A New Simplified Model for Adsorption in a Single Particle

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Studies of adsorption in a particle are commonly simplified by the use of linear driving force model (Akulov and Ustinov, 1981; Liaw et al., 1979; Rice, 1982). The linear driving force model was derived from the assumption of a parabolic profile for the intraparticle concentration. Its validity has been recently studied by Do and Rice (1986), and they have shown that the parabolic profile assumption is only applicable when the nondimensional time τ is greater than 0.05. In terms of fractional uptake, the uptake has to be greater than 60% before the linear driving force model is applicable. This means that the time domain of validity for the linear driving force model is very restricted.

The aim of this note is to develop a new simplified, and better, model of adsorption in a single particle that design engineers and researchers can use in their systems without unnecessary and complicated mathematical analysis.

Theory

The nondimensional model equations for adsorption inside a particle are

$$\frac{\partial A}{\partial \tau} = \frac{1}{x^2}\frac{\partial}{\partial x}\left(x^2 \frac{\partial A}{\partial x}\right) \tag{1a}$$

$$\tau = 0; \quad A = 0 \tag{1b}$$

$$x = 0; \quad \partial A/\partial x = 0 \tag{1c}$$

$$x = 1; \quad \partial A/\partial x = Bi(1 - A) \tag{1d}$$

The nondimensional variables and parameters for the two adsorption models are given in Table 1.

When the parabolic profile of the intraparticle concentration is assumed, i.e.,

$$A = a_o(t) + a_2(t)x^2 \tag{2}$$

the following equation for the mean concentration is obtained (Do and Rice, 1986)

$$\frac{d\overline{A}}{d\tau} = \frac{15(1 - \overline{A})}{(1 + 5/Bi)}. \tag{3}$$

Rewriting in dimensional terms, Eq. 3 can quickly be rearranged to yield the well-known linear driving force model for adsorption.

Knowing the mean concentration $\overline{A}$, from solution of Eq. 3, the intraparticle concentration can be obtained as

$$A = 1 - \left[1 + \frac{3/2}{(1 + 5/Bi)}\right]\exp\left[-\frac{15\tau}{(1 + 5/Bi)}\right] + \frac{(5/2)x^2}{(1 + 5/Bi)}\exp\left[-\frac{15\tau}{(1 + 5/Bi)}\right] \tag{4}$$

When the external mass transfer resistance is negligible (i.e., $k_m \rightarrow \infty$), the intraparticle concentration profile simplifies to

$$A = 1 - \tfrac{5}{2}(1 - x^2)e^{-15\tau} \tag{5}$$

It is clear from this equation that when $\tau < 0.061$, a portion of the concentration profile is negative. This physical inconsistency invalidates the applicability of the linear driving force model (Do and Rice, 1986) making it a poor approximation.

Examination of the profiles of the exact solution, Figure 1,

Table 1. Definitions of Variables and Parameters.

Variables, Parameters	Pore Diffusion Model	Solid Diffusion Model
A	C/C_o	q/KC_o
x	r/R	r/R
τ	$D_e t/R^2(\epsilon_p + \rho_p K)$	$D_s t/R^2$
Bi	$k_m R/D_e$	$k_m R/\rho_p K D_s$

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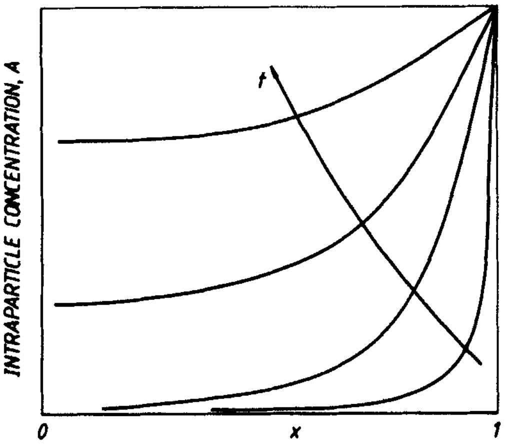

Figure 1. Intraparticle concentration profiles.

suggests that the intraparticle concentration profile should take the form

$$A = a_o + a_n x^n \tag{6}$$

where a_o, a_n, and n are all functions of time. Experience dictates that n should decrease to zero from a large initial value. It is noted that for noneven values of n, the symmetrical condition at the particle center is violated. However bear in mind that the profile serves as a vehicle to obtain the mean concentration within the particle. It is this mean concentration that we wish to predict, not the nature of the profile at $x = 0$.

Reapplying the analysis of Do and Rice to this new form of the particle profile we obtain:

$$\frac{d\bar{A}}{d\tau} = \frac{3(n+3)}{\left[1 + \frac{(n+3)}{Bi}\right]}(1 - \bar{A}) \tag{7}$$

At this point it is important to determine how n varies with respect to time. We first assume n to be constant. If we let this constant be n^*, the resultant solution of Eq. 7 is

$$\bar{A} = 1 - \exp\left\{-\frac{3(n^* + 3)\tau}{\left[1 + \frac{(n^* + 3)}{Bi}\right]}\right\} \tag{8}$$

The exact solution of Eq. 1 obtained by either Laplace transforms or the separation of variables method is

$$\bar{A} = 1 - 6\sum_{n=1}^{\infty} \frac{(\sin \xi_n - \xi_n \cos \xi_n)^2 e^{-\xi_n^2 \tau}}{\xi_n^4\left[1 + \frac{\cos^2 \xi_n}{(Bi - 1)}\right]} \tag{9}$$

where ξ_n is the solution of the following transcendental equation:

$$\xi_n \cos \xi_n = (1 - Bi) \sin \xi_n. \tag{10}$$

By comparing the exact solution, Eq. 9, to the approximate solution, Eq. 8, (that is, by equating the average concentration, $\bar{A}$, of the approximate model, Eq. 8, to that of the exact model, Eq. 9) one can obtain n^* as a function of time. Table 2 shows that dependence, and the result is shown graphically in Figure 2. Clearly, the value of n^* is large initially and decreases with increasing τ.

Additionally it should be noted that n^* is the integral mean of n from $\tau = 0$ to the time τ at which it is evaluated, i.e.,

$$n^* = \frac{1}{\tau}\int_0^\tau n \, d\tau \tag{11}$$

A log-log plot of n^* *vs.* τ, Figure 2, reveals a linear dependence that reduces to the following relationship:

$$n^* = 0.385\,\tau^{-0.68} \tag{12}$$

Substituting Eq. 12 into Eq. 11 and taking the derivative with respect to τ, we obtain the relationship for the instantaneous value of n.

$$n = 0.123\,\tau^{-0.638} \tag{13}$$

Substituting of n back into Eq. 7 allows us to generate the following solution for the average particle concentration.

$$\bar{A} = 1 - \exp\left[-(9\tau + 1.153\,\tau^{0.32})\right] \tag{14}$$

The ratio of the fractional uptake calculated from the approximate method, Eq. 14, to that calculated from the exact method, Eq. 9, is

$$R = \frac{1 - \exp\left[-(9\tau + 1.153\,\tau^{0.32})\right]}{1 - 6\sum_{n=1}^{\infty} \frac{e^{-\xi_n^2 \tau}}{\xi_n^2}} \tag{15}$$

Plotting this ratio *vs.* τ, Figure 3, indicates tremendous improvement over the conventional parabolic profile assumption. See Table 3.

Although the instantaneous value of n is found as a function of time, it is to be noted that this dependence is indirect. The

Table 2. Dependence of n^* and n on Nondimensional Time, τ

τ	$\bar{A}_{exact}$	n^*	n Calc. by Eq. 13
0.001	0.104	33.6	13.5
0.002	0.145	23.2	8.4
0.005	0.224	13.9	4.5
0.01	0.309	9.3	2.8
0.02	0.419	6.0	1.76
0.05	0.607	3.2	0.94
0.1	0.770	1.9	0.59
0.15	0.861	1.4	0.45
0.2	0.915	1.12	0.367

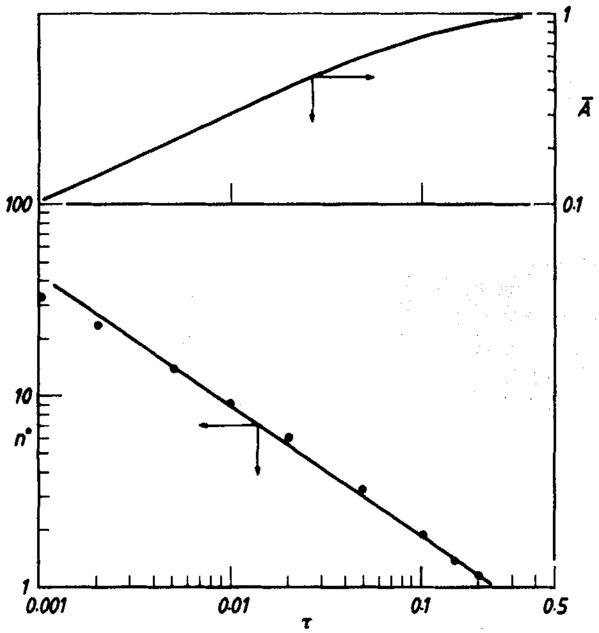

Figure 2. Plot of n^* and $\bar{A}_{exact}$ *vs* τ.

direct relationship should be that between n and the mean concentration $\bar{A}$. This relationship can be obtained by eliminating τ between Eqs. 13 and 14. We obtain:

$$\frac{0.046}{n^{1.47}}(9 + 9.37n) = \ln\left(\frac{1}{1-\bar{A}}\right) \tag{16}$$

Thus the new model for adsorption for a single particle is given by Eq. 7 where n is determined implicitly from Eq. 16.

In dimensional terms, the new model equations for adsorption in a single particle can be summarized as

$$\frac{0.046}{n^{1.47}}(9 + 9.37n) = \ln\left(\frac{C_o}{C_o-\bar{C}}\right) \tag{17a}$$

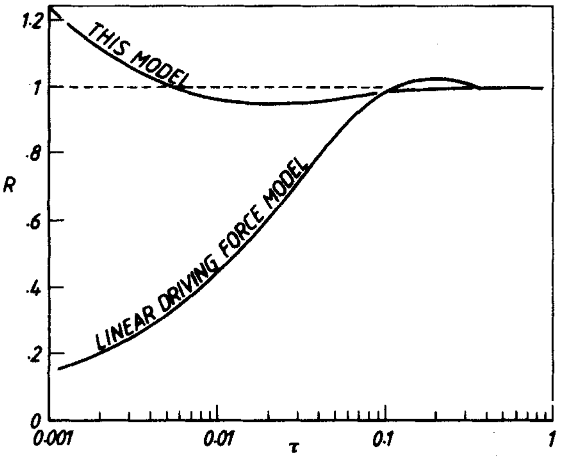

Figure 3. Plot of ratio of approximate to exact fractional uptake, Eq. 15, *vs.* τ.

Table 3. Comparison with Parabolic Profile Work of Do and Rice (1986)

		This Work		Parabolic Profile	
τ	$\bar{A}_{exact}$	$\bar{A}_{approx}$	Rel. Error*	$\bar{A}_{approx}$	Rel. Error*
0.001	0.104	0.127	19	0.015	85.6
0.002	0.145	0.161	11	0.029	80
0.005	0.224	0.226	0.9	0.072	68
0.01	0.309	0.298	3.5	0.139	55
0.02	0.419	0.400	4.5	0.259	38
0.05	0.607	0.590	2.8	0.528	13
0.1	0.770	0.766	0.5	0.777	1
0.15	0.861	0.862	0.1	0.895	4
0.2	0.915	0.917	0.2	0.950	4

*Relative error = $\left|\frac{\bar{A}_{approx} - \bar{A}_{exact}}{\bar{A}_{exact}}\right| \times 100$

$$\frac{d\bar{C}}{dt} = \frac{3(n+3)D_e}{R^2(\epsilon_p + \rho_p K)\left[1 + \frac{(n+3)D_e}{k_m R}\right]}(C_o - \bar{C}) \tag{17b}$$

where the pore diffusion model is used, and

$$\frac{0.046}{n^{1.47}}(9 + 9.37n) = \ln\left(\frac{C_o}{C_o - \bar{q}/K}\right) \tag{18a}$$

$$\frac{d\bar{q}}{dt} = \frac{3(n+3)D_s}{R^2\left[1 + \frac{(n+3)K\rho_p D_s}{k_m R}\right]}(KC_o - \bar{q}) \tag{18b}$$

where the solid diffusion model applies.

Although the results presented in Eq. 17 and 18 show significant improvement over the linear driving force model, a more explicit form would be desirable. To facilitate this let n take the following arbitrary functional form:

$$n = n_o \cdot \frac{(1-\bar{A})}{\bar{A}} \tag{19a}$$

Note that it satisfies the behavior at two extremes, i.e.,

$$n \rightarrow \infty \quad \text{when } \bar{A} \rightarrow 0 \text{ (or } \tau \rightarrow 0) \tag{19b}$$

$$n \rightarrow 0 \quad \text{when } \bar{A} \rightarrow 1 \text{ (or } \tau \rightarrow \infty) \tag{19c}$$

Substituting Eq. 19a into Eq. 7 and simplifying to the case where $Bi \rightarrow \infty$ yields

$$\frac{d\bar{A}}{d\tau} = 9\left[(1-\bar{A}) + \left(\frac{n_o}{3}\right)\frac{(1-\bar{A})^2}{\bar{A}}\right] \tag{20}$$

The solution of Eq. 20 is

$$\ln\left(\frac{1}{(1-\bar{A})}\right) - \frac{n_o}{(3-n_o)}\ln\left[1 + \frac{(3-n_o)}{n_o}\bar{A}\right] = 9\tau \tag{21}$$

Minimization of error between this approximate solution and the exact solution, Eq. 9, yields an optimal value of n_o of 1.6. Consequently, the equation for adsorption is

$$\frac{d\bar{A}}{d\tau} = 9\left[(1 - \bar{A}) + 0.533\,\frac{(1 - \bar{A})^2}{\bar{A}}\right] \tag{22}$$

In dimensional terms, Eq. 22 can be rewritten as:

$$\frac{d\bar{C}}{dt} = 9\left[\frac{D_e}{R^2(\epsilon_p + \rho_p K)}(C_o - \bar{C}) + \frac{0.533 D_e}{R^2(\epsilon_p + \rho_p K)} \cdot \frac{(C_o - \bar{C})^2}{\bar{C}}\right] \tag{23}$$

for the pore diffusion model, and as

$$\frac{d\bar{q}}{dt} = 9\left[\frac{D_s}{R^2}(KC_o - \bar{q}) + \frac{0.533 D_s}{R^2} \cdot \frac{(KC_o - \bar{q})^2}{\bar{q}}\right] \tag{24}$$

for the solid diffusion model. It is to be noted that Eqs. 23 and 24 contain quadratic forms of the concentration driving force. The quadratic form closely resembles Vermeulen's quadratic driving force form (Perry, 1973, pp. 16–19). In this respect, we may have uncovered the underlying principle for Vermeulen's quadratic approximation.

Conclusion

A new, more simplified model describing adsorption in a single particle, Eqs. 17 and 18, has been derived. Considerable improvement over the linear driving force model, first proposed about 40 years ago, has been clearly demonstrated. In addition the simplicity of the model equations lends itself to the analysis of more complex bimodal particle and fixed-bed problems.

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Notation

$\underline{A}$ = intraparticle concentration, Table 1
$\bar{A}$ = mean concentration
Bi = Biot number for mass transfer
C = intraparticle concentration
C_o = bulk concentration
D_e = effective diffusivity
D_s = surface diffusivity
k_m = external mass transfer coefficient
n = exponent, Eq. 7
n^* = defined in Eq. 14
n_o = defined in Eq. 24a
q = adsorbed concentration
$\bar{q}$ = mean adsorbed concentration
q^* = equilibrium adsorbed concentration, Eq. 4b
R = particle radius
x = nondimensional spatial variable
ξ = eigenvalue, Eq. 13
ρ = particle density
τ = time, Table 1

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