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Mass-Transfer Calculation Methods for Transient Diffusion within Particles

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Modeling of diffusion within spherical particles is often an important part of modeling of many processes relevant to chemical engineering such as adsorption. The accurate solution of the differential equations describing diffusion is quite a complicated task involving calculation of infinite series. A rational approximation to the diffusion equation is presented in this article leading to a solution that is both very easy to use and very accurate. The present method was compared to the exact solution for diffusion and adsorption in spheres, and it was found that the present solution is practically indistinguishable from the exact solution. This method is also applicable to multicomponent systems in a straightforward manner.

Introduction

Many important processes in chemical engineering include modeling of diffusion within particles or fluid spheroids. Accurate, but still computationally simple, solutions to these diffusion equations are, therefore, of great importance. Diffusion in adsorption processes has been subject to many studies since the classical approximate solution by Glueckauf (1955). In that solution, the mass transfer within the spherical particles is described by assuming that the mass-transfer rate depends linearly on the difference between the average concentration within the sphere and the surface concentration, along with the assumption of a constant (time-independent) mass-transfer coefficient. Since then that assumption has been used widely in the adsorber modeling. Furthermore, it has been shown that the linear driving force assumption (LDF) is equivalent to assuming a concentration profile within the particles. Both these approaches are used to ease the complicated solution of the time-dependent material balances in the adsorbers (Goto et al., 1990; Ching, Lu, 1998; Haas et al., 1988; Liaw et al., 1979; Li and Yang, 1999).

The LDF approximation is a very useful simplification in the adsorber modeling. However, it is not very accurate, especially for short contact times. In the present work, the exact solution of the particle diffusion equation is approximated by a rational function. The present approximation has correct short and long time asymptotes, and the intermediate times are described by a five-parameter rational function. This makes the present approach very accurate for all contact times.

Diffusion Model

Diffusion and adsorption in a sphere can be described with the following partial differential equation

$$\epsilon\frac{\partial c}{\partial t} = \epsilon\frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right) - (1-\epsilon)K\frac{\partial c}{\partial t} \tag{1}$$

with the boundary conditions

$$\begin{aligned} &t = 0,\ c = c_0 \\ &r = 0,\ \frac{\partial c}{\partial r} = 0 \\ &r = R,\ c = c^* \end{aligned} \tag{2}$$

Here it is assumed that the adsorption from the fluid in particle pores to the pore walls is in equilibrium at all times. The adsorption equilibrium is assumed linear, or linearized so that $K = dc_{\text{adsorbed}}/\text{dc}$. The initial concentration is assumed constant. The development to follow is applicable to fluid spheres, such as bubbles and drops with immobile surfaces, as well, if the mass transfer inside the fluid spheres is considered. In these cases we only set $\epsilon = 1$ and $K = 0$.

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The diffusion equation can be put in the following convenient non-dimensional form by using the modified Fourier number (the dimensionless time) definition

$$Fo = \frac{Dt}{R^2\left(1+\frac{1+\epsilon}{\epsilon}K\right)} \tag{3}$$

The concentration is scaled as $q = c - c_0$ and the radius as $z = r/R$.

The resulting partial differential equation is

$$\frac{\partial q}{\partial Fo} = \frac{1}{z^2}\frac{\partial}{\partial r}\left(z^2\frac{\partial q}{\partial z}\right) \tag{4}$$

The boundary conditions are now

$$\begin{aligned} Fo &= 0,\ q = 0 \\ z &= 0,\ \frac{\partial q}{\partial z} = 0 \\ z &= 1,\ q = q^* \end{aligned} \tag{5}$$

This formulation is referred often as the pore diffusion model.

It must be noted that in all these equations, the diffusion coefficient D and the distribution coefficient K are assumed both time and radius invariant. In practice, average values can be used in the cases where these coefficients are weak functions of time and/or radius. For strong time and/or radius dependence of these coefficients, the following development must be considered with caution.

For the adsorber mass balance, the volume-average (or cup-mixing) compositions within the adsorbent particles are needed. These composition are defined as

$$\bar{q} = 3\int_0^1 q(z,t)z^2dz \tag{6}$$

Some analytical solutions to the diffusion equation (4) are available in the literature (Crank, 1975, pp. 89–98). When the surface concentration, q^*, is time-independent, the solution for fractional approach to equilibrium is

$$F = \frac{\bar{q}}{q^*} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-n^2\pi^2 Fo) \tag{7}$$

For situations where the surface concentration is not constant, some special solutions are available. In these solutions, however, numerical solutions for the eigenvalues of the series expansions are needed. This may be quite an awkward task for slowly converging series expansion, and the solution of the adsorber model becomes quite complicated. Hence, the adsorber modeling is best accomplished by solving the time-dependent adsorber material balance and the diffusion equations with proper simplifications.

The time-dependent modeling can be done conveniently by expressing the equations with the Sherwood number and the Fourier number. In terms of the cup-mixing compositions, we have

$$\frac{\partial \bar{q}}{\partial Fo} = \frac{3}{2}Sh(q^* - \bar{q}) \tag{8}$$

In the definition of the Sherwood number, the driving force for diffusion inside the particle is taken to be the difference between the cup-mixing concentration and the surface concentration (Clift, Grace, and Weber, p. 57).

Solution to the diffusion equation in terms of the Sherwood number is then

$$Sh = \frac{2\pi^2}{3}\frac{\sum_{n=1}^{\infty}\exp(-n^2\pi^2 Fo)}{\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-n^2\pi^2 Fo)}. \tag{9}$$

For short contact times the solution is

$$Sh = \frac{2}{\sqrt{\pi Fo}} \tag{10}$$

and for long contact times the asymptotic solution is

$$Sh = \frac{2\pi^2}{3}. \tag{11}$$

A time-average Sherwood number can be calculated with

$$Sh_{\text{ave}} = \frac{-2\ln(1-F)}{3Fo}. \tag{12}$$

Here the Sherwood number is averaged over the contact time.

For short contact times the solution is

$$Sh_{\text{ave}} = \frac{4}{\sqrt{\pi Fo}}. \tag{13}$$

For long contact times, the asymptotic solution for the time averaged Sherwood number is the same as for the instantaneous case (Eq. 11). This time-averaged Sherwood number is not usually needed, since for the case of constant surface concentration, the fractional approach to equilibrium can be calculated straight from Eq. 7 for any given adsorption time.

Simplified Solutions to the Transient Adsorption Equation

To avoid the calculation of the infinite series in Eq. 9, simplified solutions are welcomed. The most classical and widespread simplification in the adsorber modeling is the classical LDF solution to Glueckauf (1955). It stands as

$$\frac{\partial \bar{q}}{\partial Fo} = 15(q^* - \bar{q}). \tag{14}$$

Comparing Eqs. 8 and 14, it can be seen that in the Glueckauf's solution a constant Sherwood number $Sh = 10$ is assumed.

Lee and Kim (1998) presented a different kind of approximation. They calculated the time-dependent cup-mixing compositions with the Padé approximations to the Laplace transformed diffusion equation. The most accurate method in their work was the Padé [2,3] rational approximation. It can be written with the present notation (for time domain) as

$$\frac{d\bar{q}}{dFo} = -378\bar{q} + q_2 + 81q^*$$
$$\frac{dq_2}{dFo} = -17{,}325\bar{q} + q_3 + 8316q^* \qquad (15)$$
$$\frac{dq_3}{dFo} = 135{,}135(q^* - \bar{q}).$$

Here q_2 and q_3 are additional state variables. This approach was shown to be superior compared to the classical LDF approach. In fact, Lee and Kim showed that the classical LDF solution is a first-order Padé approximation.

Here a completely different approach is adopted. Equation 9 for the Sherwood number is approximated by a rational function. Both short contact time and long contact time asymptotes (Eqs. 10 and 11) are set correct. The intermediate contact times are represented by a rational approximation, where five adjustable parameters are fitted to give the best representation of the exact solution. The following equation was found to follow the exact solution very accurately.

$$Sh = \frac{a_0}{\sqrt{\pi Fo}} + \frac{a_1 \cdot \sqrt{Fo} + a_2 \cdot Fo + \dfrac{2\pi^2}{3} a_5 \cdot Fo^{1.5}}{1 + a_3 \cdot \sqrt{Fo} + a_4 \cdot Fo + a_5 \cdot Fo^{1.5}}, \qquad (16)$$

where

$a_0 = 2$, $a_1 = 117{,}346$, $a_2 = 39{,}596$, $a_3 = 62{,}166$, $a_4 = 31{,}169$, and $a_5 = 337{,}258$.

For the constant surface concentration, the following approximation can be used to any given contact time without any integration. The functional form of the time-averaged Sherwood number is the same as for the instantaneous case, but the adjustable parameters are the following: $a_0 = 4$, $a_1 = 63{,}237$, $a_2 = 71{,}892$, $a_3 = 33{,}616$, $a_4 = 45{,}628$, and $a_5 = 116{,}673$.

The cup-mixing compositions are then calculated from

$$F = \frac{\bar{q}}{q^*} = 1 - \exp(-1.5 \cdot Fo \cdot Sh_{\text{ave}}). \qquad (17)$$

In this case, no series expansions or numerical integrations are needed. However, as mentioned earlier, constant surface concentration is only a special case, and hence the more general time-dependent modeling is recommended for varying surface concentration q^*.

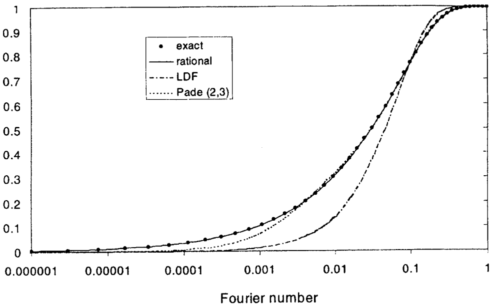

Figure 1. Approximate and exact solutions to the fractional approach to the equilibrium in a sphere.

Numerical Comparisons

The accuracy of the three approximate solutions, LDF, Padé, and the solution presented here, are validated numerically. The time-dependent diffusion equations are integrated numerically with respect to the Fourier number, and the resulting approaches to equilibrium are compared to the exact solution.

In Figure 1, the approximate solutions are compared to the exact solution. From the two approximations presented in this work, the instantaneous Sherwood number approach is used because of its generality. However, almost indistinguishable results are obtained if the time averaged form (17) is used. The instantaneous case is used here also to convince that the approximation errors are not accumulated during the time integration.

Hence, the three approximations are the LDF (Eq. 14), the Padé [2,3] approximation (Eq. 15), and the instantaneous Sherwood number approximation of this work (Eq. 8 and 16).

As can be seen, the presented approximation is almost indistinguishable from the exact solution. The Padé approximation works well for the long contact times, but there are deviations in the short contact time behavior. Of course, the order of the Padé approximation can be increased to make the solution more accurate, but this complicates the solution. The present approximation follows the exact solution very accurately even for short contact times, since the asymptote was set to the theoretical value in the parameter fit. The LDF approximation cannot be considered very accurate.

The sum of squared absolute errors are calculated at dimensionless times $Fo = 10^{-N}$, where $N = 0$, 1, 2, 3, 4, 5, 6 and 7. The results are shown in Table 1.

It must be noted that no additional state variables were needed in the present solution. In the high order Padé ap-

Table 1. Sum of Squared Absolute Residuals at Dimensionless Times $Fo = 10^{-N}$, where $N = 0, 1, 2, 3, 4, 5, 6$ and 7

Method	Sum of Squared Errors
LDF (Eq. 13)	0.037775707
Padé [2,3] approximation	0.001967182
Present work	1.33866×10^{-6}

proximations, additional state variables are needed. This obviously complicates the solution.

If relative errors were considered in Table 1, the differences between the different models would be even more pronounced. This is because the present approach is superior to the other approximations especially for short contact times. At short contact times, the fractional approach to equilibrium is low, resulting in higher relative errors.

Generalizations to Multicomponent Systems

The exact solution can be generalized to multicomponent systems in a straightforward manner. In multicomponent systems, a diffusion coefficient matrix is generally needed instead of scalar coefficients, and the component concentrations are represented as a vector. For further discussion of this subject (Taylor and Krishna, 1993, p. 235; Toor, 1964).

Since this approximation is a function of the diffusion coefficient matrix only, it is readily generalized to the following multicomponent form

$$\begin{aligned}[Sh] = {} & \frac{a_0}{\sqrt{\pi}}[Fo]^{-1/2} \\ & + \left(a_1 \cdot [Fo]^{0.5} + a_2 \cdot [Fo] + \frac{2\pi^2}{3} a_5 \cdot [Fo]^{1.5}\right) \\ & \cdot \left([I] + a_3 \cdot [Fo]^{0.5} + a_4 \cdot [Fo] + a_5 \cdot [Fo]^{1.5}\right)^{-1} \end{aligned} \tag{18}$$

Here the matrix of Fourier numbers is defined similarly to the scalar number, except that the scalar diffusion coefficient is replaced by a matrix.

This matrix function can be easily calculated with the approximate matrix function formula of Alopaeus and Nordén (1999).

Conclusions

The linear driving force model (LDF) has been widely used to model batch adsorbers. However, especially for short contact times, the LDF approach deviates significantly from the exact solution. In this work, a rational approximation to the interparticle mass transfer coefficient is presented. It has the correct asymptotic values for both short and long contact times. The intermediate contact times are modeled by a five-parameter rational function. This approach avoids the use of the series expansions needed in the exact solutions, leading to significant ease to be computational burden. The accuracy of the present method compared to the exact solution is excellent. In fact, the two solutions are almost indistinguishable.

Acknowledgments

Financial support from Neste OY Foundation is gratefully acknowledged.

Notation

c, c^*, c_0 = concentrations within the pores: general, surface, initial, mol/m^3
c_{adsorbed} = concentration in absorbent, mol/m^3
D = diffusion coefficient, m^2/s
F = fractional approach to equilibrium, $F = \bar{q}/q^*$
Fo = (modified) Fourier number
K = distribution coefficient, mol/m^3 (solid)/mol/m^3(fluid)
$q, q^*, \bar{q}$ = scaled concentrations: general, surface cupmixing (mol/m^3) (volume average)
q_2, q_3 = state variables, mol/m^3
r = radial distance from the center, m
R = radius of the spherical particle, m
Sh = Sherwood number
Sh_{ave} = time-averaged Sherwood number
t = time, s
z = dimensionless radius

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Manuscript received Dec. 30, 1999, and revision received May 14, 2000.