



Film Model Approximation for Multicomponent Adsorption

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Abstract. An approximate rate equation based on a film-model representation of diffusional mass transfer is 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. Starting with an irreversible thermodynamics description of multicomponent diffusion, the flux relationships are integrated across the film yielding analytical expressions for the rate of mass transfer in a multicomponent adsorption system, when adsorption equilibria are described by the extended Langmuir isotherm. The new approximate rate equation can be conveniently used in the numerical simulation of adsorption systems with concentration-dependent micropore or surface diffusivity, and describes the effects of diffusional flux coupling. Results of accuracy comparable with that obtained when using the classical linear-driving-force approximation for systems with constant diffusivities are obtained with this new rate equation for both batch and fixed-bed adsorption calculations. A generalization of the approach based on the Gibbs adsorption isotherm describes mass transfer rates in terms of the spreading-pressure gradient and provides an extension to other multicomponent isotherm forms.

Keywords: multicomponent adsorption, diffusion, Maxwell-Stefan model, linear driving force approximation, Langmuir isotherm

Introduction

Approximate rate equations are extensively used to reduce the numerical complexities encountered in fixed-bed adsorption calculations (Ruthven, 1984; Yang, 1987; LeVan et al., 1997). The most widely used of these simplified rate laws is the so-called linear driving force (LDF) approximation, which was originally obtained by Glueckauf (1955) for solid (or surface) diffusion with a *constant* diffusivity. Accordingly, for an adsorbate with diffusivity $D_{s,i}^0$, this rate law can be written as:

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

where \bar{n}_i is the average adsorbate concentration in the particle, n_i^s is the adsorbate concentration at the particle surface, and r_p is the particle radius.

In many adsorption systems, however, the micropore- or surface-diffusion flux is more appropriately expressed in terms of the adsorbate's chemical potential gradient. As discussed by several authors (Garg and Ruthven, 1972; Kapoor and Yang, 1991; Chen et al., 1994) this leads to a concentration-dependent diffusivity except for the case where the equilibrium isotherm is linear. A further consequence of this effect is that in a multicomponent adsorption system the adsorbates' fluxes are coupled (Habgood, 1958; Rounds et al., 1966; Kärger and Bülow, 1975). Thus, the diffusional flux of one adsorbate depends upon the concentration gradient of all of the adsorbates. Following the irreversible thermodynamics formulation, this coupling can in general be described through the multicomponent adsorption isotherm (Krishna and Wesselingh, 1997). As a result, the kinetic behavior is influenced by the shape of the isotherm and

different kinetic behaviors 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.

Recently, Carta and Cincotti (1998) and Carta et al. (1999), have introduced a “film model” approach 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 in both batch and fixed-bed adsorption and ion-exchange systems.

The objective of this paper is to extend the film-model approximation to the case of multicomponent adsorption, when the adsorbate flux is expressed in terms of the chemical potential gradient. Analytical expressions are obtained for the case of Langmuirian adsorption equilibrium behavior. These expressions permit the replacement of the partial differential equations describing intraparticle diffusion with explicit rate equations. The results obtained through the film-model formulation quantitatively predict the effects of adsorbate flux coupling. When compared to results obtained by numerically integrating the full intraparticle diffusion model, the film-model approximation is shown to yield accuracy comparable to that obtained when using the classical LDF approximation for systems with constant diffusivity. A formal generalization of the treatment to permit extension to other multicomponent isotherms is obtained using the Gibbs adsorption isotherm.

Theoretical Development

Rigorous Model

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

$$J_i = -\rho_p \frac{D_{s,i}^0}{RT} n_i \frac{\partial \mu_i}{\partial r} \quad (2)$$

where $D_{s,i}^0$ is the so-called “corrected” or “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, $\mu_i = \mu_i^0 + RT \ln p_i$. Thus, for a system with M components Eq. (2) can be written as:

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

where the derivatives $\partial p_i / \partial n_j$ are obtained from the isotherm. An equivalent expression is obtained following the Maxwell-Stefan approach if all non-diagonal terms in the diffusivity matrix are assumed to be zero, a case corresponding to the so-called “single file” diffusion mechanism (van den Broeke and Krishna, 1995; Krishna and Wesselingh, 1997).

For a Langmuirian system where the multicomponent isotherm is given by:

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

we obtain the expression:

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

In the infinite dilution case, the second term in parenthesis approaches zero, and the flux expression reduces to that for the constant-diffusivity case. In dimensionless form this equation can be written as follows:

$$J_i^* = -\frac{1}{\alpha_i} \left(\frac{\partial y_i}{\partial \rho} - y_i \frac{\partial \ln y_I}{\partial \rho} \right) \quad (6)$$

where $J_i^* = r_p J_i / n_m \rho_p D_{s,\text{ref}}^0$ is a dimensionless flux, $\alpha_i = D_{s,\text{ref}}^0 / D_{s,i}^0$ is the ratio of corrected diffusivities, $y_i = n_i / n_m$ is the dimensionless adsorbed phase concentration, $\rho = r / r_p$ is the dimensionless radius, and $y_I = 1 - \sum_{k=1}^M y_k$ is the fraction of the saturation or monolayer capacity which is free of adsorbates. Finally, $D_{s,\text{ref}}^0$ is the corrected diffusivity of a reference adsorbate. This flux equation may be used in conjunction with the following dimensionless conservation equations to describe adsorption in a fixed bed.

For the particles:

$$\frac{\partial y_i}{\partial \tau} = -\frac{1}{\rho^2} \frac{\partial}{\partial \rho} (\rho^2 J_i^*) \quad (7)$$

$$\rho = 0: \quad \frac{\partial y_i}{\partial \rho} = 0 \quad (7a)$$

$$\rho = 1: \quad y_i = y_i^s \quad (7b)$$

$$\tau = 0: \quad y_i = y_i^0 \quad (7c)$$

$$\bar{y}_i = 3 \int_0^1 y_i \rho^2 d\rho \quad (7d)$$

where $\tau = t D_{s,\text{ref}}^0 / r_p^2$ is the dimensionless time and y_i^s and y_i^0 are the surface and initial adsorbate concentrations.

For the fixed-bed:

$$\frac{\partial \bar{y}_i}{\partial \tau'} + \frac{\partial x_i}{\partial \xi} = 0 \quad (8)$$

$$\frac{\partial \bar{y}_i}{\partial \tau'} = \frac{\partial \bar{y}_i}{\partial \tau} = -3 J_i^* \big|_{\rho=1} \quad (8a)$$

$$\xi = 0: \quad x_i = x_i^F \quad (8b)$$

$$\tau' = 0: \quad \bar{y}_i = y_i^0 \quad (8c)$$

where $x_i = c_i / c_{\text{ref}}$ is the dimensionless fluid phase concentration, $\xi = z \Lambda D_{s,\text{ref}}^0 / v r_p^2$ is the dimensionless bed length, $\Lambda = \rho_b n_m / \varepsilon c_{\text{ref}}$ is a partition ratio, and $\tau' = \tau - \xi / \Lambda$. External mass transfer resistance and axial dispersion are neglected in these equations, and the fluid velocity is assumed to be constant. Obviously, these assumptions can be relaxed and a more complex model can be used. However, this is beyond the scope of this paper. Dimensional forms of these equations can be found in a variety of standard texts (Ruthven, 1984; Yang, 1987; LeVan et al., 1997). Numerical calculations were carried out with a finite difference scheme as discussed by Carta and Cincotti (1998) and Carta et al. (1999).

Film Model Approximation

To develop this approximation, the intraparticle diffusional resistance is represented by pseudo-steady-state diffusion through a hypothetical flat film of thickness equal to one fifth of the particle radius (Carta and Cincotti, 1998). With these assumptions, Eq. (6) yields

the following result for each of the M adsorbates:

$$\frac{d J_i^*}{d \rho} = -\frac{1}{\alpha_i} \left(\frac{d^2 y_i}{d \rho^2} - \frac{d y_i}{d \rho} \frac{d \ln y_i}{d \rho} - y_i \frac{d^2 \ln y_i}{d \rho^2} \right) = 0 \quad (9)$$

Since for Eq. (9) to be satisfied the term in parenthesis must be zero, summing over all the adsorbates we obtain the differential equation

$$y_I \frac{d^2 y_I}{d \rho^2} - \left(\frac{d y_I}{d \rho} \right)^2 = 0 \quad (10)$$

with boundary conditions:

$$\rho = 1: \quad y_I = y_I^s = 1 - \sum_{j=1}^M y_j^s \quad (10a)$$

$$\rho = 1 - \frac{1}{5}: \quad y_I = \bar{y}_I = 1 - \sum_{j=1}^M \bar{y}_j \quad (10b)$$

Equation (10) has solution of the form $y_I = \gamma \exp(\beta \rho)$ where the integration constants γ and β are determined from Eqs. (10a) and (10b). Inserting this result in Eq. (6) provides the following expression for the dimensionless adsorbate flux:

$$J_i^* = -\frac{5}{\alpha_i} \cdot \frac{y_i^s \bar{y}_I - \bar{y}_i y_I^s}{(y_I^s - \bar{y}_I) / \ln(y_I^s / \bar{y}_I)} \quad (11)$$

Finally, combining this result with the overall mass balance for a spherical particle (Eq. (8a)) yields the film model approximation:

$$\frac{\partial \bar{y}_i}{\partial \tau} = \frac{15}{\alpha_i} \cdot \frac{y_i^s \bar{y}_I - \bar{y}_i y_I^s}{(y_I^s - \bar{y}_I) / \ln(y_I^s / \bar{y}_I)} \quad (12)$$

It can be seen that in the limit of low adsorbate loadings, when y_I^s and \bar{y}_I approach unity, this equation reduces to the classical LDF approximation $\partial \bar{y}_i / \partial \tau = (15 / \alpha_i) (y_i^s - \bar{y}_i)$. In other situations, however, Eq. (12) describes the effect of concentration-dependent diffusivity and diffusional coupling in multicomponent adsorption, and can be used with well-established numerical computation schemes.

Application Examples

To ascertain the usefulness of the film-model approximation for multicomponent adsorption, numerical

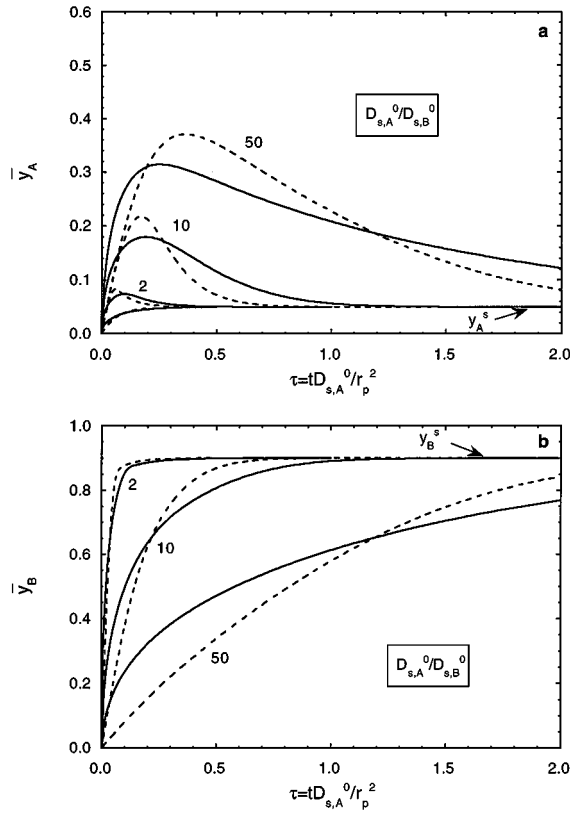


Figure 1. Comparison of numerical solution of rigorous model (solid lines) and film-model approximation (dashed lines) for binary adsorption on a single particle with constant surface concentrations and different values of the diffusivity ratio. The solid lines coincide with the results of Round et al. (1966). $y_A^s = 0.05$, $y_B^s = 0.9$.

calculations were carried out for a binary adsorption system, with adsorbates A and B, for batch uptake with a constant surface concentration, and for an adsorption bed with constant initial and feed concentrations.

Figure 1 shows a comparison of the numerical solution of the rigorous model for batch uptake (Eqs. (6) and (7)) with the corresponding film-model approximation (Eq. (12)) for a binary system with $y_A^s = 0.05$ and $y_B^s = 0.9$ using different values of the diffusivity ratio $D_{s,A}^0/D_{s,B}^0$. The system simulated is the same as that considered by Round et al. (1966) and our numerical results agree with the ones obtained by those authors. As shown in Fig. 1(a), the adsorbent loading with the faster diffusing species, A, shows a maximum at intermediate times before declining to the final equilibrium value. The maximum increases in magnitude as the diffusivity ratio is increased since more A is adsorbed in the early stages of the process. The bottom curve

in this figure corresponds to the case where A alone is adsorbed, where, of course, there is no maximum. The rate of uptake of B, as shown in Fig. 1(b), is influenced by the simultaneous uptake of A and becomes slower as the diffusivity ratio is increased. This occurs because of the coupling of diffusion fluxes that slows down the adsorption of B as a result of the counter-diffusion of A which follows the A-loading overshoot above the equilibrium value. As seen in Fig. 1, the film-model approximation is in qualitative agreement with the shape of the uptake curves for each value of the diffusivity ratio. In fact, for each value of the diffusivity ratio, the agreement between the film-model approximation and the rigorous model is comparable with that obtained when using the classical LDF approximation for a constant-diffusivity system. More importantly, however, the film-model approximation provides a quantitative prediction of the effects of a concentration-dependent diffusivity and of diffusional coupling in multicomponent adsorption.

Figure 2 shows numerical results comparing two-component breakthrough curves based on the rigorous model (Eq. (6)), the LDF approximation with constant diffusivities (Eq. (1) with diffusivities assumed equal to the corrected diffusivity for each adsorbate species), and the film-model approximation developed in this work (Eq. (12)). Conditions chosen for these sample calculations are: $D_{s,A}^0/D_{s,B}^0 = 10$, $b_A = 2$, $b_B = 1$, $c_A^F = 0.5$, $c_B^F = 18$, $\Lambda = 20$, and $\xi = 1$. For these conditions, at equilibrium, $y_A^s = 0.05$ and $y_B^s = 0.9$ as for the case considered in Fig. 1. As seen in Fig. 2, the

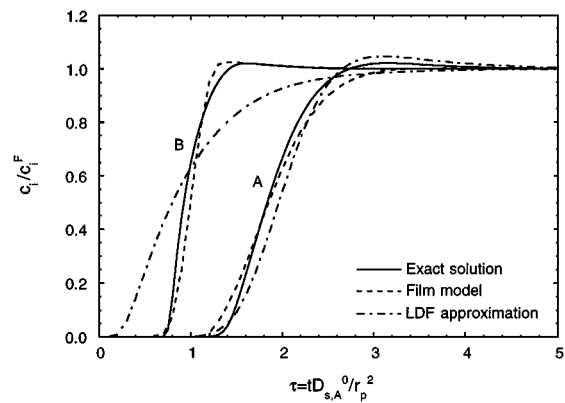


Figure 2. Breakthrough curves for binary adsorption calculated from the numerical solution of the rigorous model, the LDF approximation with constant diffusivities, and the film-model approximation (Eq. (12)). $D_{s,A}^0/D_{s,B}^0 = 10$, $b_A = 2$, $b_B = 1$, $c_A^F = 0.5$, $c_B^F = 18$, $\Lambda = 20$, and $\xi = 1$.

film-model approximation is in good agreement with the rigorous model, predicting the breakthrough curves with an accuracy consistent with that of the classical LDF approximation for constant diffusivity systems. As seen in this figure, however, although the LDF approximation is reasonably close to the breakthrough curve of the faster diffusing and lower-concentration adsorbate, A, it completely fails to predict the breakthrough of the slower diffusing and higher concentration adsorbate, B. This occurs because of the concentration dependence of the diffusivity and of the coupling of solute fluxes which are not accounted for in the LDF approximation. Conversely, the film-model approximation correctly predicts these effects and gives reasonable predictions of the two-component breakthrough curves for both A and B.

The effect of increasing the diffusivity ratio to $D_{s,A}^0/D_{s,B}^0 = 50$ is shown in Fig. 3. In this more extreme case, the agreement between the film model and the exact solution is not as good as in the previous case for the more strongly adsorbed and faster-diffusing species A. However, compared to the LDF approximation with constant diffusivity, the film model is still superior providing a reasonable approximation of the profile for the less strongly adsorbed and slower diffusing species B and the correct shape for A.

The last effect considered is the isotherm non-linearity. Figure 4 shows predicted profiles for a case where the ratio $D_{s,A}^0/D_{s,B}^0 = 10$ but the feed concentrations are changed to $c_A^F = 2$, $c_B^F = 4$ giving $y_A^s = y_B^s = 0.44$ at equilibrium. The film model is again in good agreement with the exact solution. In particular,

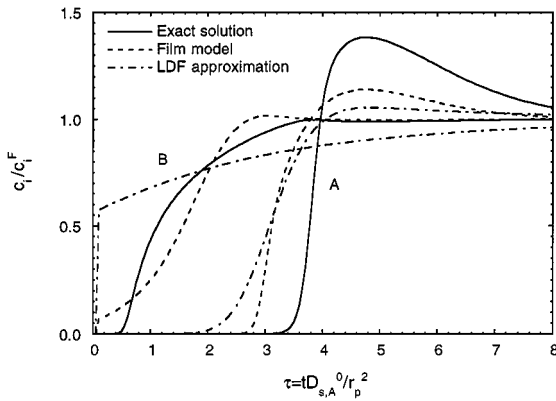


Figure 3. Breakthrough curves for binary adsorption calculated from the numerical solution of the rigorous model, the LDF approximation with constant diffusivities, and the film-model approximation (Eq. (12)). $D_{s,A}^0/D_{s,B}^0 = 50$, $b_A = 2$, $b_B = 1$, $c_A^F = 0.5$, $c_B^F = 18$, $\Lambda = 20$, and $\xi = 1.5$.

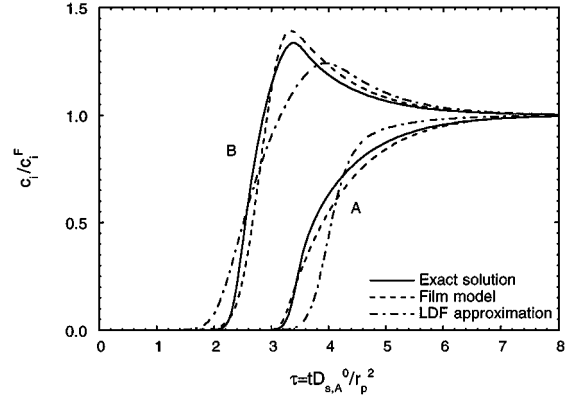


Figure 4. Breakthrough curves for binary adsorption calculated from the numerical solution of the rigorous model, the LDF approximation with constant diffusivities, and the film-model approximation (Eq. (12)). $D_{s,A}^0/D_{s,B}^0 = 10$, $b_A = 2$, $b_B = 1$, $c_A^F = 2$, $c_B^F = 4$, $\Lambda = 20$, and $\xi = 1$.

it correctly predicts the shape of the profile for the more strongly adsorbed species characterized by a sharp initial rise followed by much more gradual approach to the feed concentration. This occurs because within the adsorption bed, the adsorbed phase concentration of A exceeds the equilibrium value for short times (see Fig. 1). For longer times, desorption of A must occur against a counter-diffusion flux of the more slowly diffusing species B generating a slow approach to equilibrium. The LDF approximation with constant diffusivity predicts a shallower profile for B and an incorrect shape for A.

Generalization

Having demonstrated the predictive capability of the film-model approximation for systems where multi-component adsorption equilibrium is described by the extended Langmuir isotherm, we now turn our attention to generalizing the approach to other isotherms. For the general case, with M adsorbates, the Gibbs adsorption isotherm is (Young and Crowell, 1962):

$$A d\pi = \sum_{j=1}^M n_j d\mu_j \quad (13)$$

where A is the adsorbent area and π is the spreading or surface pressure. From Eq. (2), assuming pseudo-steady-state diffusion across the film, we obtain:

$$\frac{dJ_i}{dr} = -\rho_p \frac{D_{s,i}^0}{RT} \left(\frac{dn_i}{dr} \frac{d\mu_i}{dr} + n_i \frac{d^2\mu_i}{dr^2} \right) = 0 \quad (14)$$

From Eq. (13) we also have:

$$A \frac{d^2 \pi}{dr^2} = \sum_{j=1}^M \left(\frac{dn_j}{dr} \frac{d\mu_j}{dr} + n_j \frac{d^2 \mu_j}{dr^2} \right) \quad (15)$$

Thus, combining Eqs. (14) and (15) yields:

$$\frac{d^2 \pi}{dr^2} = 0 \quad (16)$$

which implies that the spreading pressure is a linear function of distance in the film. Thus, $\pi = \gamma r + \beta$ with $\gamma = 5(\pi^s - \bar{\pi})/r_p$. Here π^s and $\bar{\pi}$ are the particle-surface and bulk spreading pressure values.

The chemical potential of a component in the adsorbed phase can be written as follows (Suwanayuen and Danner, 1980):

$$\mu_i = \mu_i^* + \Re T \ln a_i + \hat{A}_i \pi \quad (17)$$

where μ_i^* is the adsorbate's chemical potential at infinite dilution, a_i is the activity, and \hat{A}_i is the adsorbate's partial molar area. If we assume that the adsorbed phase is ideal and that the adsorbate's partial molar area is constant, from Eqs. (2) and (17) we obtain:

$$\begin{aligned} J_i &= -\rho_p \frac{D_{s,i}^0}{\Re T} n_i \left(\Re T \frac{d \ln n_i}{dr} + \hat{A}_i \frac{d\pi}{dr} \right) \\ &= -\rho_p D_{s,i}^0 \left(\frac{dn_i}{dr} + n_i \frac{\hat{A}_i}{\Re T} \frac{d\pi}{dr} \right) \\ &= -\rho_p D_{s,i}^0 \left[\frac{dn_i}{dr} + n_i \frac{5}{r_p} \frac{\hat{A}_i (\pi^s - \bar{\pi})}{\Re T} \right] \end{aligned} \quad (18)$$

Finally, integrating this equation across the film as was done for Eq. (10), yields the following expressions for the flux and the rate equation:

$$J_i = -\frac{5\rho_p D_{s,i}^0}{r_p} \cdot \frac{\hat{A}_i (\pi^s - \bar{\pi})}{\Re T} \cdot \frac{n_i^s \exp[\hat{A}_i (\pi^s - \bar{\pi})/\Re T] - \bar{n}_i}{\exp[\hat{A}_i (\pi^s - \bar{\pi})/\Re T] - 1} \quad (19)$$

$$\frac{\partial \bar{n}_i}{\partial t} = \frac{15 D_{s,i}^0}{r_p^2} \cdot \frac{\hat{A}_i (\pi^s - \bar{\pi})}{\Re T} \cdot \frac{n_i^s \exp[\hat{A}_i (\pi^s - \bar{\pi})/\Re T] - \bar{n}_i}{\exp[\hat{A}_i (\pi^s - \bar{\pi})/\Re T] - 1} \quad (20)$$

We can verify that for the special case of an ideal Langmuirian system with equal partial molar volumes

($n_{m,i} = n_{m,j} = n_m$, $\hat{A}_i = \hat{A}_j = \hat{A}$) these equations reduce to Eqs. (11) and (12). In this case, from the Gibbs isotherm we have (Myers, 1986):

$$\begin{aligned} \frac{A\pi}{\Re T} &= \int_0^{p'_i(\pi)} \frac{n_i}{p_i} dp_i = \int_0^{n'_i(\pi)} \frac{d \ln p_i}{d \ln n_i} dn_i \\ &= n_{m,i} \ln \left[\frac{n_{m,i}}{n_{m,i} - n'_i(\pi)} \right] \end{aligned} \quad (21)$$

where $p'_i(\pi)$ and $n'_i(\pi)$ are for the pure component at the same spreading pressure of the mixture. Solving Eq. (21) for $n'_i(\pi)$ and using the condition that there is no area change upon mixing (Myers and Prausnitz, 1965) the following result is obtained:

$$1 = \sum_{j=1}^M \frac{n_j}{n'_j(\pi)} = \sum_{j=1}^M \left[\frac{n_j}{n_{m,j}} \cdot \frac{\exp(A\pi/n_{m,j}\Re T)}{\exp(A\pi/n_{m,j}\Re T) - 1} \right] \quad (22)$$

In general, this equation has to be solved numerically to find π for given values of the n_i 's. However, when the saturation capacities are equal, this equation can be solved explicitly giving the result:

$$\exp\left(\frac{\hat{A}\pi}{\Re T}\right) = \frac{n_m}{n_m - \sum_{j=1}^M n_j} \quad (23)$$

where we have taken $\hat{A} = \hat{A}_i = A/n_m$. When Eq. (23) is inserted in Eq. (20), we obtain:

$$\begin{aligned} \frac{\partial \bar{n}_i}{\partial t} &= \frac{15 D_{s,i}^0}{r_p^2} \cdot \frac{n_i^s (n_m - \sum_j \bar{n}_j) - \bar{n}_i (n_m - \sum_j n_j^s)}{((n_m - \sum_j n_j^s) - (n_m - \sum_j \bar{n}_j)) / \ln\left(\frac{n_m - \sum_j n_j^s}{n_m - \sum_j \bar{n}_j}\right)} \end{aligned} \quad (24)$$

which is the same as Eq. (12).

Comparison with Extended LDF Approximation

An empirical extension of the classical LDF approximation to account for diffusional coupling of fluxes in a multicomponent system has been suggested by Marutovsky and Bülow (1987) and Sircar (1991) and has been further developed by Sundaram and

Yang (1998) to predict the effects of concentration-dependent diffusivities on pressure-swing-adsorption calculations for two- and three-component Langmuirian systems. The basis for the extended LDF model used by Sundaram and Yang is the assumption that the intraparticle concentration profiles are parabolic. In this case, as shown by Liaw et al. (1979), we obtain:

$$\left. \frac{\partial n_i}{\partial r} \right|_{r=r_p} = \frac{5}{r_p} (n_i^s - \bar{n}_i) \quad (25)$$

Thus, for the case of a Langmuirian system, the following result is obtained from Eq. (5):

$$J_i|_{r=r_p} = -\frac{5\rho_p D_{s,i}^0}{r_p} \left[(n_i^s - \bar{n}_i) + \frac{n_i^s}{n_m - \sum_{k=1}^M n_k^s} \times \sum_{j=1}^M (n_j^s - \bar{n}_j) \right] \quad (26)$$

The latter, combined with an overall balance for the particle yields the rate equation:

$$\frac{\partial \bar{n}_i}{\partial t} = \frac{15D_{s,i}^0}{r_p^2} \left[(n_i^s - \bar{n}_i) + \frac{n_i^s}{n_m - \sum_{k=1}^M n_k^s} \times \sum_{j=1}^M (n_j^s - \bar{n}_j) \right] \quad (27)$$

For the case of two components ($M = 2$), this equation gives:

$$\frac{\partial \bar{n}_1}{\partial t} = \frac{15D_{s,1}^0}{r_p^2} \left[\frac{n_m - n_2^s}{n_m - n_1^s - n_2^s} (n_1^s - \bar{n}_1) + \frac{n_1^s}{n_m - n_1^s - n_2^s} (n_2^s - \bar{n}_2) \right] \quad (28a)$$

$$\frac{\partial \bar{n}_2}{\partial t} = \frac{15D_{s,2}^0}{r_p^2} \left[\frac{n_2^s}{n_m - n_1^s - n_2^s} (n_1^s - \bar{n}_1) + \frac{n_m - n_1^s}{n_m - n_1^s - n_2^s} (n_2^s - \bar{n}_2) \right] \quad (28b)$$

which coincides with the result of Sundaram and Yang (1998). These equations include a dependence of the “effective” diffusivity on the adsorbates’ concentrations at the particle surface, n_1^s and n_2^s . On the other

hand, it is apparent that their validity is necessarily limited to special cases where the intraparticle concentration profiles can indeed be approximated as parabolic. This occurs when the adsorbates’ concentrations are very low. In this case, however, the effective diffusivities become constant and there is no coupling of solute fluxes. For other situations, the intraparticle concentration profiles can be far from parabolic and Eq. (27) or Eq. (28) can give erroneous results unless they are used in an empirical way with limiting diffusivity values fitted to multicomponent adsorption rate data (Sundaram and Yang, 1998). For example, we can consider binary desorption from a particle with the boundary condition $n_1^s = n_2^s = 0$. In this case, from the extended LDF approximation (Eq. (28)) one would obtain the result:

$$\frac{\partial \bar{n}_1}{\partial t} = -\frac{15D_{s,1}^0}{r_p^2} \cdot \bar{n}_1 \quad (29a)$$

$$\frac{\partial \bar{n}_2}{\partial t} = -\frac{15D_{s,2}^0}{r_p^2} \cdot \bar{n}_2 \quad (29b)$$

which, contrary to expectations, would predict constant effective diffusivities with no flux coupling. On the other hand, the film model approximation developed in this work, for the case of a Langmuirian system (Eq. (12) or (24)), yields the result:

$$\frac{\partial \bar{n}_1}{\partial t} = -\frac{15D_{s,1}^0}{r_p^2} \cdot \frac{n_m \bar{n}_1}{(\bar{n}_1 + \bar{n}_2) / \ln[n_m / (n_m - \bar{n}_1 - \bar{n}_2)]} \quad (30a)$$

$$\frac{\partial \bar{n}_2}{\partial t} = -\frac{15D_{s,2}^0}{r_p^2} \cdot \frac{n_m \bar{n}_2}{(\bar{n}_1 + \bar{n}_2) / \ln[n_m / (n_m - \bar{n}_1 - \bar{n}_2)]} \quad (30b)$$

This result retains the expected concentration dependence and flux coupling of the diffusing adsorbates and produces results consistent with detailed numerical simulations.

Conclusion

A film-model approximation has been developed to simplify numerical calculations of multicomponent adsorption in batch and fixed-bed adsorbers. The new rate expression introduced in this paper, based on an equivalent film resistance model, provides a simple tool for numerical calculations pertaining to processes

using spherical adsorbent particles. The approximation 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 latter approximation can, in fact, be considered as a special case of the more general film-model approximation. Although only a limited set of cases was considered explicitly in this paper, it is clear that the new rate equation can be conveniently used for adsorption calculations in more complex situations in concert with various available numerical algorithms. A formal generalization of the approach, based on the Gibbs adsorption isotherm, provides a framework for extending the treatment to other multicomponent isotherm expressions. An analogous formulation has also been developed for multicomponent ion exchange based on the Nernst-Planck flux equations and is presented in Carta and Lewus (1999). 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.

Nomenclature

a_i	Thermodynamic activity
A	Surface area of adsorbent, m ² /kg
\hat{A}_i	Partial molar area of i , m ² /mol
b_i	Langmuir isotherm parameter, 1/Pa
c_i	Fluid phase concentration of adsorbate species, mol/m ³
c_{ref}	Reference fluid phase concentration, mol/m ³
$D_{s,i}^0$	"Corrected" or "limiting" adsorbate diffusivity, m ² /s
J_i	Adsorbate flux, mol/m ² s
J_i^*	Dimensionless adsorbate flux ($=r_p J_i / \rho_p n_m D_{s,\text{ref}}^0$)
n_i	Moles of adsorbate i in adsorbed phase, mol/kg
$n_{m,i}$	Maximum number of moles of adsorbate i in adsorbed-phase, mol/kg
p_i	Partial pressure of i , Pa
r	Particle radial coordinate, m
r_p	Particle radius, m
\mathcal{R}	Ideal gas constant, J/mol K

t	Time, s
T	Temperature, K
v	Fluid velocity, m/s
x_i	Dimensionless fluid-phase adsorbate concentration ($=c_i/c_{\text{ref}}$)
y_i	Dimensionless adsorbate concentration in adsorbate phase ($=n_i/n_m$)
y_I	Fraction of saturation capacity free of adsorbates ($=1 - \sum_{k=1}^M y_k$)
z	Bed length or bed axial coordinate, m

Greek Letters

α_i	Ratio of limiting diffusivities ($=D_{s,\text{ref}}^0/D_{s,i}^0$)
ε	Bed void fraction
Λ	Partition ratio ($=\rho_b n_m / \varepsilon c_{\text{ref}}$)
μ_i	Chemical potential, J/mol
π	Spreading pressure, N/m
ρ	Dimensionless radial coordinate ($=r/r_p$)
ρ_b	Bed density ($=\rho_p(1 - \varepsilon)$), kg/m ³
ρ_p	Particle density, kg/m ³
τ	Dimensionless time ($=t D_{s,\text{ref}}^0 / r_p^2$)
τ'	Dimensionless time ($=\tau - \xi / \Lambda$)
ξ	Dimensionless bed length or axial coordinate ($=z \Lambda D_{s,\text{ref}}^0 / v r_p^2$)

Superscripts

F	Feed value
0	Initial value
s	Value at particle surface
$-$	Average over the particle

Subscript

ref	Value for reference adsorbate
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References

- Carta, G. and A. Cincotti, "Film Model Approximation for Non-Linear Adsorption and Diffusion in Spherical Particles," *Chem. Engng. Sci.*, **53**, 3483 (1998).
- Carta, G., A. Cincotti, and G. Cao, "Film Model Approximation for Binary Ion Exchange," *Sep. Sci. Technol.*, **34**, 1 (1999).

- Carta, G. and R.K. Lewus, "Film Model Approximation for Particle-Diffusion-Controlled Multicomponent Ion Exchange," *Sep. Sci. Technol.*, **34**, 2685 (1999).
- Chen, N.Y., R.T. Yang, and P. Uawithya, "Diffusion of Oxygen, Nitrogen and their Mixtures in Carbon Molecular Sieve," *AIChE J.*, **40**, 577 (1994).
- Farooq, S. and D.M. Ruthven, "Numerical Simulation of a Kinetically Controlled Pressure Swing Adsorption Bulk Separation Process Based on a Diffusion Model," *Chem. Engng. Sci.*, **46**, 2213 (1991).
- Farooq, S., M.N. Rathor, and K. Hidajat, "A Predictive Model for a Kinetically Controlled Pressure Swing Adsorption Separation Process," *Chem. Engng. Sci.*, **48**, 4129 (1993).
- Garg, D.R. and D.M. Ruthven, "The Effect of Concentration Dependence of Diffusivity on Zeolite Sorption Curves," *Chem. Engng. Sci.*, **27**, 417 (1972).
- Glueckauf, E., "Theory of Chromatography 10: Formulae for Diffusion into Spheres and their Application to Chromatography," *Trans. Faraday Soc.*, **51**, 1540 (1955).
- Habgood, H.W., "The Kinetics of Molecular Sieve Action. Sorption of Nitrogen-Methane Mixtures by Linde Molecular Sieve 4A," *Can. J. Chem. Engng.*, **36**, 1384 (1958).
- Kapoor, A. and R.T. Yang, "Contribution of Concentration-dependent Surface Diffusion to Rate of Adsorption," *Chem. Engng. Sci.*, **45**, 1995 (1991).
- Kärger, J. and M. Bülöw, "Theoretical Prediction of Uptake Behaviour in Adsorption Kinetics of Binary Gas Mixtures using Irreversible Thermodynamics," *Chem. Engng. Sci.*, **30**, 893 (1975).
- Krishna, R. and J.A. Wesselingh, "The Maxwell-Stefan Approach to Mass Transfer," *Chem. Engng. Sci.*, **52**, 861 (1997).
- LeVan, M.D., G. Carta, and C.M. Yon, "Adsorption and Ion Exchange," *Perry's Chemical Engineers Handbook*, Section 16, 7th ed., D.W. Green (Ed.), McGraw-Hill, New York, 1997.
- Liaw, C.H., J.S.P. Wang, R.H. Greenkorn, and K.C. Chao, "Kinetics of Fixed-Bed Adsorption: a New Solution," *AIChE J.*, **25**, 376 (1979).
- Marutovsky, R.M. and M. Bülöw, "Determination of the Matrix of Kinetic Coefficients for Internal Mass Transport of Two-Component Mixtures in Porous Solids," *Chem. Engng. Sci.*, **42**, 2745 (1987).
- Myers, A.L., "Thermodynamics of Adsorption Phenomena," *J. Non-Equil. Thermodyn.*, **11**, 35 (1986).
- Myers, A.L. and J.M. Prausnitz, "Thermodynamics of Mixed-Gas Adsorption," *AIChE J.*, **11**, 121 (1965).
- Nakao, S. and M. Suzuki, "Mass Transfer Coefficient in Cyclic Adsorption and Desorption," *J. Chem. Eng. Japan*, **16**, 114-119 (1982).
- Round, G.F., H.W. Habgood, and R. Newton, "A Numerical Analysis of Surface Diffusion in a Binary Adsorbed Film," *Sep. Sci.*, **1**, 219 (1966).
- Ruthven, D.M., *Principles of Adsorption and Adsorption Processes*, Wiley, New York, 1984.
- Sircar, S., "Pressure Swing Adsorption: Research Needs by Industry," *Fundamentals of Adsorption*, A.B. Mersmann and S.E. Scholl (Eds.), pp. 815-843, Engineering Foundation, New York, 1991.
- Sundaram, N. and R.T. Yang, "Effects of Main and Cross Term Diffusivities on Kinetic Separations by Pressure Swing Adsorption," *Chem. Engng. Sci.*, **53**, 1901 (1998).
- Suwanayuen, S. and R.P. Danner, "A Gas Adsorption Isotherm Equation Based on Vacancy Solution Theory," *AIChE J.*, **26**, 68 (1980).
- van den Broeke, L.J.P. and R. Krishna, "Experimental Verification of the Maxwell-Stefan Theory for Micropore Diffusion," *Chem. Engng. Sci.*, **50**, 2507 (1995).
- Yang, R.T., *Gas Separation by Adsorption Processes*, Butterworths, Boston, 1987.
- Young, D.M. and A.D. Crowell, *Physical Adsorption of Gases*, Butterworths, Washington, DC, 1962.