

A Kinetic Model Framework for Combined Diffusion and Adsorption Processes

E.A. BRINKMANN and R.P. KING

Department of Metallurgy and Materials Engineering, University of the Witwatersrand, Johannesburg

A kinetic model framework for single particle kinetics in combined diffusion and adsorption processes is presented. The framework applies to the general case in which both diffusion and the adsorption reaction play important roles in determining the overall rate in processes where the migrating species can both adsorb and accumulate. The technique, which should be applicable to a wide range of reaction mechanisms, consists of an iterative integration procedure for the coupled diffusion and reaction equations. The case of a reversible linear adsorption reaction rate is developed. In order to verify the technique as a legitimate method of model development, an analytical solution for the identical case is derived and compared to the numerical solution.

Excellent agreement exists between the two solutions.

Introduction

Interactions between migrating species in a fluid and a porous particulate phase, whereby some of the migrating species become immobilized with respect to further fluid migration as diffusion proceeds, are fairly common in adsorption-type processes such as carbon in pulp, resin ion exchange and removal of gaseous pollutants. The transport-reaction mechanisms operative in processes where the migrating species can both adsorb and accumulate are: (1) external mass transfer from the bulk fluid to the outer surface of the porous particle, (2) intraparticle mass transfer through the pore fluid and along the walls of the pores, and (3) adsorption at a site interior to the particle.

A variety of models based on the above mechanisms have been developed, frequently with the assumption that the adsorption reaction is intrinsically rapid with respect to the mass transfer processes such

that equilibrium is maintained at all times between the free and adsorbed components of the diffusing species at the adsorption site. When the approach to system equilibrium is much slower than can be accounted for by diffusion control alone or when the controlling mechanisms in a process are uncertain, the validity of this assumption becomes questionable.

In the present paper, a model framework is presented for the general case where both mass transfer and the adsorption reaction may play important roles in determining the overall rate. The main objectives are: (1) to illustrate the solution technique, which can be used for a variety of reversible adsorption reaction types, and (2) to verify the numerical technique results by comparison with an analytical solution for the case of a first-order reversible adsorption reaction.

Basic equations

The problem consists of a porous spherical particle of radius R comprised of a solid that is capable of adsorbing a fluid-diffusing reactant species at concentration C . The specific case where the species can both adsorb and accumulate is considered. In order to minimize the complexity of the problem, intraparticle diffusion has been attributed entirely to pore diffusion. Thus, as diffusion proceeds, the migrating species (at concentration C) is adsorbed and immobilized, producing a non-diffusing adsorbed product species at concentration S .

Under these conditions, the dynamic mass balance for the adsorbate is

$$\frac{\partial}{\partial r} \left(r^2 D_p \frac{\partial C}{\partial r} \right) - r^2 \frac{\rho}{\epsilon_p} \frac{\partial S}{\partial t} = r^2 \frac{\partial C}{\partial t} \quad [1]$$

with boundary conditions

$$C(r=R) = C_b \quad [2]$$

$$\frac{\partial C}{\partial r}(r=0) = 0 \quad [3]$$

For reversible adsorption, the reaction rate is governed by

$$\frac{\partial S}{\partial t} = f(C, S) \quad [4]$$

with the initial condition

$$S(t=0) = 0 \quad [5]$$

The assumptions of quasi-stationary behaviour and dilute solution permit the reformulation of Eq.[1]

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) = \frac{r^2}{D_p} \frac{\rho}{\epsilon_p} \frac{\partial S}{\partial t} \quad [6]$$

Evidently, the external mass transfer resistance has been neglected. In a well-mixed adsorber, this resistance may be ascribed primarily to diffusion through a hydrodynamic boundary layer at the outer surface of the particle. Therefore, the assumption of negligible external mass transfer resistance can be readily relaxed and the appropriate boundary condition can be accommodated within this framework. For

the sake of simplicity, the bulk concentration of the fluid phase was assumed to be constant. These factors were not included as the objective is to consider the respective roles of internal diffusional effects and the adsorption reaction rate expression in the overall rate process. Obviously, the exclusion of external mass transfer effects and variable bulk fluid concentration causes serious limitations under certain conditions, e.g. a batch environment.

Solution technique

The solution technique consists of an iterative integration procedure similar to that described by Saltelli and Offerman¹ for the coupled equations Eq.[4] and Eq.[6]. In this procedure, the migrating species is first allowed to diffuse with no adsorption taking place. Then, after each time step of diffusion, adsorption is allowed to occur before taking the next time step of diffusion. In each adsorption calculation, the solution obtained from the previous integration is used as the initial condition.

In order to illustrate the solution technique, provide numerical results and verify the technique, the case of a first-order reversible adsorption reaction is considered. In this case, Eq.[4] becomes

$$\frac{\partial S}{\partial t} = \frac{\epsilon_p}{\rho} k_a C - k_d S \quad [7]$$

and Eq.[6] becomes

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) = r^2 \frac{k_a}{D_p} C - r^2 \frac{\rho}{\epsilon_p} \frac{k_d}{D_p} S \quad [8]$$

Pseudo-analytical solution

In order to illustrate the solution technique, a pseudo-analytical solution over two diffusion time steps is presented for the case of reversible adsorption with a linear rate.

First time step

According to Eq.[5] the value of S at time zero is equal to zero such that the second term on the right of Eq.[8] is eliminated. After integration of the modified Eq.[8] and application of the boundary conditions in Eqs.[2] and [3] the concentration of the diffusing species in the pore fluid was obtained

$$C(r, t_1) = C_b \frac{R}{r} \frac{\sinh(r\sqrt{(k_a/D_p)})}{\sinh(R\sqrt{(k_a/D_p)})} \quad [9]$$

As the bulk fluid concentration was assumed constant, the adsorbed species concentration at time t_1 was obtained by the substitution of Eq.[9] into Eq.[7], integration and application of the initial condition given by Eq.[5]

$$S(r, t_1) = C_b \frac{\epsilon_p}{\rho} \frac{R}{r} \frac{k_a}{k_d} \frac{\sinh(r\sqrt{(k_a/D_p)})}{\sinh(R\sqrt{(k_a/D_p)})} * [1 - \exp(-k_d t_1)] \quad [10]$$

Second time step

The concentration of the diffusing species in the pore fluid at time t_2 was determined by substitution of Eq.[10] into Eq.[8] followed by integration and application of the boundary conditions given by Eqs.[2] and [3]

$$\begin{aligned} C(r, t_2) = & C_b \frac{R}{r} \frac{\sinh(r\sqrt{(k_a/D_p)})}{\sinh(R\sqrt{(k_a/D_p)})} \\ & + C_b \frac{R^2}{2r} \sqrt{(k_a/D_p)} \coth(R\sqrt{(k_a/D_p)}) \\ & * \frac{\sinh(r\sqrt{(k_a/D_p)})}{\sinh(R\sqrt{(k_a/D_p)})} [1 - \exp(-k_d t_1)] \\ & - C_b \frac{R}{2} \sqrt{(k_a/D_p)} \frac{\cosh(r\sqrt{(k_a/D_p)})}{\sinh(R\sqrt{(k_a/D_p)})} \\ & * [1 - \exp(-k_d t_1)] \quad [11] \end{aligned}$$

The concentration of the adsorbed species at time t_2 was calculated by substitution of Eq.[11] into Eq.[7], integration and application of the initial condition given by Eq.[10]

$$\begin{aligned} S(r, t_2) = & C_b \frac{\epsilon_p}{\rho} \frac{k_a}{k_d} \frac{R}{r} \frac{\sinh(r\sqrt{(k_a/D_p)})}{\sinh(R\sqrt{(k_a/D_p)})} \\ & * [1 - \exp(-k_d t_2)] \\ & + C_b \frac{\epsilon_p}{\rho} \frac{k_a}{k_d} \frac{R^2}{2r} \sqrt{(k_a/D_p)} \coth(R\sqrt{(k_a/D_p)}) \\ & * \frac{\sinh(r\sqrt{(k_a/D_p)})}{\sinh(R\sqrt{(k_a/D_p)})} * [F] \\ & - C_b \frac{\epsilon_p}{\rho} \frac{k_a}{k_d} \frac{R}{2} \sqrt{(k_a/D_p)} \\ & * \frac{\cosh(r\sqrt{(k_a/D_p)})}{\sinh(R\sqrt{(k_a/D_p)})} * [F] \quad [12] \end{aligned}$$

where

$$F = 1 - \exp(k_d t_1 - k_d t_2) - \exp(-k_d t_1) + \exp(-k_d t_2) \quad [13]$$

The process could be repeated, with the initial condition given by $S(r, t_{i-1})$ being used to evaluate $S(r, t_i)$.

Numerical solution

In order to provide numerical results which can be utilized in the verification of the solution technique, the case of reversible adsorption with a linear rate is presented. The number of independent parameters to be considered for numerical analysis was minimized by making Eqs.[7] and [8] dimensionless. Four dimensionless variables and one dimensionless parameter were chosen:

(a) dimensionless radial coordinate, λ ,

$$\lambda = \frac{r}{R} \quad [14]$$

(b) dimensionless migrating species concentration of the pore fluid, α ,

$$\alpha = \frac{C}{C_b} \quad [15]$$

(c) dimensionless concentration of adsorbed species, β ,

$$\beta = \frac{S}{S_{\text{equil}}} = \frac{S}{C_b} \frac{\rho}{\epsilon_p} \frac{k_d}{k_a} \quad [16]$$

(d) dimensionless time, θ ,

$$\theta = k_d t \quad [17]$$

(e) and dimensionless parameter, ψ ,

$$\psi = \sqrt{(R^2 k_a / D_p)} \quad [18]$$

The numerical solution procedure for the case of reversible linear kinetics mimics the pseudo-analytical technique through time by application of a finite difference technique for the evaluation of α with β being evaluated 'analytically'. A modified tridiagonal Gaussian elimination technique² was used to solve the set of simultaneous equations.

Numerous program runs were executed in order to evaluate the effects of the number of spacing intervals along the particle radius (i.e. the number of nodal points in the finite difference analog) and the incremental size of the dimensionless time step. In all cases it was found that, for a particular value of θ , β values asymptotically decreased as the number of nodal points increased and asymptotically increased as the incremental size of the time step decreased. Although the solution converged, it was concluded that approximately 100 nodal points and dimensionless time increments as small as 0,001 were required.

Analytical solution

In order to evaluate the numerical solution technique, an analytical solution was developed for the case of a reversible linear adsorption reaction rate. For the purpose of comparison with the numerical results, the analytical solution was evolved in terms of the dimensionless quantities described by Eqs.[14-18].

Solutions for the dimensionless migrating species concentration in the pore fluid, α , and the dimensionless adsorbed species concentration, β , were obtained by application of the Laplace transformation with respect to the dimensionless time

variable, θ . The method of solution follows that outlined by Wilson³ and Crank⁴.

The dimensionless equivalents of Eqs.[7] and [8] are

$$\frac{\partial \beta}{\partial \theta} = \alpha - \beta \quad [19]$$

$$\frac{\partial}{\partial \lambda} (\lambda^2 \frac{\partial \alpha}{\partial \lambda}) = \psi^2 \lambda^2 (\alpha - \beta) \quad [20]$$

with corresponding boundary conditions

$$\alpha(\lambda=1) = 1 \quad [21]$$

$$\frac{\partial \alpha}{\partial \lambda}(\lambda=0) = 0 \quad [22]$$

and initial condition

$$\beta(\theta=0) = 0 \quad [23]$$

After transformation into the Laplace domain, Eqs.[19-22] become

$$\bar{\beta} = \bar{\alpha} \frac{s}{s+1} \quad [24]$$

$$\frac{\partial^2 \bar{\alpha}}{\partial \lambda^2} + \frac{2}{\lambda} \frac{\partial \bar{\alpha}}{\partial \lambda} = \psi^2 \bar{\alpha} \frac{s}{s+1} \quad [25]$$

$$\bar{\alpha}(\lambda=1) = \frac{1}{s} \quad [26]$$

$$\frac{\partial \bar{\alpha}}{\partial \lambda}(\lambda=0) = 0 \quad [27]$$

As differentiations of $\bar{\alpha}$ with respect to s do not appear in Eq.[25], the equation may be solved as an ordinary differential equation. After integration and application of the boundary conditions, the solution to Eq.[25] was obtained

$$\bar{\alpha}(\lambda, s) = \frac{1}{s\lambda} \frac{\sinh[\psi\lambda\sqrt{(s/(s+1))}]}{\sinh[\psi\sqrt{(s/(s+1))}]} \quad [28]$$

The inverse transform of $\bar{\alpha}$ was determined by summing the residues at the poles⁵

$$\alpha(\lambda, \theta) = 1 + \frac{2\psi^2}{\pi\lambda} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} * \frac{\sin(n\pi\lambda)}{\psi^2 + n^2 \pi^2} \exp \left[\frac{-n^2 \pi^2 \theta}{\psi^2 + n^2 \pi^2} \right] \quad [29]$$

and the inverse transform of $\bar{\beta}$ was obtained after application of the convolution theorem⁶

$$\beta(\lambda, \theta) = 1 - \exp(-\theta) + \frac{2}{\pi\lambda} \sum_{n=1}^{\infty} \frac{(-1)^n}{n}$$

$$* \sin(n\pi\lambda) \exp \left[\frac{-n^2 \pi^2 \theta}{\psi + n^2 \pi^2} \right]$$

$$- \frac{2}{\pi\lambda} \exp(-\theta) \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin(n\pi\lambda) \quad [30]$$

Technique verification

The numerical and analytical solutions obtained for the case of reversible linear kinetics provide dimensionless time dependent profiles of dimensionless adsorbed species concentration versus dimensionless radial coordinate of the porous particle. In Figures 1-3, the numerical results obtained by application of the solution technique are compared to those obtained from the analytical solution at different values of the dimensionless parameter, ψ . In the numerical solution, 100 nodal points in the finite difference analog and constant dimensionless time steps of 0,001 were used. The evaluation of the infinite series portion of the analytical solution

was terminated when the n th term of the generated pseudo pattern⁷ was less than 10^{-5} . Excellent agreement exists between the two solutions at all three values of the dimensionless parameter, ψ . Thus, it is concluded that the solution technique provides a valid means of model development which should be applicable for a wide range of reaction rate expressions in combined diffusion and adsorption processes.

Additional remarks

A model framework, which should be applicable to a wide range of adsorption reaction rates, has been described and verified as a viable technique for processes in which the migrating species can both adsorb and accumulate by comparison with an analytical solution for the case of a reversible linear adsorption reaction rate. As the model framework is still under development, no attempt has yet been

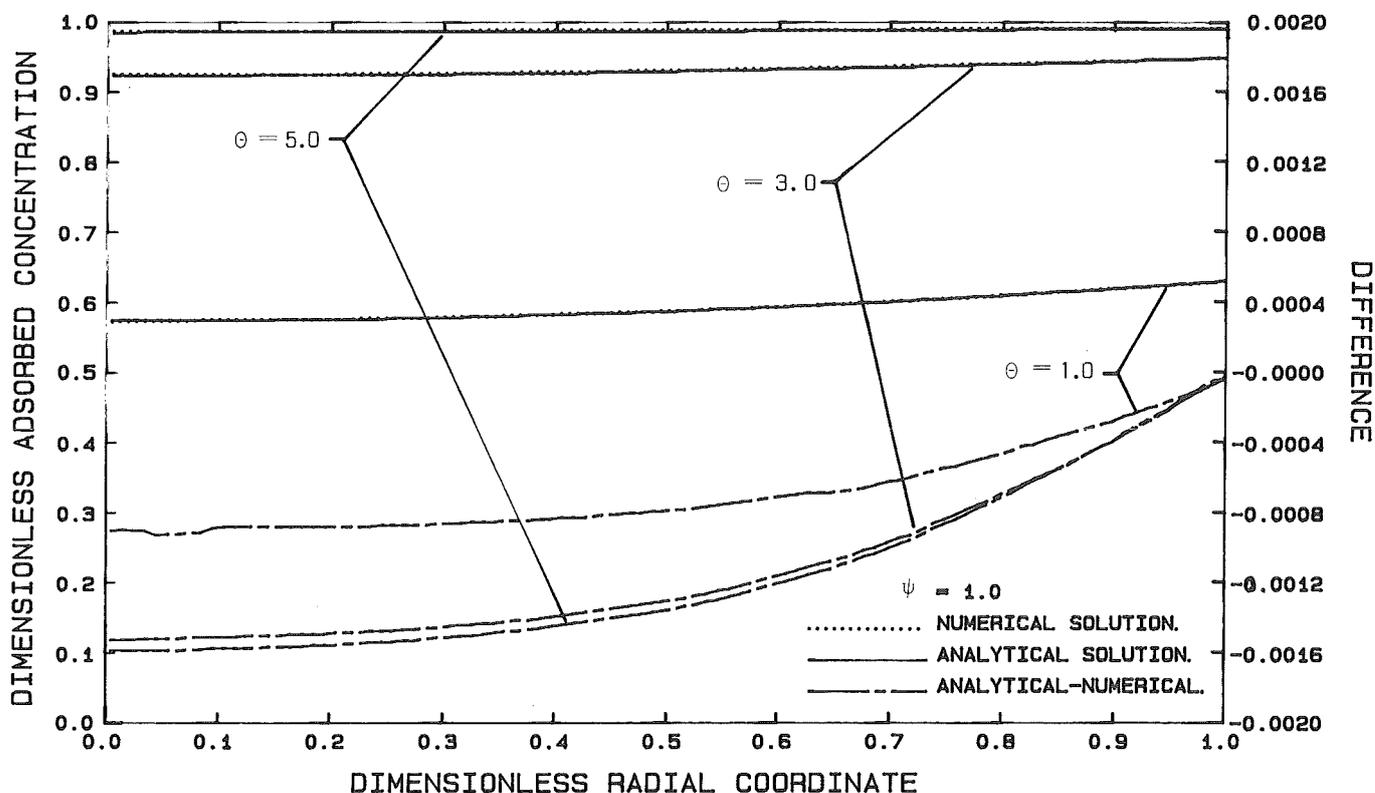


FIGURE 1. Dimensionless adsorbed species profiles for reversible linear kinetics. $\psi = 1.0$; comparison of numerical and analytical solutions

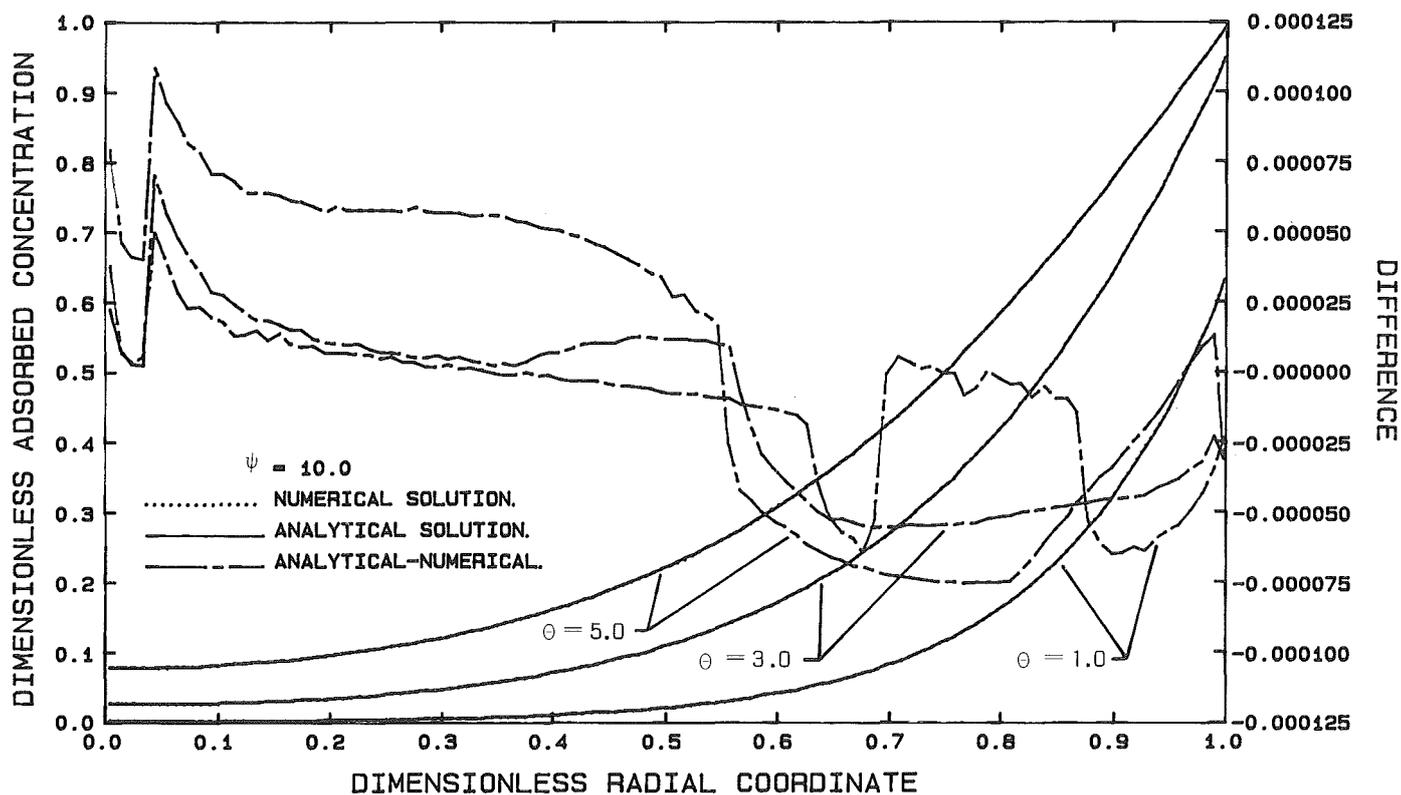


FIGURE 2. Dimensionless adsorbed species profiles for reversible linear kinetics. $\psi = 10.0$; comparison of numerical and analytical solutions

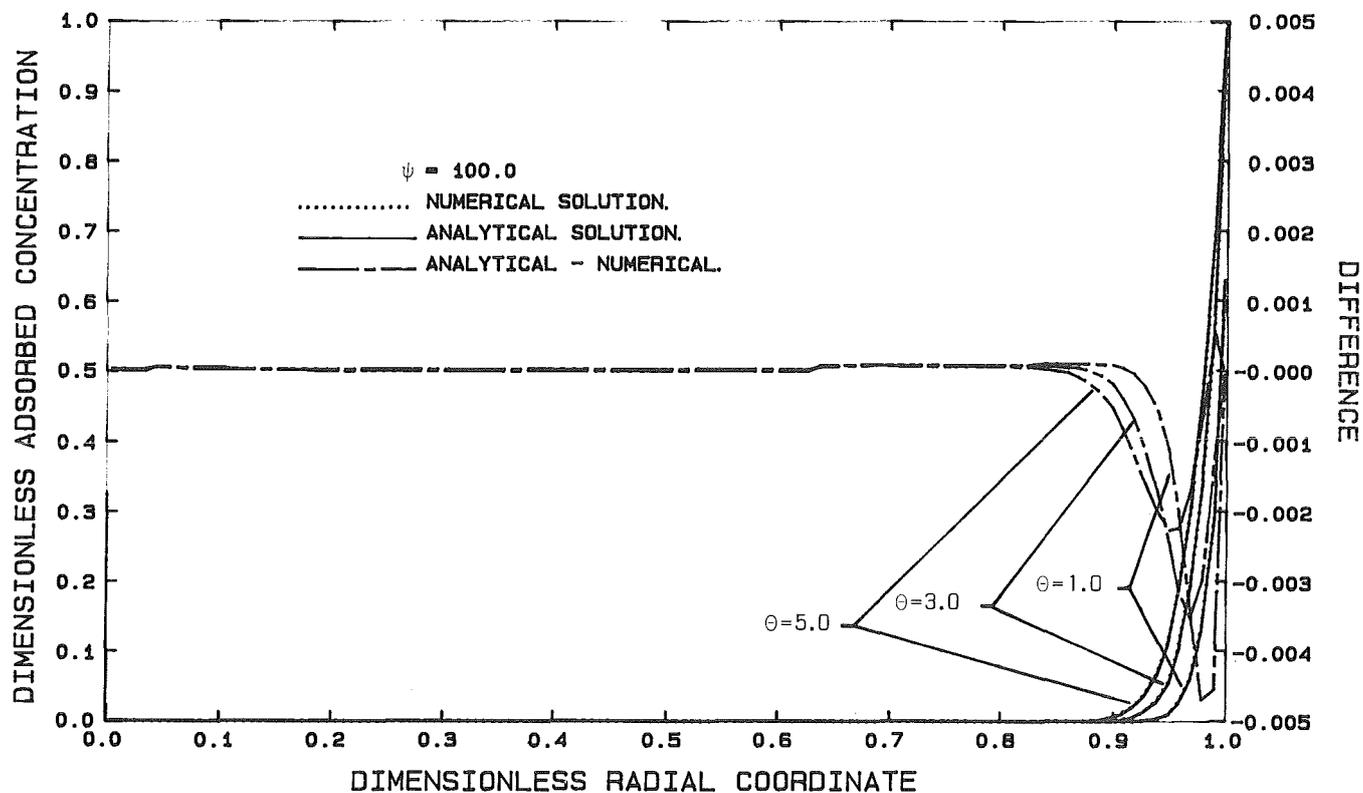


FIGURE 3. Dimensionless adsorbed species profiles for reversible linear kinetics. $\psi = 100.0$; comparison of numerical and analytical solutions

made to compare model results obtained by the technique with published experimental data on combined diffusion and adsorption processes. Improvements in the framework can be obtained in several ways:

- (a) Inclusion of external mass transfer effects.
- (b) Implementation of an improved numerical procedure (i.e. variable size of node spacing and dimensionless time steps).
- (c) Expansion to other reaction mechanisms.

Notation

- C = migrating species concentration in the pore fluid, $g_{ms} cm_f^{-3}$; C_b = migrating species concentration in the bulk fluid
- D_p = effective intraparticle diffusivity (based on void and solid area of the particle), $cm_{f+s}^2 s^{-1}$
- F = function of time defined by Eq.[13]
- k_a = adsorption rate constant, s^{-1}
- k_d = desorption rate constant, s^{-1}
- r = radial distance from the center of the porous particle, cm_{f+s}
- R = radius of the porous particle, cm_{f+s}
- s = transform variable
- S = concentration of adsorbed species, $g_{as} g_s^{-1}$
- t = time, s

Greek letters

- α = dimensionless migrating species concentration of pore fluid, defined by Eq.[15]
- $\bar{\alpha}$ = Laplace transform of $\alpha(\lambda, \theta)$

- β = dimensionless concentration of adsorbed species, defined by Eq.[16]
- $\bar{\beta}$ = Laplace transform of $\beta(\lambda, \theta)$
- ϵ_p = internal porosity of the porous particle, $cm_f^3 cm_{f+s}^{-3}$
- θ = dimensionless time, defined by Eq.[17]
- λ = dimensionless radial coordinate, defined by Eq.[14]
- ρ = apparent density of the porous particle, $g_s cm_{f+s}^{-3}$
- ψ = dimensionless parameter, defined by Eq.[18]

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