)\\ &\quad - \frac{e^{\lambda_n \tau}}{\lambda_n^2}\frac{df}{d\tau} + \left.\frac{1}{\lambda_n^2}\frac{df}{d\tau}\right|_{\tau=0} + \frac{e^{\lambda_n \tau}}{\lambda_n^3}\frac{d^2f}{d\tau^2} - \left.\frac{1}{\lambda_n^3}\frac{d^2f}{d\tau^2}\right|_{\tau=0} - + \cdots\end{aligned} \tag{13}$$

Substitution of Eq. 13 into Eq. 12 gives

$$\begin{aligned}\overline{C}(\tau) &= f(\tau)\sum_{n=1}^{\infty}\frac{6}{\lambda_n} - \frac{df}{d\tau}\sum_{n=1}^{\infty}\frac{6}{\lambda_n^2}\\ &\quad + \frac{d^2f}{d\tau^2}\sum_{n=1}^{\infty}\frac{6}{\lambda_n^3} - + \cdots + \sum_{n=1}^{\infty}\frac{e^{-\lambda_n \tau}}{\lambda_n}\\ &\quad \cdot\left(-f(0) + \left.\frac{1}{\lambda_n}\frac{df}{d\tau}\right|_{\tau=0} - \left.\frac{1}{\lambda_n^2}\frac{d^2f}{d\tau^2}\right|_{\tau=0} + - \cdots\right)\end{aligned} \tag{14}$$

At large τ, the terms with $e^{-\lambda_n \tau}$ become negligible and may be dropped out, and Eq. 14 becomes

$$\overline{C}(\tau) = s_1 f(\tau) - s_2\frac{df}{d\tau} + s_3\frac{d^2f}{d\tau^2} - s_4\frac{d^3f}{d\tau^3} + - \cdots \tag{15}$$

where

$$s_i = \sum_{n=1}^{\infty}\frac{6}{\lambda_n^i} \tag{16}$$

For a constant surface concentration $f(\tau) = A$ and $\tau \to \infty$, Eqs. 12 and 15 give the same result, i.e., $\overline{C} = s_1 A$. Thus $s_1\,[=\Sigma_{n=1}^{\infty}(6/\lambda_n)]$ can be seen as the ratio of the volume-averaged fluid-phase concentration in the catalyst particle at steady-state to the surface concentration. Even when the surface concentration varies with time, the internal volume-averaged concentration $\overline{C}$ will move in the direction toward $s_1 f(\tau)$, and may eventually become $s_1 f(\tau)$ if the dynamics of the mass transfer inside the catalyst is sufficiently rapid. In this respect, we let

$$f_0(\tau) = s_1 f(\tau) \tag{17}$$

Then rearranging Eq. 15 gives

$$(f_0 - \overline{C}) = \frac{s_2}{s_1}\frac{df_0}{d\tau} - \frac{s_3}{s_1}\frac{d^2f_0}{d\tau^2} + \frac{s_4}{s_1}\frac{d^3f_0}{d\tau^3} - + \cdots \tag{18}$$

Differentiation of Eq. 15 with respect to τ gives

$$\frac{d\overline{C}}{d\tau} = \frac{df_0}{d\tau} - \frac{s_2}{s_1}\frac{d^2f_0}{d\tau^2} + \frac{s_3}{s_1}\frac{d^3f_0}{d\tau^3} - \frac{s_4}{s_1}\frac{d^4f_0}{d\tau^4} + - \cdots \tag{19}$$

Eq. 19 expresses the rate of the mean concentration change in terms of the derivatives of $f_0(\tau)$. The coefficient of the derivative s_i rapidly decreases as the index i increases (see Table 1), and, in general, the derivative of f_0 also becomes less important as the order of the derivative increases; thus we may approximate $d\overline{C}/d\tau$ by simply truncating the series Eq. 19 after a finite terms. As shown below, however, we can obtain more refined formulas for given orders of approximations by combining Eqs. 18 and 19.

With Eq. 18 it is possible to eliminate any one derivative of f_0 from Eq. 19. If the first-order term is to be eliminated, a combination of Eqs. 18 and 19 yields

$$\begin{aligned}\frac{d\overline{C}}{d\tau} &= \frac{s_1}{s_2}(f_0 - \overline{C}) - \left(\frac{s_2}{s_1} - \frac{s_3}{s_2}\right)\frac{d^2f_0}{d\tau^2}\\ &\quad + \left(\frac{s_3}{s_1} - \frac{s_4}{s_2}\right)\frac{d^3f_0}{d\tau^3} - + \cdots\end{aligned} \tag{20}$$

Table 1. Coefficients of the Expansion Eq. 15

ϕ	s_1	s_2	s_3	s_4
0	1	$1/15$	0.006349	0.0006349
1	0.9391	0.05565	0.004773	0.0004322
2	0.8060	0.03550	0.002331	0.0001639
5	0.4801	0.007212	0.0001694	4.448×10^{-6}
10	0.2700	0.001200	8.250×10^{-6}	6.375×10^{-8}
20	0.1425	0.0001688	3.047×10^{-7}	6.152×10^{-10}
50	0.05880	1.1152×10^{-5}	3.408×10^{-9}	1.123×10^{-12}
100	0.02970	1.470×10^{-6}	1.095×10^{-10}	9.075×10^{-15}

If we truncate after the first term, we obtain

$$\frac{d\bar{C}}{d\tau} = \frac{s_1}{s_2}(f_0 - \bar{C}) \tag{21}$$

which is in fact correct to the first order $df_0/d\tau$ and at the same time consists of only zero-order terms at its right hand side. Further, it can be verified that the coefficients of the derivatives in Eq. 20 are smaller than the corresponding coefficients in Eq. 19. Hence Eq. 21 is more accurate and mathematically more tractable than the first-order approximation by Eq. 19 alone. To obtain a second-order approximation, we eliminate the second-order derivative from Eq. 19 by combining Eq. 18. Then

$$\frac{d\bar{C}}{d\tau} = \frac{s_2}{s_3}(f_0 - \bar{C}) + \left(1 - \frac{s_2^2}{s_1 s_3}\right)\frac{df_0}{d\tau} + \left(\frac{s_3}{s_1} - \frac{s_2 s_4}{s_1 s_3}\right)\frac{d^3 f_0}{d\tau^3} - + \cdots \tag{22}$$

We truncate the terms with derivatives of orders higher than three and obtain

$$\frac{d\bar{C}}{d\tau} = \frac{s_2}{s_3}(f_0 - \bar{C}) + \left(1 - \frac{s_2^2}{s_1 s_3}\right)\frac{df_0}{d\tau} \tag{23}$$

By this way we may derive as many approximations as necessary, but approximations with orders higher than the one in Eq. 23 are of little practical use, since the resulting increased complexity in the expressions is often unwieldy and the accuracy of Eq. 23 is sufficient for most practical purposes.

We revert to the real-time scale in view of Eq. 5. The surface concentration is then $F(t)$ and if we let $F_0(t) = s_1 F(t)$, then we have

$$\frac{d\bar{C}}{dt} = \frac{\epsilon_p D}{R^2[\epsilon_p + (1 - \epsilon_p)K]}\frac{s_1}{s_2}(F_0 - \bar{C}) \tag{24}$$

$$\frac{d\bar{C}}{dt} = \frac{\epsilon_p D}{R^2[\epsilon_p + (1 - \epsilon_p)K]}\frac{s_2}{s_3}(F_0 - \bar{C}) + \left(1 - \frac{s_2^2}{s_1 s_3}\right)\frac{dF_0}{dt} \tag{25}$$

The rate of unsteady-state mass transfer between the catalyst and its surroundings is now given as $[\epsilon_p + (1 - \epsilon_p)K](d\bar{c}/dt) + (1 - \epsilon_p)k\bar{C}$.

Discussion

In the case of no reaction, $\phi = 0$, Eqs. 24 and 25 become

$$\frac{d\bar{C}}{dt} = 15\frac{\epsilon_p D}{R^2[\epsilon_p + (1 - \epsilon_p)K]}(F - \bar{C}) \tag{26}$$

$$\frac{d\bar{C}}{dt} = 10.5\frac{\epsilon_p D}{R^2[\epsilon_p + (1 - \epsilon_p)K]}(F - \bar{C}) + 0.3\frac{dF}{dt} \tag{27}$$

When $K = 1$, Eq. 26 is equivalent to Eq. 2, but Eq. 27 is different from the corresponding Glueckauf formula, Eq. 3. The reason for the difference lies in the series expansion of $d\bar{C}/d\tau$ for the respective approximations: the present formula (Eq. 27) originates from the series Eq. 22, in which the second-order derivative has been vanished, whereas, as can be examined in Glueckauf's work (1955), Eq. 3 is from a series which has all orders of the derivatives. In this respect, although both formulas are expressed with terms up to the first order, Eq. 25 and Eq. 27 are exact to the second order, while the Glueckauf's formula, Eq. 3 is exact only to the first order. Hence, enhanced approximation accuracy can be expected with the present formulas. In Figure 1, Eqs. 2, 3 and 27 are compared with the exact solution Eq. 12, for a unit step change in the surface concentration. Fair agreement is obtained with Eq. 2 or Eq. 26 with $\epsilon_p D/\{R^2[\epsilon_p + (1 - \epsilon_p)K]\} = 1$. Except at very small t values, the agreement is excellent either with Eq. 3 or Eq. 27, and between the two, Eq. 27 gives better quantitative results, as expected.

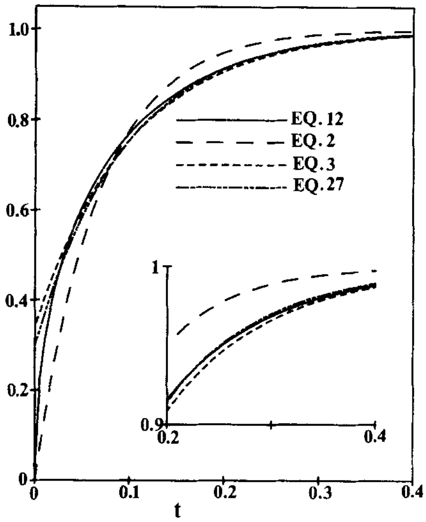

Figure 1. Comparison of exact solution and LDF formulas for unit step change in surface concentration.
Values: $D/R^2 = 1$ for Eqs. 2 and 3, $(\epsilon_p D)/R^2[\epsilon_p + (1 - \epsilon_p)K] = 1$ for Eqs. 12 and 27.

In Table 1, s_i values are listed for various ϕ values, and in Table 2, the coefficients in the LDF formulas are given. The coefficients for $(F_0 - \bar{C})$ rapidly increase with increasing ϕ, while the coefficient for dF_0/dt in Eq. 25 remains virtually the same, irrespective of the ϕ values. At large ϕ values, the concentration profiles of the reactant become stiff as a result of rapid consumption of the reactant in the catalyst outer shell. Then the stiff profiles give rise to rapid mass transfer rates between the catalyst and its surroundings, and the rapidity in the mass trans-

Table 2. Coefficients in LDF Formulas

ϕ	s_1/s_2	s_2/s_3	$1 - (s_2^2/s_1 s_3)$
0	15	10.5	0.3
1	16.88	11.66	0.3092
2	22.70	15.23	0.3291
5	66.56	42.56	0.3606
10	225.0	145.5	0.3535
20	844.4	553.8	0.3441
50	5,104	3,380	0.3377
100	20,202	13,425	0.3355

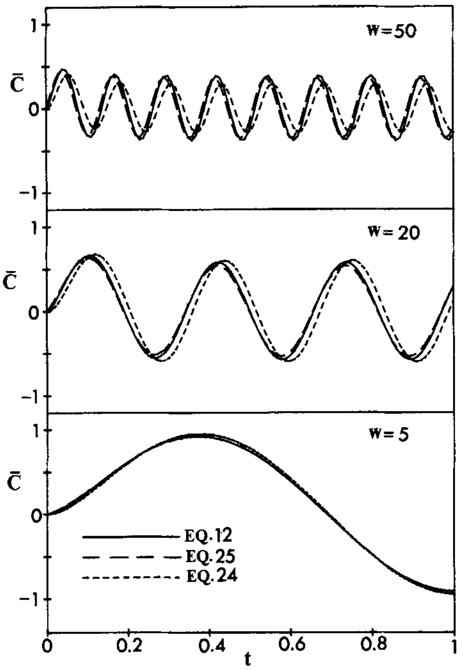

Figure 2. Comparison of exact solution and LDF formulas for sinusoidal surface concentration ($F(t)$ = sin wt), effect of frequency.

Values: $(\epsilon_p D)/R^2[\epsilon_p + (1 - \epsilon_p)K] = 1, \phi = 0$

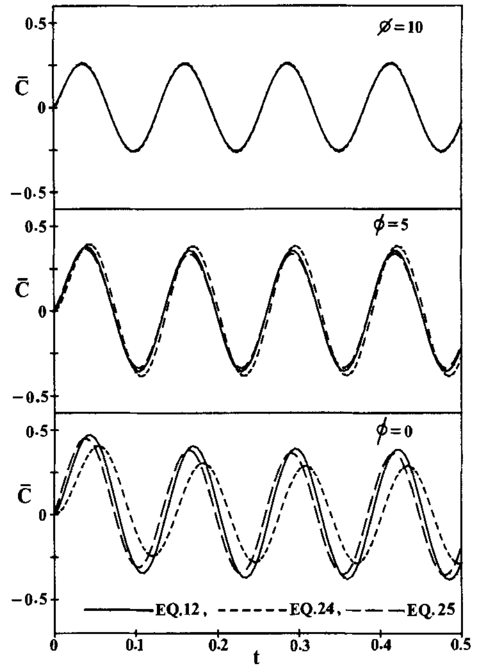

Figure 3. Comparison of exact solution and LDF formulas for sinusoidal surface concentration ($F(t)$ = sin wt), effect of ϕ.

Values: $(\epsilon_p D)/R^2[\epsilon_p + (1 - \epsilon_p)K] = 1, w = 50$

fer rates is reflected in large coefficients of the LDF formulas. But in this case, the coefficients of $(F_0 - \bar{C})$ alone become large since the rapidity has not been caused by the variation of the surface concentration such as $dF_0/d\tau$, but by the stiff internal concentration profiles.

Responses of LDF formulas and the exact solution for sinusoidal changes in the surface concentration are compared in Figure 2. For a slowly varying surface concentration, agreement with either Eq. 24 or Eq. 25 is excellent, but as the rate of change in the surface concentration increases, agreement with Eq. 24 becomes less satisfactory while Eq. 25 still gives acceptable results. In Figure 3, the effect of ϕ on the predictions of the LDF formulas are shown for a sinusoidal surface concentration. As ϕ increases, the approximation accuracy of the LDF formulas also increases. Even Eq. 24, which gives unacceptable results at $\phi = 0$, produces nearly perfect results at $\phi = 10$. This is not striking because, as discussed before, the effect of the term involving $(F_0 - \bar{C})$ becomes more pronounced and almost dominant when ϕ is large.

For the case of equilibrium adsorption with a nonlinear isotherm, the present formulas can also be employed if the perturbation in the surface concentration is small so that the isotherm can be linearized. In this case, $\bar{C}$ and $F(t)$ should be interpreted as deviations from the steady state, and K as the linearization coefficient of the nonlinear isotherm.

Notation

C = fluid-phase concentration in the catalyst
$\bar{C}$ = volume-averaged fluid-phase concentration in the catalyst
D = effective diffusivity
$F(t), f(\tau)$ = time-varying surface concentration
$F_0(t), f_0(\tau)$ = volume-averaged fluid-phase concentration in the catalyst at pseudo steady-state ($F_0(t) = s_1F(t)$, $f_0(\tau) = s_1(\tau)$)
K = adsorption equilibrium constant
k = reaction rate constant
R = radius of the catalyst particle
r = radial variable in the catalyst
s_i = defined in Eq. 16
t = time
x = dimensionless radial variable in the catalyst ($=r/R$)

Greek letters

ϵ_p = porosity in the catalyst particle
λ_n = eigenvalue ($=\phi^2 + n^2\pi^2$)
ϕ = Thiele modulus ($=R\sqrt{(1 - \epsilon_p)k/(\epsilon_p D)}$)
τ = dimensionless time ($=\epsilon_p Dt/\{R^2[\epsilon_p + (1 - \epsilon_p)K]\}'$)

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