Adsorption Calculations Using the Film Model Approximation for Intraparticle Mass Transfer

GIORGIO CARTA

Department of Chemical Engineering, University of Virginia, Charlottesville, VA 22903-2442, USA

gc@virginia.edu

Abstract. An approximate rate equation based on a film-model representation of diffusional mass transfer has been developed to describe the kinetics of multicomponent adsorption. The model describes mass transfer as a pseudo-steady state diffusion process through a flat film of thickness equal to one fifth of the particle radius. The flux relationships are integrated across the film yielding analytical expressions for the rate of mass transfer in a multicomponent adsorption system. The usefulness of the film model approximation is tested by carrying out calculations for three different practical adsorption systems: the adsorption of n-pentane and n-heptane mixtures on NaCaA zeolite discussed by Marutovsky and Bülow (1987); the adsorption of air in molecular sieve RS-10 discussed by Farooq et al. (1993); and the separation of air in a kinetically-controlled nitrogen PSA process discussed by Farooq and Ruthven (1990) and Sundaram and Yang (1998). In each case, the film model approximation predicts the expected trends accounting for the coupling of diffusion fluxes in the adsorbed phase.

Keywords: multicomponent adsorption, coupled diffusion, linear driving force approximation, pressure swing adsorption

Introduction

Approximate rate equations are extensively used in fixed-bed adsorption calculations (Ruthven, 1984; Yang, 1987; LeVan et al., 1997). The linear driving force (LDF) approximation is frequently used because of its simplicity. As originally derived by Glueckauf (1955), the LDF approximation expresses the adsorption rate as:

$$\frac{\partial \bar{n}_i}{\partial t} = \frac{15 D_{s,i}^0}{r_p^2} \left(n_i^s - \bar{n}_i \right) \qquad (1)$$

where $\bar{n}_i$ is the average adsorbate concentration in the particle, n_i^s is the adsorbate concentration at the particle surface, $D_{s,i}^0$ is the intraparticle diffusivity, and r_p is the particle radius. Equation (1) can be derived by assuming that the intraparticle concentration profile of the adsorbate is a parabolic function (Liaw et al.,

1979). However, Sircar and Hufton (2000) have recently shown that Eq. (1) is in fact compatible with any monotonic and continuous intraparticle concentration profile within a spherical particle, provided a numerical constant other than 15 is used. For example, when the radial dependence of the intraparticle concentration profile is given by the function $(r)^p$ with $p \geq 2$, the factor 15 in Eq. (1) is replaced by $3(3 + p)$.

In general, however, the shape of the concentration profile is not known a priori and it can change for different conditions. For example, when the diffusivity is concentration-dependent, although a parabolic profile may be a good approximation for adsorption it may not be an adequate description for desorption or vice-versa, since adsorption and desorption profiles are not necessarily mirror images (Ruthven, 1984). Moreover, in a multicomponent adsorption system the adsorbates' fluxes are coupled (Habgood, 1958; Round et al., 1966; Kärger and Bülow, 1975). As a result, the shape of

the isotherm influences the kinetic behavior and, thus, the shape of the intraparticle concentration profiles and different results are obtained at different mixture compositions. Several authors (e.g. Farooq and Ruthven, 1991; Farooq et al., 1993; van den Broeke and Krishna, 1995; Krishna and Wesselingh, 1997) have reported experimental evidence of these effects in microporous adsorbents.

A "film model" approximation has recently been developed by Carta and Cincotti (1998) and Carta and Lewus (2000) as a framework to develop approximate rate laws for cases where the diffusivity is concentration-dependent. The film-model approach is based on the observation that the intraparticle diffusional resistance can be considered equivalent to the resistance offered by a flat film of thickness equal to one fifth of the particle radius. By representing transport through this film as a pseudo-steady-state diffusion process, in certain cases, analytical expressions for the adsorbate flux can be obtained and have been shown to provide a consistent prediction of the effects of concentration-dependent diffusivity on adsorption rates.

The objective of this paper is to determine the ability of the film model approximation to describe practical adsorption systems. Three different cases are considered. The first is the adsorption of n-pentane and n-heptane mixtures on NaCaA zeolite reported by Marutovsky and Bülow (1987), which exhibits a loading overshoot for the more weakly adsorbed and faster diffusing species. We show that the film model approximation provides a thermodynamically consistent way of fitting these experimental results, including the observed overshoot. The second system is O_2-N_2 adsorption in molecular sieve RS-10 reported by Farooq et al. (1993), which was shown to be consistent with a concentration-dependent diffusivity model. We show that the film model approximation provides a prediction of the binary breakthrough curves obtained by these authors in good agreement with detailed calculations based on the full intraparticle diffusion model. Finally, the third system is a nitrogen PSA process described by Farooq and Ruthven (1990) for which Sundaram and Yang (1998) have shown the importance of diffusional flux coupling. For this system we develop both a simple transient PSA model as well as a continuous countercurrent flow (CCF) analog based on the film-model approximation. The results exhibit trends consistent with those observed by Sundaram and Yang using an empirical kinetic model.

Theoretical Development

Particle Diffusion Model

The adsorption model used in this work is based on the following flux equation:

$$J_i = -\frac{D_{s,i}^0}{\Re T} n_i \frac{\partial \mu_i}{\partial r} \tag{2}$$

where $D_{s,i}^0$ is the "limiting" diffusivity (which is related to the adsorbate's mobility in the adsorbed phase), n_i is the adsorbate concentration, and μ_i is the adsorbate's chemical potential. Assuming that the adsorbed species behave ideally in the fluid phase, $\mu_i = \mu_i^0 + \Re T \ln p_i$. Thus, for a system with M components Eq. (2) can be written as:

$$J_i = -D_{s,i}^0 n_i \frac{\partial \ln p_i}{\partial r} = -D_{s,i}^0 \frac{n_i}{p_i} \sum_{j=1}^{M} \left(\frac{\partial p_i}{\partial n_j} \frac{\partial n_j}{\partial r} \right) \tag{3}$$

where the derivatives $\partial p_i / \partial n_j$ are obtained from the isotherm. For a thermodynamically-consistent Langmuirian system where the multicomponent isotherm is given by:

$$p_i = \frac{n_i}{b_i \left(n_m - \sum_{k=1}^{M} n_k \right)} \tag{4}$$

we obtain the expression:

$$J_i = -D_{s,i}^0 \left(\frac{\partial n_i}{\partial r} + \frac{n_i}{n_m - \sum_{k=1}^{M} n_k} \sum_{k=1}^{M} \frac{\partial n_k}{\partial r} \right) \tag{5}$$

The latter can also be written as:

$$J_i = -D_{s,i}^0 \left(\frac{\partial n_i}{\partial r} - n_i \frac{\partial \ln n_I}{\partial r} \right) \tag{6}$$

where $n_I = n_m - \sum_{k=1}^{M} n_k$. For spherical particles, the following conservation equation and boundary conditions describe the adsorption kinetics:

$$\frac{\partial n_i}{\partial t} = -\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 J_i) \tag{7}$$

$$r = 0: \quad \frac{\partial n_i}{\partial r} = 0 \tag{7a}$$

$$r = r_p: \quad n_i = n_i^s \tag{7b}$$

$$t = 0: \quad n_i = n_i^0 \tag{7c}$$

$$\bar{n}_i = \frac{3}{r_p^3} \int_0^{r_p} n_i r^2 \, dr \tag{7d}$$

where n_i^0 is the initial adsorbate concentration. The adsorption rate is given by:

$$\frac{\partial \bar{n}_i}{\partial t} = -\frac{3}{r_p} J_i \Big|_{r=r_p} \quad (8)$$

The external mass transfer resistance is neglected in these equations but this assumption can be relaxed and a more complex model can be used.

Film Model Approximation

The film model approximation for adsorption was developed by Carta and Cincotti (1998) and Carta and Lewus (2000). Thus, only an outline of the development is given here for the special case of the multi-component Langmuir isotherm. In this approximation, transport is represented by pseudo-steady-state diffusion through a hypothetical flat film of thickness equal to one fifth of the particle radius. Because of the pseudo-steady-state assumption, the flux is invariant with r. Thus, taking the derivative of Eq. (6) with respect to r yields:

$$\frac{dJ_i}{dr} = -D_{s,i}^0 \left(\frac{d^2 n_i}{dr^2} - \frac{dn_i}{dr}\frac{d\ln n_I}{dr} - n_i \frac{d^2 \ln n_I}{dr^2} \right) = 0$$
$$\text{for } i = 1, 2 \ldots M \quad (9)$$

Since the term in parenthesis must be zero, summing over all the adsorbates we obtain the differential equation

$$n_I \frac{d^2 n_I}{dr^2} - \left(\frac{dn_I}{dr} \right)^2 = 0 \quad (10)$$

with boundary conditions:

$$r = r_p: \quad n_I = n_I^s = n_m - \sum_{k=1}^M n_k^s \quad (10a)$$

$$r = \left(1 - \frac{1}{5}\right) r_p: \quad n_I = \bar{n}_I = n_m - \sum_{k=1}^M \bar{n}_k \quad (10b)$$

The solution of this equation has the form $\ln n_I = \alpha + \beta r$ where α and β are integration constants. This result

gives:

$$\frac{d\ln n_I}{dr} = \beta = \frac{1}{5r_p} \ln \frac{n_I^s}{\bar{n}_I} \quad (11)$$

The final result is obtained by inserting Eq. (11) in Eq. (6) and integrating across the film with a constant J_i. The adsorption rate is then found from:

$$\frac{\partial \bar{n}_i}{\partial t} = -\frac{3}{r_p} J_i \quad (12)$$

The following rate equation is obtained:

$$\frac{\partial \bar{n}_i}{\partial t} = \frac{15 D_{s,i}^0}{r_p^2}$$
$$\cdot \frac{\dfrac{n_i^s \left(n_m - \sum_{k=1}^M \bar{n}_k \right) - \bar{n}_i \left(n_m - \sum_{k=1}^M n_k^s \right)}{\left(n_m - \sum_{k=1}^M n_k^s \right) - \left(n_m - \sum_{k=1}^M \bar{n}_k \right)}}{\ln \left(\dfrac{n_m - \sum_{k=1}^M n_k^s}{n_m - \sum_{k=1}^M \bar{n}_k} \right)}$$
$$(13)$$

It can be seen that in the limit of low adsorbate loadings, i.e. when n_I^s and $\bar{n}_I$ approach the adsorbent capacity, this equation reduces to the classical LDF approximation, Eq. (1). In other situations, however, Eq. (13) describes the effect of concentration-dependent diffusivity and diffusional coupling in multicomponent adsorption, and can be used with well-established numerical computation schemes. Carta and Lewus (2000) give a more general rate equation based on a spreading pressure gradient driving force for an arbitrary multicomponent isotherm.

Application Examples

Adsorption of n-Pentane and n-Heptane Mixtures on NaCaA Zeolite

The sorption uptake curves for the adsorption of a gaseous mixture of n-pentane and n-heptane on NaCaA zeolite obtained by Marutovsky and Bülow (1987) are shown in Fig. 1. The faster diffusing species, n-pentane, exhibits an overshoot above the equilibrium value. Marutovsky and Bülow and later Sircar (1991) suggested the following empirical model to describe these data with n-pentane $= 1$ and n-heptane $= 2$:

$$\frac{d\bar{n}_1}{dt} = k_{11}\left(n_1^s - \bar{n}_1\right) + k_{12}\left(n_2^s - \bar{n}_2\right) \quad (14a)$$

$$\frac{d\bar{n}_2}{dt} = k_{21}\left(n_1^s - \bar{n}_1\right) + k_{22}\left(n_2^s - \bar{n}_2\right) \quad (14b)$$
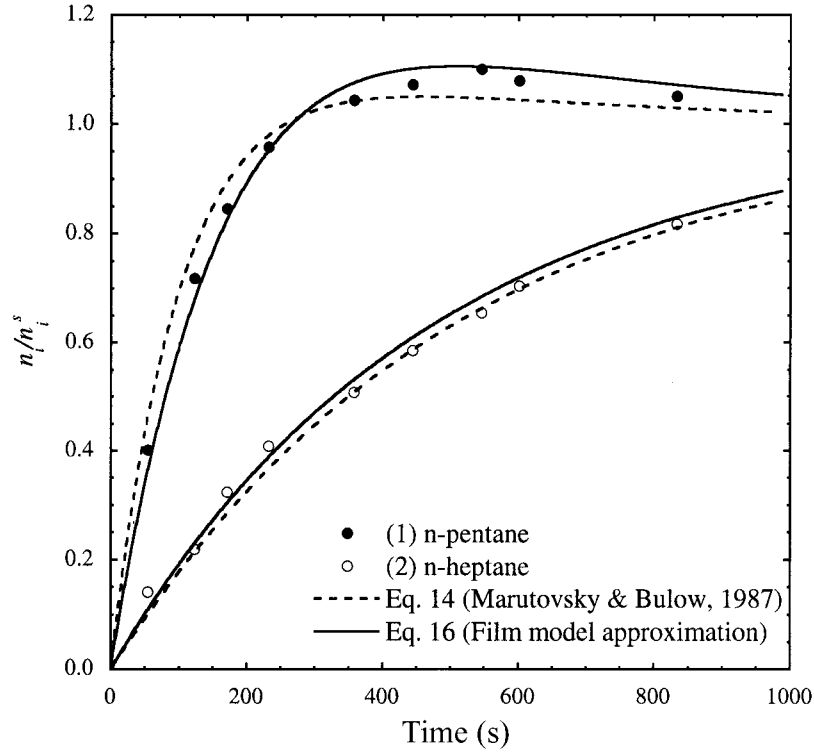
Figure 1. Sorption uptake data for n-pentane and n-heptane mixtures on NaCaA zeolite of Marutovsky and Bülow (1987). $n_1^s = 0.270$ mol/kg, $n_2^s = 0.508$ mol/kg, $n_m = 2.2$ mol/kg, $r_p = 2.4 \times 10^{-4}$ cm.

where the k_{ij} are related to the corresponding elements of the diffusivity matrix by:

$$k_{ij} = \frac{15}{r_p^2} D_{i,j} \qquad (15)$$

The fitted diffusivity values were $D_{11} = 2.73 \times 10^{-11}$, $D_{12} = 0.337 \times 10^{-11}$, $D_{21} = -2.45 \times 10^{-11}$, and $D_{22} = 0.917 \times 10^{-11}$ cm^2/s. Calculated lines are shown in Fig. 1. While these equations can obviously approximate the experimental behavior, there are certain drawbacks. On one hand, negative cross-coefficients were required to fit the binary uptake data. While this has been observed for other systems, the physical significance of negative cross-terms is unclear. On the other hand, Eqs. (14) do not have the appropriate limits when one of the components vanishes. In that case, the concentration dependence of the adsorption rate coefficient vanishes altogether, which is not expected.

The corresponding rate equations based on the film-model approximation for the two component system

are given by:

$$\frac{\partial \bar{n}_1}{\partial t} = \frac{15 D_{s,1}^0}{r_p^2}$$
$$\cdot \frac{n_1^s(n_m - \bar{n}_1 - \bar{n}_2) - \bar{n}_1\left(n_m - n_1^s - n_2^s\right)}{\frac{\left(n_m - n_1^s - n_2^s\right) - (n_m - \bar{n}_1 - \bar{n}_2)}{\ln\left(\frac{n_m - n_1^s - n_2^s}{n_m - \bar{n}_1 - \bar{n}_2}\right)}} \qquad (16a)$$

$$\frac{\partial \bar{n}_2}{\partial t} = \frac{15 D_{s,2}^0}{r_p^2}$$
$$\cdot \frac{n_2^s(n_m - \bar{n}_1 - \bar{n}_2) - \bar{n}_2\left(n_m - n_1^s - n_2^s\right)}{\frac{\left(n_m - n_1^s - n_2^s\right) - (n_m - \bar{n}_1 - \bar{n}_2)}{\ln\left(\frac{n_m - n_1^s - n_2^s}{n_m - \bar{n}_1 - \bar{n}_2}\right)}} \qquad (16b)$$

A comparison of the uptake curves predicted by these equations with the experimental data is shown in Fig. 1. The adsorption capacity was not reported. However, adsorption of hydrocarbon on 5A zeolites has been shown to conform approximately to the Langmuir model (Silva and Rodrigues, 1999). A capacity value
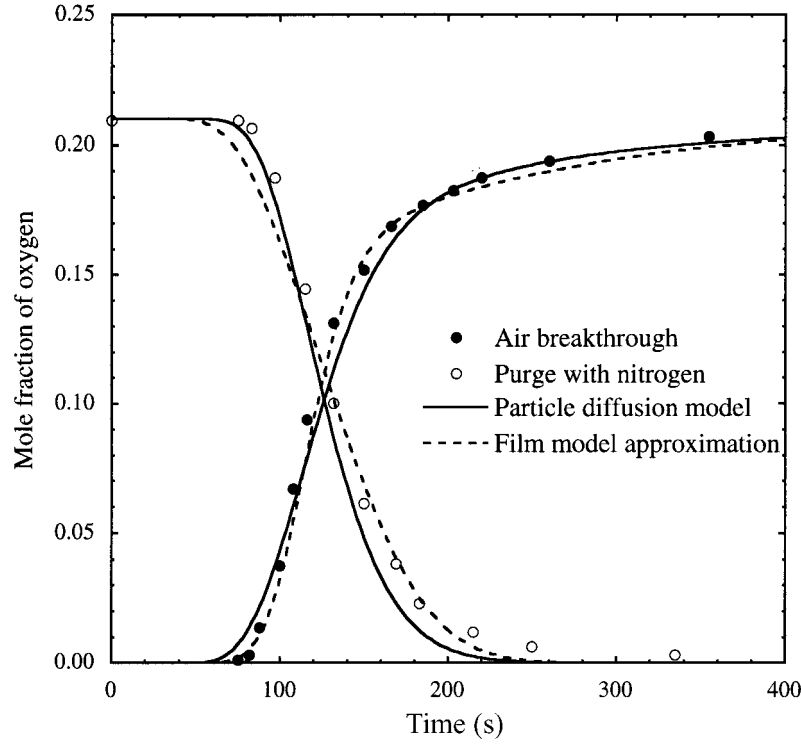
Figure 2. Binary breakthrough data for air in molecular sieve RS10 of Farooq et al. (1993). Calculated lines are based on particle diffusion model (Eqs. (17) and (18)) and film model approximation (Eqs. (16) and (18)). Parameter values are noted in text.

$n_m = 2.2$ mol/kg was assumed. Values of $D^0_{s,1} = 2.6 \times 10^{-11}$ and $D^0_{s,2} = 0.77 \times 10^{-11}$ cm^2/s were obtained by fitting. As seen in Fig. 1, the film model approximation also provides a good fit of the experimental data. In particular, these equations also predict the overshoot of the faster diffusing species, while retaining the thermodynamically correct concentration dependence of the diffusivities in the pure component limits.

O_2-N_2 Binary Breakthrough on Molecular Sieve RS-10

The adsorption of oxygen and nitrogen on zeolite molecular sieve RS-10 has been considered in detail by Farooq et al. (1993). Experimental results for break-through of oxygen by feeding air to a nitrogen-saturated bed and desorption of oxygen by feeding pure nitrogen to an air-saturated bed are shown in Fig. 2. The adsorption isotherms at 298 K are described by the Langmuir isotherm with the following parameter values: $n_m = 2.1 \times 10^{-3}$ mol/cm^3, $b_1 = 1405$ cm^3/mol, $b_2 = 2819$ cm^3/mol, $D^0_{s,1}/r^2_p = 2.75 \times 10^{-2}$ s^{-1}, and

$D^0_{s,2}/r^2_p = 7.5 \times 10^{-4}$ s^{-1} with oxygen $= 1$ and nitrogen $= 2$ (Farooq et al., 1993). As suggested by Farooq et al., the coupling of adsorbate fluxes is important for an accurate prediction of the adsorption behavior of this system. For this two-component system, the particle diffusion model is obtained by combining Eqs. (5) with (7) and (8) yielding:

$$\frac{\partial n_1}{\partial t} = \frac{D^0_{s,1}}{r^2} \frac{\partial}{\partial r}\left[r^2 \left(\frac{n_m - n_2}{n_m - n_1 - n_2} \frac{\partial n_1}{\partial r} \right. \right.$$
$$\left. \left. + \frac{n_1}{n_m - n_1 - n_2} \frac{\partial n_2}{\partial r} \right) \right] \quad (17a)$$

$$\frac{\partial n_2}{\partial t} = \frac{D^0_{s,2}}{r^2} \frac{\partial}{\partial r}\left[r^2 \left(\frac{n_2}{n_m - n_1 - n_2} \frac{\partial n_1}{\partial r} \right. \right.$$
$$\left. \left. + \frac{n_m - n_1}{n_m - n_1 - n_2} \frac{\partial n_2}{\partial r} \right) \right] \quad (17b)$$

$$\frac{\partial \bar{n}_1}{\partial t} = \frac{3D^0_{s,1}}{r_p} \left[\frac{n_m - n^s_2}{n_m - n^s_1 - n^s_2} \frac{\partial n_1}{\partial r}\bigg|_{r=r_p} \right.$$
$$\left. + \frac{n^s_1}{n_m - n^s_1 - n^s_2} \frac{\partial n_2}{\partial r}\bigg|_{r=r_p} \right] \quad (17c)$$

$$\frac{\partial \bar{n}_2}{\partial t} = \frac{3D_{s,2}^0}{r_p} \left[\frac{n_2^s}{n_m - n_1^s - n_2^s} \frac{\partial n_1}{\partial r}\bigg|_{r=r_p} \right.$$
$$\left. + \frac{n_m - n_1^s}{n_m - n_1^s - n_2^s} \frac{\partial n_2}{\partial r}\bigg|_{r=r_p} \right] \quad (17d)$$

These equations are coupled with the following bed conservation equations:

$$u\frac{\partial c_1}{\partial z} + \varepsilon\frac{\partial c_1}{\partial t} + (1-\varepsilon)\left[(1-y_1)\frac{\partial \bar{n}_1}{\partial t} - y_1\frac{\partial \bar{n}_2}{\partial t}\right] = 0$$
$$(18a)$$
$$c\frac{\partial u}{\partial z} + (1-\varepsilon)\left(\frac{\partial \bar{n}_1}{\partial t} + \frac{\partial \bar{n}_2}{\partial t}\right) = 0 \quad (18b)$$

where u is the gas superficial velocity, c is the total gas concentration, and $y_1 = c_1/c$ is the mole fraction of component 1. These equations are equivalent to the model of Farooq et al., except that axial dispersion and the boundary layer resistance are absent. This is reasonable since both of these factors were in fact negligible for the conditions simulated (Farooq et al., 1993).

The film model approximation equations are given by Eq. (16a) and (b). The bed conservation equations are, of course, the same as above. In both cases the bed conservation equations were discretized by backward finite differences. This introduces numerical dispersion that was kept essentially insignificant by using a large number of discretization points. For the particle diffusion model, the particle conservation equations were also discretized by finite differences as discussed by Carta and Cincotti (1998). The resulting system of ordinary differential equations was integrated numerically with Gear's method (subroutine DIVPAG in the IMSL library).

Experimental binary breakthrough curves and predicted profiles are compared in Fig 2. The solid lines correspond to the particle diffusion model. These curves are essentially coincident with those in Fig. 3 of Farooq et al. Conversely, the dashed lines correspond to the film model approximation. It appears that the film model approximation provides a reasonable description of the coupled diffusion process without incurring in the great numerical burden of integrating the particle diffusion equations.

Air Separation by Kinetically Controlled PSA

The third system considered in this work is nitrogen production from air by PSA with carbon molecular sieve considered by Farooq and Ruthven (1990). Air separation with carbon molecular sieve is a kinetically controlled process; thus, intraparticle mass transfer must be taken into account in order to describe the separation performance. Sundaram and Yang (1998) have pointed out the importance of diffusional flux coupling on product purity. The kinetic model used by Sundaram and Yang is based on the following rate equations:

$$\frac{\partial \bar{n}_1}{\partial t} = \frac{15D_{s,1}^0}{r_p^2} \left[\frac{n_m - n_2^s}{n_m - n_1^s - n_2^s}\left(n_1^s - \bar{n}_1\right) \right.$$
$$\left. + \frac{n_1^s}{n_m - n_1^s - n_2^s}\left(n_2^s - \bar{n}_2\right) \right] \quad (19a)$$
$$\frac{\partial \bar{n}_2}{\partial t} = \frac{15D_{s,2}^0}{r_p^2} \left[\frac{n_2^s}{n_m - n_1^s - n_2^s}\left(n_1^s - \bar{n}_1\right) \right.$$
$$\left. + \frac{n_m - n_1^s}{n_m - n_1^s - n_2^s}\left(n_2^s - \bar{n}_2\right) \right] \quad (19b)$$

The structure of these equations is analogous to that of Eqs. 17(a)–(d), with concentration-dependent terms multiplying linear-driving force terms. However, a drawback is that the concentration-dependent terms are only functions of the composition at the particle surface, n_1^s and n_2^s, and not functions of the composition in the bulk of the particle, $\bar{n}_1$ and $\bar{n}_2$. As shown by Carta and Lewus (2000) this leads to inconsistencies in certain cases. Conversely, the film model rate equations, Eqs. (16a) and (b), contain concentration dependence on both the surface and bulk compositions as might be expected.

PSA purity calculations were done with two different models for a simple four-column Skarstrom cycle. The first is a transient model and the second is a continuous countercurrent flow analog. In both cases, we consider an isothermal, plug flow system and neglect pressure drop in the beds. We also assume that the pressure remain constant during the high-pressure feed and the low-pressure purge step. Thus, the conservation equations for the transient model in these two steps are the same as Eqs. (18a) and (b). For the pressurization and blowdown steps we make the same assumptions as Raghavan and Ruthven (1985). Namely, for both of these steps we assume that the solid phase concentrations remain frozen; for blowdown we assume that at the end of blowdown the gas phase concentrations are the same as at the end of the preceding high-pressure steps multiplied times the pressure ratio, P_L/P_H; for pressurization we assume that at the end of pressurization the bed is filled with the feed gas up to a fractional
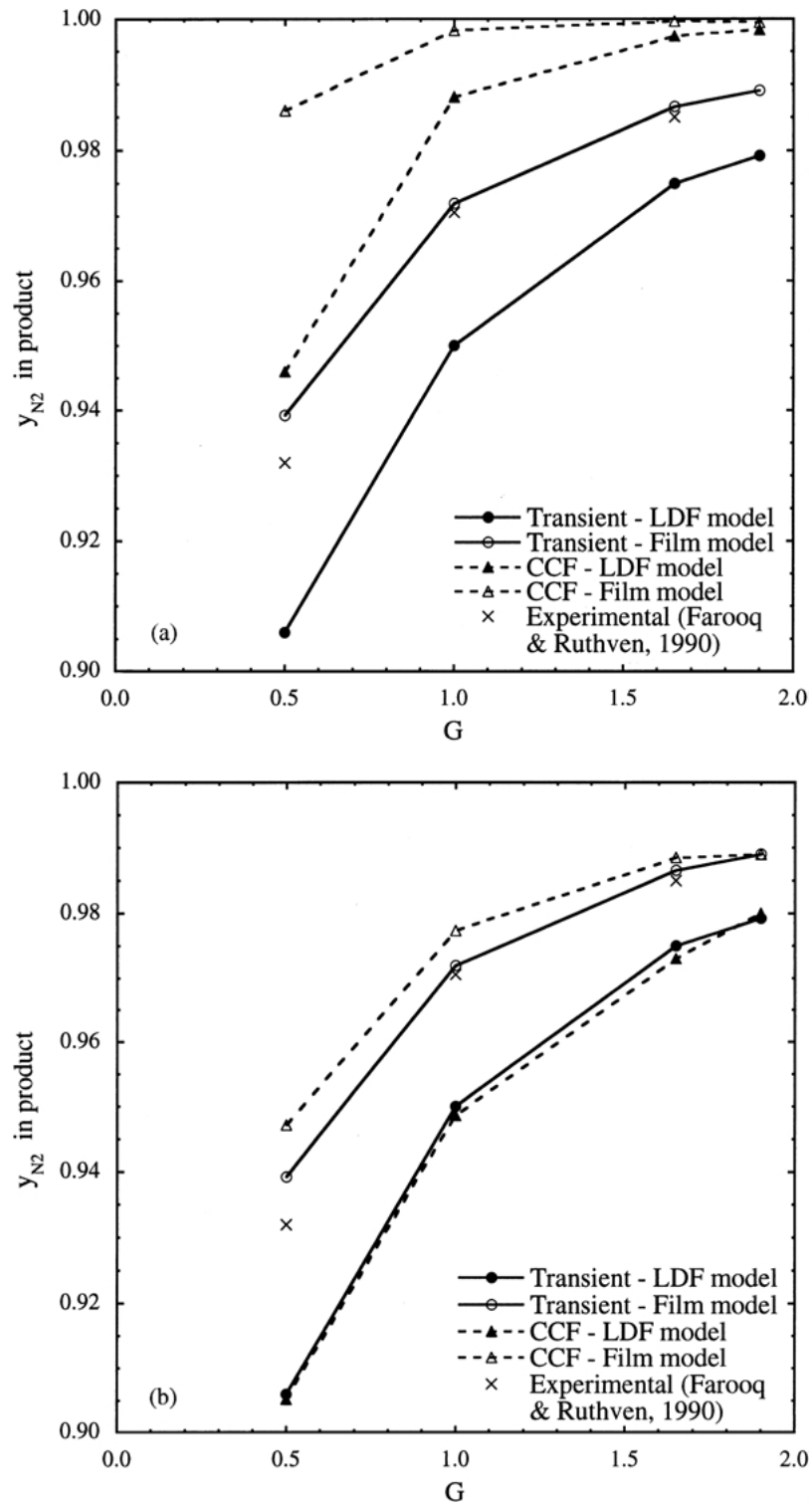
Figure 3. Predicted effect of purge-to-feed velocity ratio on product purity based on transient and CCF models. Filled symbols: LDF model with no flux coupling, Open symbols: film model approximation with coupled diffusion fluxes. (a): CCF predictions with actual $D_{s,i}^0/r_p^2$-values. (b): CCF predictions with $0.55 D_{s,i}^0/r_p^2$-values.
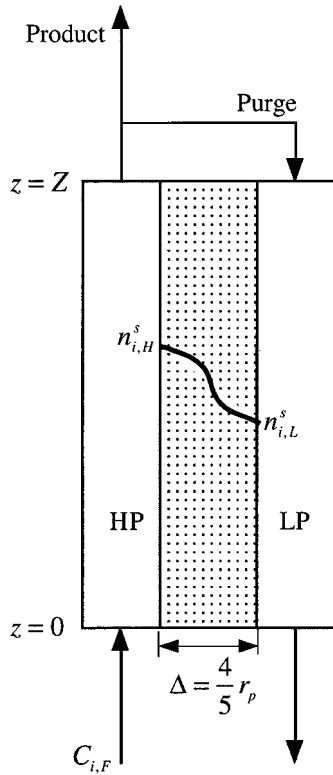
Figure 4. Continuous countercurrent flow (CCF) analog of Skarstrom PSA cycle.

distance P_L/P_H from the closed end of the bed and with the average concentrations that existed at the end of the preceding low-pressure purge step for the remaining fraction of the bed length. The transient model equations were discretized as previously described. The numerical solution was cycled over 40 cycles to ensure convergence to a cyclic steady state.

The conservation equations for the continuous countercurrent flow model can be derived with reference to Fig. 4 (Suzuki, 1985; Farooq and Ruthven, 1990). Mass transfer occurs from the high-pressure side to the low-pressure side through an adsorbent film of thickness $\Delta = 4r_p/5$. Steady-state mass balances yield:

$$\frac{d(u_H C_{1,H})}{dz} = \frac{d(u_L C_{1,L})}{dz} = -\frac{3(1-\varepsilon)}{r_p} J_1 \quad (20a)$$

$$C_H \frac{du_H}{dz} = C_L \frac{du_L}{dz} = -\frac{3(1-\varepsilon)}{r_p}(J_1 + J_2) \tag{20b}$$

where J_1 and J_2 are the mass transfer fluxes and boundary conditions are:

$$z = 0: \quad C_{1,H} = C_{1,F}, u_H = u_{H,F} \quad (20c)$$

$$z = Z: \quad C_{1,L} = C_{1,H}, u_L = Gu_{H,F} \quad (20d)$$

where G is the purge-to-feed velocity ratio. When the diffusion fluxes are uncoupled and the diffusivity is constant, the concentration profiles are linear across the film and the fluxes are given by:

$$J_1 = \frac{5D_{s,1}^0}{4r_p}\left(n_{1,H}^s - n_{1,L}^s\right) \tag{21a}$$

$$J_2 = \frac{5D_{s,2}^0}{4r_p}\left(n_{2,H}^s - n_{2,L}^s\right) \tag{21b}$$

In this case, the equations are coincident with those of Farooq and Ruthven (1990). Conversely, when the diffusion fluxes are coupled, J_1 and J_2 are obtained by integrating Eq. (10) across the film, combining the result with Eq. (6), and integrating the result again across the film with constant J_i's. The final expressions for the fluxes are:

$$J_1 = \frac{5D_{s,1}^0}{4r_p}$$
$$\cdot \frac{n_{1,H}^s\left(n_m - n_{1,L}^s - n_{2,L}^s\right) - n_{1,L}^s\left(n_m - n_{1,H}^s - n_{2,H}^s\right)}{\dfrac{\left(n_m - n_{1,H}^s - n_{2,H}^s\right) - \left(n_m - n_{1,L}^s - n_{2,L}^s\right)}{\ln\left(\frac{n_m - n_{1,H}^s - n_{2,H}^s}{n_m - n_{1,L}^s - n_{2,L}^s}\right)}}$$

$$(22a)$$

$$J_2 = \frac{5D_{s,2}^0}{4r_p}$$
$$\cdot \frac{n_{2,H}^s\left(n_m - n_{1,L}^s - n_{2,L}^s\right) - n_{2,L}^s\left(n_m - n_{1,H}^s - n_{2,H}^s\right)}{\dfrac{\left(n_m - n_{1,H}^s - n_{2,H}^s\right) - \left(n_m - n_{1,L}^s - n_{2,L}^s\right)}{\ln\left(\frac{n_m - n_{1,H}^s - n_{2,H}^s}{n_m - n_{1,L}^s - n_{2,L}^s}\right)}}$$

$$(22b)$$

The continuous countercurrent flow model equations were solved numerically as an initial value problem using Runge-Kutta, iterating to match the boundary condition at $z = Z$. The parameter values are as follows: $n_m = 2.64 \times 10^{-3}$ mol/cm^3, $b_1 = 3504$ cm^3/mol, $b_2 = 3370$ cm^3/mol, $\varepsilon = 0.4$, $\varepsilon Z/u_H = 25$ S, $D_{s,1}^0/r_p^2 = 3.73 \times 10^{-3}$ s^{-1}, $D_{s,2}^0/r_p^2 = 1.15 \times 10^{-4}$ s^{-1}, $P_H = 3$ atm, $P_L = 1$ atm, $T = 298$ K (Farooq and Ruthven, 1990). The duration of the adsorption/desorption step was 60 s.

Predicted nitrogen product purities are shown in Fig. 3(a) as a function of the purge-to-feed velocity
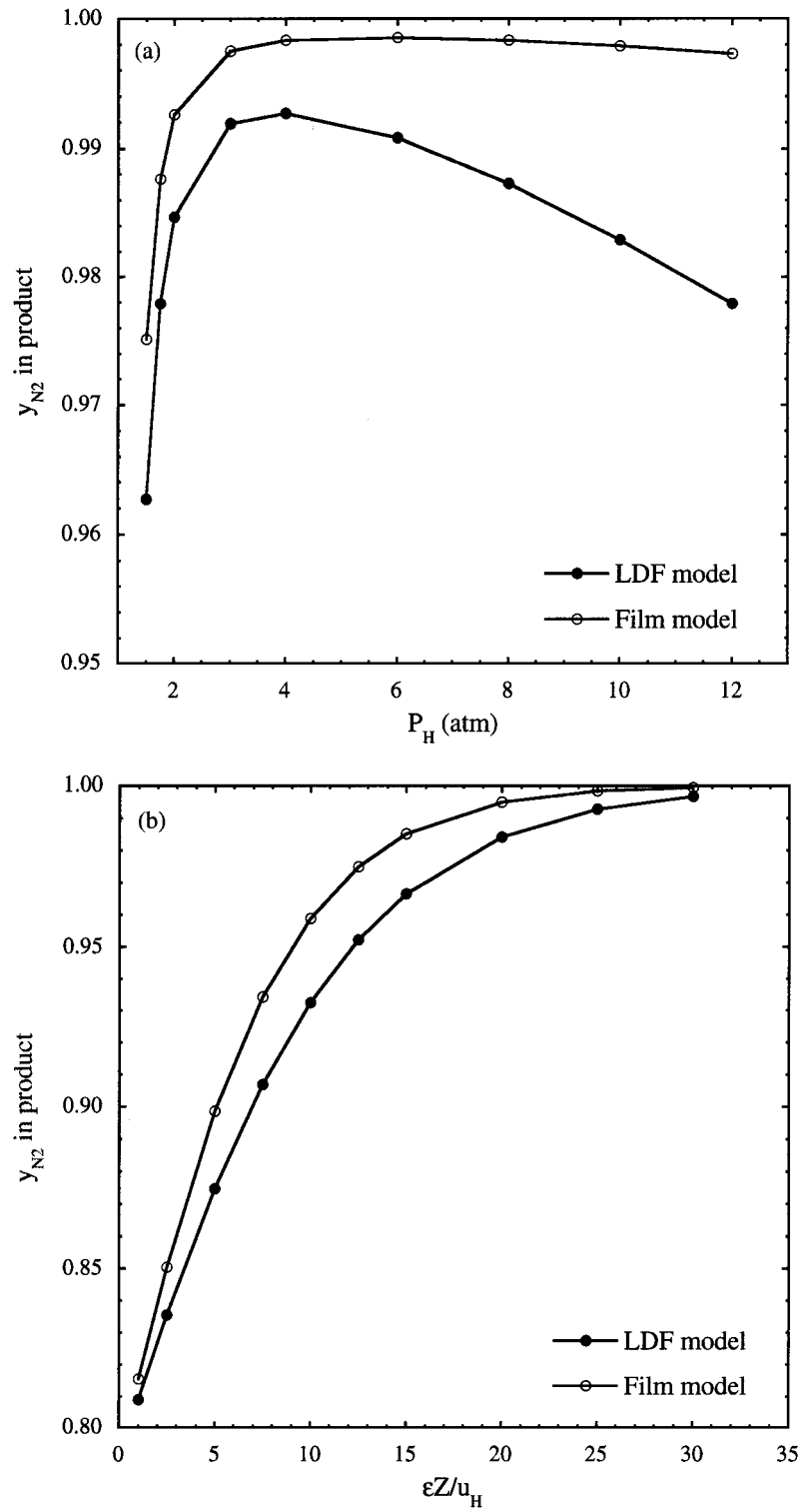
Figure 5. Effect of feed pressure (a) and length-to-velocity ratio (b) on product purity based on LDF model with no flux coupling and film model approximation for coupled diffusion fluxes using the CCF analog. Total reflux conditions. Length-to-velocity ratio = 25 in Fig. 5(a). Feed pressure = 4 atm in Fig. 5(b). Other parameters as noted in text.

ratio, G, for the transient model and the continuous countercurrent flow analog based on constant diffusivities rate equations (Eqs. (21)) and the film model rate equations (Eqs. (22)). As seen in this figure the trends predicted by the transient and the CCF model are similar, although the purity predicted by the CCF model is greater. This result is analogous to the results obtained by Farooq and Ruthven (1990) for the constant diffusivity case. We suspect that the quantitative discrepancy is due to the fact that in this separation the accumulation term in the gas phase material balance is significant, while Suzuki (1985) neglected it in the original derivation of the CCF analogy. However, we found that an almost perfect quantitative agreement between the transient model and the CCF analog could be obtained by using diffusivities that are 55% of the actual values for the CCF calculations. These results are shown in Fig. 3(b). With regards to the effects of the coupling of diffusion fluxes, the trends are consistent with the results of Farooq et al. (1993) based on a detailed particle diffusion model. The film model approximation captures these effects allowing for a greater purity than is predicted by the constant diffusivity rate equations.

Experimental results reported by Farooq and Ruthven (1990) for this system are also shown in Figs. 3(a) and (b). As seen in these figures, the transient LDF model neglecting flux coupling underestimates the nitrogen purity. However, the nitrogen purity results predicted by the transient film model approximation are in good agreement with the experimental ones. A good agreement is also observed with the CCF film model approximation when diffusivities that are 55% of the actual values are used in the calculations.

Figure 5 shows further results comparing the film model predictions with those of the constant diffusivity rate equations based on the CCF analog under total reflux condition. The results are consistent with the trends observed by Sundaram and Yang (1998). Accounting for coupling of diffusion fluxes provides a greater purity as a function of feed pressure and as a function of the length-to-velocity ratio as compared to the constant diffusivity model.

Conclusions

A film-model approximation has been developed to simplify numerical calculations of multicomponent adsorption. The new rate expression, based on an equivalent film resistance model, provides a quantitative prediction of the effects of concentration-dependent diffusivity and adsorbate flux coupling, and gives results of accuracy comparable with that obtained when using the classical LDF approximation for constant diffusivity systems. The new rate equation was used to model three practical adsorption systems. In each case, the simplified rate expression could predict the trends observed with more detailed models. It should be noted, however, that additional effects may have to be considered for the case of cyclic adsorption-desorption operations when the cycle time is very short. In this case the LDF approximation, even with constant diffusivity, deviates from the exact solution for a single particle unless the LDF coefficient is assumed to be a function of cycle time (Nakao and Suzuki, 1983). This could also affect the film model predictions. Finally, it should be pointed out that the film model approximation can be extended to other isotherm types (e.g. when the saturation capacities are different for different components) within the framework of the ideal adsorbed solution theory as discussed by Carta and Lewus (2000).

Nomenclature

b_i Langmuir isotherm parameter (1/Pa or m³/mol)

c_i Gas phase concentration of adsorbate species (mol/m³)

c Total gas phase concentration (mol/m³)

$D_{s,i}^0$ "Corrected" or "limiting" adsorbate diffusivity (m²/s)

G Purge-to-feed gas velocity ratio

J_i Adsorbate flux (mol/m² s)

k LDF rate coefficient ($=15D/r_p^2$) (1/s)

n_i Adsorbate concentration in adsorbed phase (mol/m³)

n_I Difference between adsorption capacity and total moles adsorbed (mol/m³)

n_m Adsorbent capacity (mol/m³)

$\bar{n}_i$ Average adsorbate concentration in adsorbed phase (mol/m³)

p_i Partial pressure of i (Pa)

P Total pressure (Pa)

r Particle radial coordinate (m)

r_p Particle radius (m)

$\mathfrak{R}$ Ideal gas constant (J/mol K)

t Time (s)

T Temperature (K)

u Gas superficial velocity (m/s)

y_i Mole fraction of component i

z Bed axial coordinate (m)

Z Bed length (m)

Greek Letters

ε Bed void fraction
μ_i Chemical potential (J/mol)

Superscripts

0   Initial value
s Value at particle surface

Subscripts

F Feed value
H High-pressure value
L Low-pressure value

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