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Matrix calculation of multicomponent transient diffusion in porous sorbents

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Abstract—The linearized theory of mass transfer described by Stewart and co-workers is employed to develop general matrix methods which extend approximations for unsteady-state binary diffusion in porous sorbents to cases involving multicomponent interactions. The accuracy of these extended approximations and their suitability as a simple, efficient method to account for multicomponent intraparticle diffusion when simulating sorption processes was investigated for ion-exchange mass transfer. A new approximation for binary intraparticle diffusion is also developed and evaluated.

1. INTRODUCTION

THE PERFORMANCE of sorption separation processes which employ porous particles is strongly influenced by mass-transfer effects. The rate of mass transfer from a flowing fluid to the interior of a porous particle is determined by the following resistance mechanisms: (i) diffusion from the bulk fluid to the exterior surface of the particle, (ii) diffusion in the pores of the particle, (iii) adsorption onto solid surfaces inside the particle, and (iv) diffusion in the adsorbed phase. This study will be concerned exclusively with mechanisms (ii) and (iv) since in most cases they dominate the other two transport mechanisms. Mechanisms (ii) and (iv) usually occur in parallel; i.e. the total transfer rate equals the sum of the individual transfer rates.

In general, the only way to account exactly for intraparticle diffusion when modelling a specific sorption process is to integrate numerically the differential equations describing diffusion inside the particle. However, exact numerical integration of these differential equations is computationally time consuming, unwarranted when considering the accuracy with which physical properties are generally known, and in most cases unnecessary since a sufficiently accurate representation of intraparticle diffusion can usually be achieved using approximations. For these reasons, approximate representations of intraparticle diffusion are widely used in combination with a numerical technique for solving the remainder of the differential equations describing a particular sorption process. Examples of this approach are given in refs. [1, 2] where pressure swing adsorption is simulated and in ref. [3] which considers the simulation of an ion-exchange column. It should also be noted that as small-size computers become popular for use in process simulation, it becomes increasingly important to use an approximate rather than an exact description of intraparticle diffusion so that calculations can be performed on these computers within a reasonable amount of time and with limited memory. This is particularly true for multicomponent mixtures since exact numerical methods rapidly increase in complexity as the number of interacting species increases.

Several investigators have noted the importance of interactions among components when multicomponent diffusion takes place in porous particles and have extended the simplest binary diffusion approximations to multicomponent systems. In particular, the linear driving force (LDF) approximation and the assumption of a parabolic concentration profile have been extended in this manner [1–4]. However, relatively few studies have systematically investigated approximations for multicomponent diffusion in porous particles, an exception being the recent work of Marutovsky and Bulow [5] who investigated a procedure for evaluating the matrix of transport coefficients in the LDF approximation from experimental data.

The purpose of this study is to develop general methods for extending approximations for binary diffusion in porous particles to multicomponent systems. In this way the essential features of multicomponent diffusion in porous particles can be accounted for simply and efficiently when sorption processes are modelled. The accuracy of these extended approximations will also be evaluated by comparing them to exact numerical solutions. The binary diffusion approximations considered in this study include the LDF approximation [6], a two-term approximation to the infinite series for integration by parts (i.e. Glueckauf's equation (A) [6]), the quadratic driving force (QDF) approximation [7], an approximation proposed by Do and Mayfield [8], and a new approximation developed in this study (see Appendix). This new binary diffusion approximation overcomes some of the limitations in existing methods and

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NOMENCLATURE

a_0, a_1	constants in equation (A2)
A_i	fractional change in the concentration from the initial to the final state (see equation (17))
b	parameter in equation (A6)
C_i	fluid-phase concentration [mol cm^{-3}]
D_i	diffusion coefficient [cm^2 s^{-1}]
E	parameter in equation (A2)
$[F]$	matrix of partial derivatives $\partial q_i/\partial C_j$
G	parameter defined in equation (A7)
H	parameter defined in equation (A8)
$[I]$	identity matrix
K_i	equilibrium value of dq_i/dC_i [cm^3 g^{-1}]
n	number of independent diffusional fluxes
$\mathbf{N}_i$	diffusional flux with respect to a stationary frame of reference [mol cm^{-2} s^{-1}]
$[P]$	matrix of right eigenvectors of the matrix of diffusion coefficients (see equation (6))
q_i	local concentration in a particle [mol g^{-1}]
$\Delta q_{i,\text{total}}$	total change in concentration of component i [mol g^{-1}]
r	radial position inside a particle [cm]
R	radius of particle [cm]
t	time [s]
x	dimensionless radial position inside a particle (r/R).

Greek symbols

β	parameter in equation (16)
γ	tortuosity
ε	porosity of a particle
κ_i	intraparticle mass-transfer coefficient
$[\hat{\kappa}]$	diagonal matrix composed of $\hat{\kappa}_i$ (see equation (14))
$\hat{\kappa}_i$	eigenvalue of $[\kappa]$ (see equation (15))
ρ_p	particle density [g cm^{-3}]
τ	dimensionless time, $D_{\text{ref}}t/R^2$.

Subscripts

a	quantity evaluated at the average or reference composition
ave	average or mean value
eff	effective value
fluid	property of the fluid phase
final	condition at the final state
i	component i
initial	condition at the initial state
solid	property of the solid phase
total	total change between the initial and final state
δ	quantity evaluated at the outer surface of the particle.

Additional symbols

$\hat{}$	matrix or elements of a matrix transformed using the matrix $[P]^{-1}$ or $[P_a]^{-1}$
( )	vector composed of values for all i components
[ ]	matrix composed of values for all i components (i.e. D_{ij} is the element in row i and column j of $[D]$)
$\tilde{}$	variable transformed using the matrix $[P]^{-1}$.

Abbreviations

LDF	linear driving force
QDF	quadratic driving force.

is especially useful in accurately describing the initial stages of the sorption process. The multicomponent approximations resulting from these various binary approximations should provide an adequate number of alternatives to suit most applications. However, it should be noted that there are other binary diffusion results which, if the need arises, can also be extended to multicomponent systems (see, e.g. the discussion of binary diffusion in spheres presented in ref. [9]).

2. THEORY

Consider binary intraparticle diffusion involving a single independent diffusional flux and a corresponding single driving force, e.g. diffusion of a dilute solute dissolved in a solvent. If local equilibrium exists between the pore fluid and the adjacent pore wall and if diffusion takes place in both the pores and in the adsorbed phase, Fick's law can be written in the following form (see, e.g. ref. [10]):

$$\mathbf{N}_i = -\rho_p \left\{ \frac{D_{i,\text{fluid}}\varepsilon}{\gamma \rho_p K_i} + \frac{D_{i,\text{solid}}(\rho_p K_i - \varepsilon)}{\rho_p K_i} \right\} \nabla q_i. \quad (1)$$

In equation (1), q_i is the local concentration in the particle (i.e. $q_i = \varepsilon C_{i,\text{pore}}/\rho_p + q_{i,\text{solid}}$ where $q_{i,\text{solid}}$ is the amount of solute adsorbed on, or dissolved in, the solid per unit mass), $D_{i,\text{solid}}$ the effective Fick's law diffusion coefficient for the solid based on a driving force of $\rho_{\text{solid}} \nabla q_{i,\text{solid}}$, $D_{i,\text{fluid}}$ the diffusivity in the fluid including, if appropriate, contributions from Knudsen diffusion, and K_i the local value of the isotherm slope dq_i/dC_i. The first and second terms in brackets in equation (1) are the contributions from pore diffusion and adsorbed-phase diffusion, respectively, while the entire quantity in brackets is the effective diffusion coefficient in the particle, i.e. $D_{i,\mathrm{eff}}$. The material-balance relation inside the particle can be written as

$$\frac{\partial q_i}{\partial t} = \frac{-1}{\rho_{\mathrm{p}}} \nabla \cdot \mathbf{N}_i. \tag{2}$$

When diffusion takes place in a multicomponent mixture, the relation between fluxes and driving forces must account for interactions between components. A multicomponent version of equation (1) which applies when there are n independent driving forces and n independent diffusional fluxes (i.e. n independent N_i) can be written as

$$(N) = -\rho_{\mathrm{p}} \left\{ \frac{[D_{\mathrm{fluid}}]\varepsilon[F]^{-1}}{\gamma \rho_{\mathrm{p}}} + \frac{[D_{\mathrm{solid}}](\rho_{\mathrm{p}}[I] - \varepsilon[F]^{-1})}{\rho_{\mathrm{p}}} \right\} (\nabla q). \tag{3}$$

In equation (3), $[D_{\mathrm{fluid}}]$ and $[D_{\mathrm{solid}}]$ denote $n \times n$ matrices of transport coefficients and $[F]$ denotes an $n \times n$ matrix composed of the equilibrium parameters $\partial q_i/\partial C_i$. The quantity in brackets in equation (3) is the matrix of effective Fick's law diffusion coefficients in the particle, i.e. $[D_{\mathrm{eff}}]$. Quantities in parentheses but without component subscripts denote a column vector with elements for each component; e.g. (N) denotes a column vector composed of $\mathbf{N}_i$. Note that off-diagonal elements in the matrix $[D_{\mathrm{eff}}]$ result both from equilibrium behavior (i.e. from the matrix $[F]$) and from off-diagonal elements in $[D_{\mathrm{fluid}}]$ and $[D_{\mathrm{solid}}]$. The material-balance relations corresponding to equation (3) can be written as

$$\left(\frac{\partial q}{\partial t}\right) = \frac{-1}{\rho_{\mathrm{p}}} (\nabla \cdot N). \tag{4}$$

Equations (3) and (4) apply to a wide variety of situations involving multicomponent intraparticle diffusion [11–14]. In particular, the equations apply to stoichiometric ion exchange involving $n+1$ exchangeable ions, to the sorption of n dilute solutes dissolved in a non-adsorbed diluent, to sorption from an $n+1$ component liquid mixture where there is no diluent, and to sorption from an n component gas mixture where all n components are adsorbed. Relations for the elements in $[D_{\mathrm{fluid}}]$ for this last case are given in ref. [12]. When equation (3) is applied to sorption from a gas mixture, an additional $n \times n$ matrix can be included inside the brackets in that equation to account for the (usually small) viscous flow contribution to the flux caused by pressure gradients in the sorbent particle [12].

It should be noted that for some porous sorbents the distinction between various mechanisms for diffusion becomes unclear. This is the case, e.g. in a polystyrene–divinylbenzene ion exchanger where the thermal motions of polymer segments, solvent, and solutes lead to behavior more like a concentrated polyelectrolyte solution, rather than a porous solid. Under these conditions, diffusion is usually visualized as taking place through a homogeneous, non-porous solid in which case equations (3) and (4) apply with $\varepsilon = 0$ and with $[D_{\mathrm{solid}}]$ taken as the diffusion coefficient in the homogeneous solid [3]. In addition, when solute uptake takes place by dissolution in pores filled with fluid immiscible with the interparticle fluid (as in gas–liquid chromatography) equation (3) again applies but with $\varepsilon = 0$ and with $[D_{\mathrm{solid}}]$ taken as the diffusivity in the pore fluid divided by the tortuosity.

In this study the diffusional relations for multicomponent systems will be linearized by evaluating all physical properties at an average composition in the particle such that the following relation applies:

$$(N) = -\rho_{\mathrm{p}} \left\{ \frac{[D_{\mathrm{fluid,a}}]\varepsilon[F_{\mathrm{a}}]^{-1}}{\gamma \rho_{\mathrm{p}}} + \frac{[D_{\mathrm{solid,a}}](\rho_{\mathrm{p}}[I] - \varepsilon[F_{\mathrm{a}}]^{-1})}{\varepsilon \rho_{\mathrm{p}}} \right\} (\nabla q). \tag{5}$$

For fixed values of the physical properties, equations (4) and (5) can be solved using matrix methods [15–17]. In particular, these equations can be decoupled by pre-multiplying with the inverse of the matrix of right eigenvectors of $[D_{\mathrm{eff,a}}]$ (i.e. $[P]^{-1}$)

$$[P]^{-1}(N) = -\rho_{\mathrm{p}}[P]^{-1}[D_{\mathrm{eff,a}}][P][P]^{-1}(\nabla q). \tag{6}$$

Thus, equations (4) and (5) can be written as

$$\left(\frac{\partial \tilde{q}}{\partial t}\right) = \frac{-1}{\rho_{\mathrm{p}}} (\nabla \cdot \tilde{N}) \tag{7}$$

$$(\tilde{N}) = -\rho_{\mathrm{p}}[\hat{D}](\nabla \tilde{q}) \tag{8}$$

where

$$(\tilde{N}) = [P]^{-1}(N) \tag{9}$$

$$(\tilde{q}) = [P]^{-1}(q) \tag{10}$$

$$[\hat{D}] = [P]^{-1}[D_{\mathrm{eff,a}}][P]. \tag{11}$$

Since the elements of the diagonal matrix $[\hat{D}]$ (i.e. $\hat{D}_i$) are constant, equations (7) and (8) reduce to a set of uncoupled equations

$$\frac{\partial \tilde{q}_i}{\partial t} = \hat{D}_i \nabla^2 \tilde{q}_i. \tag{12}$$

Given a set of boundary conditions for the original problem (i.e. the problem defined by equations (3) and (4)) and a reference composition for determining physical properties, corresponding boundary conditions for equation (12) can be determined using equation (10). The solutions of equation (12) then yield a solution of the original set of equations using the inverse of equation (10).

In this study, approximate solutions of equation (12) for diffusion in a sphere will be used to determine approximate solutions for equations (3) and (4). In particular, the average composition in the particle, $q_{i,\mathrm{ave}}$, can be determined by integrating the relation

Table 1. Expressions for the intraparticle mass-transfer coefficients and the corresponding driving forces

Model	$\hat{\kappa}_i$	$\Delta\tilde{q}_i$
LDF	$5\hat{D}_i/R$	$\tilde{q}_{i,\delta}-\tilde{q}_{i,\mathrm{ave}}$
QDF	$\pi^2\hat{D}_i/3R$	$(\tilde{q}_{i,\delta}^2-\tilde{q}_{i,\mathrm{ave}}^2)/2\tilde{q}_{i,\mathrm{ave}}$
Approximation of Do and Mayfield [8] [see equation (16) of that work] and this work (see Appendix)	$(3+E)\hat{D}_i/R$	$\tilde{q}_{i,\delta}-\tilde{q}_{i,\mathrm{ave}}$
Glueckauf's equation (A) [6]	$\tilde{N}_{i,\delta}=(\rho_p\pi^2\hat{D}_i/3R)(\tilde{q}_{i,\delta}-\tilde{q}_{i,\mathrm{ave}})+(R\rho_p/3)(1-\pi^2/15)(\mathrm{d}\tilde{q}_{i,\delta}/\mathrm{d}t)$	

$$\left(\frac{\mathrm{d}q_{\mathrm{ave}}}{\mathrm{d}t}\right)=\frac{3}{R\rho_p}[P](\tilde{N}_\delta) \tag{13}$$

where the flux is given by

$$(\tilde{N}_\delta)=\rho_p[\hat{\kappa}](\Delta\tilde{q}). \tag{14}$$

In equation (14), $[\hat{\kappa}]$ is a diagonal matrix consisting of the transformed intraparticle mass-transfer coefficients and $(\Delta\tilde{q})$ the vector of transformed driving forces composed of elements $\tilde{q}_{i,\delta}-\tilde{q}_{i,\mathrm{ave}}$. Specific forms of $\hat{\kappa}_i$ and $\Delta\tilde{q}_i$ for the various approximate methods under consideration are given in Table 1. The matrix of intraparticle mass-transfer coefficients is given by the inverse transformation of $[\hat{\kappa}]$

$$[\kappa]=[P][\hat{\kappa}][P]^{-1}. \tag{15}$$

However, it is generally unnecessary to evaluate $[\kappa]$ explicitly since usually only the fluxes are needed for the purpose of integrating the material-balance equations. Note that the matrix transformation procedure for calculating $[\kappa]$ for the LDF approximation is equivalent to applying the LDF approximation to each element in the matrix $[D_{\mathrm{eff}}]$.

Equation (13) can be integrated using standard numerical methods in which the averaged properties are assumed to remain constant over a small time interval and then are updated for the next time interval (see Appendix). Implicit in this development is the assumption that the transformation procedure applies even though the average composition used to evaluate physical properties is allowed to vary with time, i.e. the pseudo-steady-state approximation is employed when determining fluxes from equation (14). In this way, the flux at the surface of the particle for completely arbitrary changes in surface concentration can be determined without solving the differential equations for diffusion inside the particle. As mentioned previously, such a procedure leads to a large saving in computational effort—often an order-of-magnitude reduction in computation time and memory requirement—when incorporated into a numerical simulation method for the overall process (see ref. [1] and references therein for comparisons for binary systems). It should be noted that the method described in this section, including the use of the pseudo-steady-state approximation, is equivalent to the method described in ref. [17] in which the linearized theory of mass transfer was used to solve the problem of multicomponent transient diffusion into a semi-infinite gas. It should also be noted that the multicomponent extensions of the LDF approximation and Glueckauf's equation (A) become exact solutions of the multicomponent diffusion equations in the limit of small driving forces.

3. NUMERICAL COMPARISONS

A variety of comparisons between approximate and exact solutions were conducted in this study. Each comparison involves a surface concentration given by the relation

$$A_{i,\delta}=1-\exp(-\beta\tau) \tag{16}$$

where A_i denotes the fractional change in the concentration of component i from the initial to the final state, i.e.

$$A_i=\frac{q_i-q_{i,\mathrm{initial}}}{q_{i,\mathrm{final}}-q_{i,\mathrm{initial}}}\equiv\frac{\Delta q_i}{\Delta q_{i,\mathrm{total}}}. \tag{17}$$

A number of previous investigators [7, 8] used $\beta=\infty$ exclusively when developing approximations for binary diffusion. Note that $\beta=\infty$ corresponds to a surface concentration change from its initial to its final value at $t=0$ as would be the case for a particle suddenly immersed in a well-stirred fluid of constant composition or for the case where irreversible sorption takes place in a fixed bed of sorbent particles. In this study more practical cases will be simulated by varying the value of β in equation (16). It should also be noted that an exact analytical solution of equations (1) and (2) with a constant diffusion coefficient and with equation (16) as a boundary condition is given in ref. [6].

In many sorption processes, including sorption in fixed beds, the value of $A_{i,\mathrm{ave}}$ for all components changes simultaneously in a single monotonic transition from an initial state to a final state. For simplicity, this study deals only with cases in which the surface concentrations for all components are characterized by the same value of β. This situation is representative of a number of practical cases, including sorption in fixed beds, since $A_{i,\delta}$ (as well as $A_{i,\mathrm{ave}}$) often tends to be a similar function of τ for every component even when the components have widely differing diffusion coefficients and equilibrium behavior [18]. It should be noted, however, that the procedure developed in Section 2 can accommodate cases where the dependence of $A_{i,\delta}$ on τ varies among

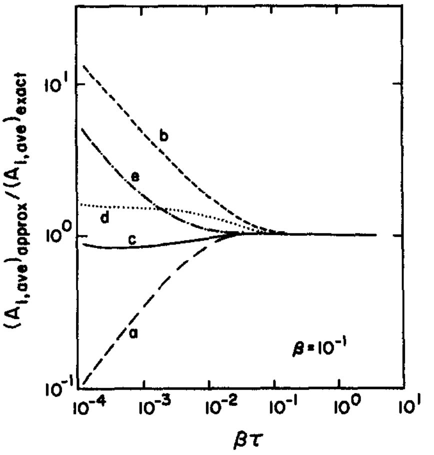

FIG. 1. Comparison of exact results for ternary ion exchange to various approximations used to determine the average concentration for component 1. Calculations correspond to a gradual increase in surface concentration with $\beta = 0.1$, $D_2/D_1 = 2.0$, $D_3/D_1 = 5.0$, $z_1 = z_2 = z_3$, $\tau = D_1 t/R^2$. The initial and final compositions correspond to $\Delta q_{1,\text{total}}/Q = 0.6$, $\Delta q_{2,\text{total}}/Q = 0.4$, and $\Delta q_{3,\text{total}}/Q = -1$. (a) LDF; (b) Do and Mayfield's approximation; (c) this work; (d) QDF; (e) Glueckauf's equation (A).

components. Since the results for individual components in multicomponent systems are generally very similar, only the results for one component will be reported in this study.

The matrix generalization method developed in Section 2 can be applied to a variety of systems. For simplicity in interpreting the results, stoichiometric ion exchange involving n independent diffusional fluxes and $n+1$ exchangeable ions was chosen for study in this investigation since multicomponent interactions in these systems are relatively simple to account for. It will be assumed that there is no co-ion or solvent uptake by the sorbent and that the Nernst–Planck equation applies. A discussion of the diffusional relations which apply with these assumptions is given in ref. [3]. Under these conditions, the $n \times n$ matrix $[D_{\text{eff}}]$ is given by

$$\underset{i \neq n+1}{D_{ii}} = D_i \left[1 + \frac{q_i z_i (D_{n+1} - D_i)}{\sum_{k=1}^{n+1} q_k z_k D_k} \right] \tag{18}$$

$$\underset{\substack{i \neq j \\ i \neq n+1}}{D_{ij}} = \frac{D_i z_i q_i (D_{n+1} - D_j)}{\sum_{k=1}^{n+1} q_k z_k D_k} \tag{19}$$

where D_i is the mobility of ion i.

4. DISCUSSION

Figures 1–3 and 4–8 illustrate computational results for multicomponent and binary systems, respectively. In Figs. 1–3, the results are displayed as the ratio $(A_{1,\text{ave}})_{\text{approx}}/(A_{1,\text{ave}})_{\text{exact}}$ as a function of time for a ternary ion-exchange system. Binary diffusion results are plotted in a similar way in Figs. 4–8. Note that the abscissa of these figures is the product $\beta\tau$, except in Fig. 8 where it is τ. Although the LDF and QDF approximations are often used with correction factors so that a better overall accuracy is achieved in column calculations [19], there appears to be no simple means to estimate these correction factors for multicomponent systems. These correction factors are therefore ignored in this study.

Figures 1–8 indicate that the accuracy of the LDF approximation decreases as the rate of change of surface concentration increases, as expected from the assumptions underlying this approximation (see

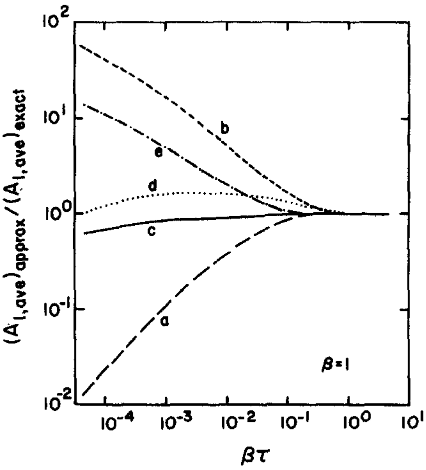

FIG. 2. Comparison of exact results for ternary ion exchange to various approximations used to determine the average concentration for component 1. Calculations correspond to a gradual increase in surface concentration with $\beta = 1$. Other conditions are the same as in Fig. 1. (a) LDF; (b) Do and Mayfield's approximation; (c) this work; (d) QDF; (e) Glueckauf's equation (A).

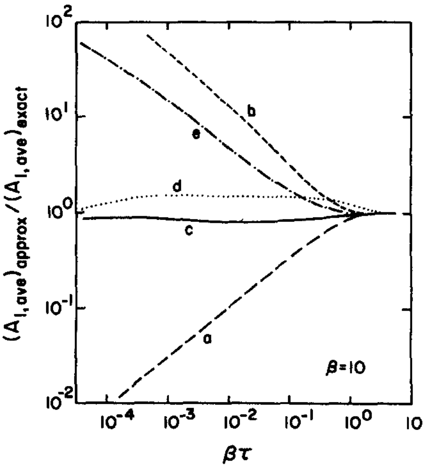

FIG. 3. Comparison of exact results for ternary ion exchange to various approximations used to determine the average concentration for component 1. Calculations correspond to a gradual increase in surface concentration with $\beta = 10$. Other conditions are the same as in Fig. 1. (a) LDF; (b) Do and Mayfield's approximation; (c) this work; (d) QDF; (e) Glueckauf's equation (A).

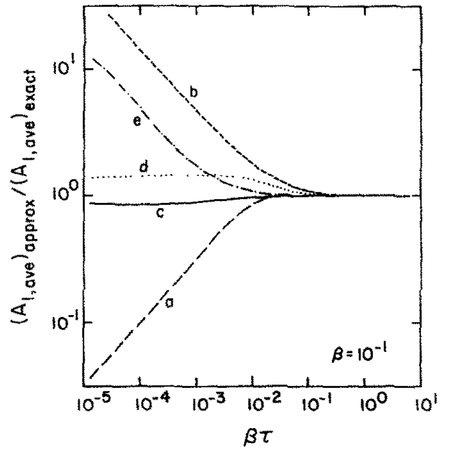

FIG. 4. Comparison of exact results for binary mass transfer to various approximations used to determine the average concentration for component 1. Calculations correspond to a gradual increase in surface concentration with $\beta = 0.1$. (a) LDF; (b) Do and Mayfield's approximation; (c) this work; (d) QDF; (e) Glueckauf's equation (A).

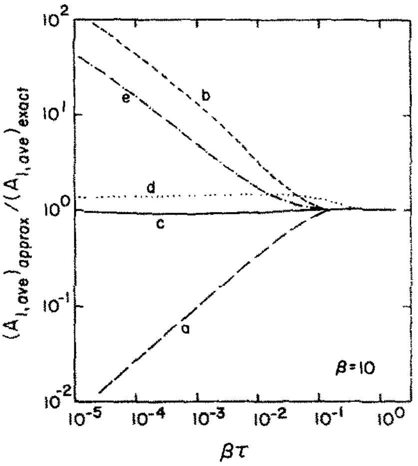

FIG. 6. Comparison of exact results for binary mass transfer to various approximations used to determine the average concentration for component 1. Calculations correspond to a gradual increase in surface concentration with $\beta = 10$. (a) LDF; (b) Do and Mayfield's approximation; (c) this work; (d) QDF; (e) Glueckauf's equation (A).

Appendix). The LDF approximation yields acceptable accuracy only when the rate of change of surface concentration is extremely slow. Glueckauf's equation (A) [6] yields the best results for moderate to large values of τ for a wide range of β but leads to significant errors at very small times. The QDF approximation yields the best results at small times, except when β is large in which case Do and Mayfield's approximation [8] yields better results. Note that Do and Mayfield's approximation [8] and the binary approximation developed in this study (see Appendix) have the disadvantage that they require the initial and final values for the composition to be known at the start of the calculation, which may be inconvenient for certain applications.

The new binary approximation developed in this study is similar to Glueckauf's equation (A) [6] (see Table 1). Both approximations take into account the effect of the rate of change of the surface concentration. However, the binary approximation developed in this study appears to be the more accurate of the two since it is based on the complete solution of the governing equations, rather than a two-term approximation to this solution. The new approximation leads to significant error only when the surface concentration changes at a high rate such as when the components of a multicomponent mixture have widely differing sorption selectivities. Under these conditions Do and Mayfield's approximation [8] appears more reliable.

Figures 1–8 indicate that the general trends

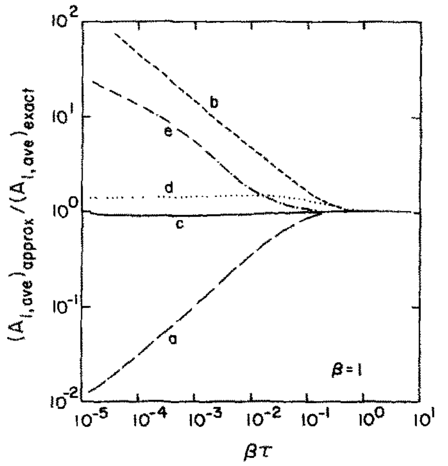

FIG. 5. Comparison of exact results for binary mass transfer to various approximations used to determine the average concentration for component 1. Calculations correspond to a gradual increase in surface concentration with $\beta = 1$. (a) LDF; (b) Do and Mayfield's approximation; (c) this work; (d) QDF; (e) Glueckauf's equation (A).

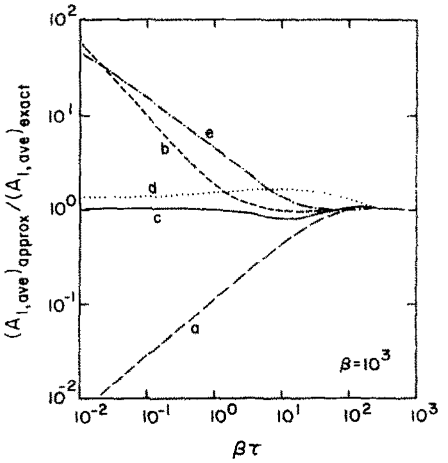

FIG. 7. Comparison of exact results for binary mass transfer to various approximations used to determine the average concentration for component 1. Calculations correspond to a gradual increase in surface concentration with $\beta = 10^3$. (a) LDF; (b) Do and Mayfield's approximation; (c) this work; (d) QDF; (e) Glueckauf's equation (A).

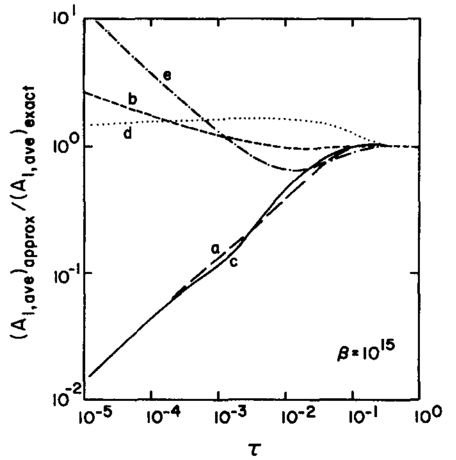

FIG. 8. Comparison of exact results for binary mass transfer to various approximations used to determine the average concentration for component 1. Calculations correspond to a gradual increase in surface concentration with $\beta = 10^{15}$. (a) LDF; (b) Do and Mayfield's approximation; (c) this work; (d) QDF; (e) Glueckauf's equation (A).

observed in constant-diffusivity binary systems also apply to multicomponent systems in spite of the presence of composition-dependent diffusion coefficients in the latter case. It would appear, therefore, that the effect of multicomponent interactions dominates over the influence of variable diffusion coefficients such that the matrix decoupling method described in Section 2 usually leads to good results.

As mentioned earlier, the new binary approximation developed in this study is more accurate than existing approximations at small values of τ; thus, it is expected to be particularly useful in the prediction of the small time behavior except when β is large, i.e. when there are large differences in selectivity among components. In this case Do and Mayfield's approximation [8] should be used. Glueckauf's equation (A) [6] is perhaps the optimal choice when both accuracy and convenience are considered. However, the LDF approximation has the important advantage that it does not require the determination of eigenvalues. It should be used if high accuracy is not required since the computational difficulties associated with computing eigenvalues increase rapidly with the size of the matrix.

5. CONCLUSIONS

A procedure utilizing the linearized mass-transfer theory of Stewart and co-workers is developed for extending approximations for transient binary diffusion in spherical porous particles to systems with multicomponent diffusional interactions. Calculations performed for ion exchange indicate that these methods yield acceptable accuracy for most purposes. A new approximation for binary intraparticle diffusion is developed which appears to be especially useful in representing the small time behavior, as does the matrix extension of this method. The matrix extension of a two-term approximation to integration by parts is a useful compromise method which leads to good accuracy while at the same time is convenient to use. Matrix extensions of the linear driving force approximation are the least accurate of the methods investigated but are still useful when high accuracy is not needed. Do and Mayfield's approximation becomes the preferred choice for systems with very large differences in adsorption selectivity among components.

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APPENDIX

Derivation of a new approximation for binary intraparticle diffusion

When the diffusion coefficient is constant, equations (1) and (2) can be combined to yield

$$\frac{\partial q_i}{\partial t} = D_{i,\text{eff}}\nabla^2 q_i. \tag{A1}$$

The LDF approximation, when used to solve equation (A1), assumes that the rate of change of the average concentration in the particle is the same as that of the surface concentration. Hence, the accuracy of this approximation is highest for systems that are near equilibrium. It can also be shown that the LDF approximation is equivalent to assuming a parabolic concentration profile in the particle [1], which is a poor assumption in the early stages of solute uptake. The QDF approximation, on the other hand, predicts the initial concentration change better because the steep initial concentration profile is better represented by the quadratic driving force. However, both approximations lack generality since no flexibility is allowed in either of the formulations.

Instead of modifying the order of the driving force, as in the QDF approximation, Do and Mayfield [8] proposed that the order of the polynomial representation of the profile be allowed to vary with time. The proposed profile can be written as

$$A_i = a_0 + a_1 x^E \tag{A2}$$

where a_0, a_1 and E are functions of time. It should be mentioned that this equation is only a means to obtain a better approximation of the interfacial flux; it may not in fact describe the true shape of the profile. Manipulation of equations (A1) and (A2) (see ref. [8]) yields

$$\frac{\mathrm{d}A_{i,\text{ave}}}{\mathrm{d}\tau} = 3(E+3)(A_{i,\delta} - A_{i,\text{ave}}). \tag{A3}$$

It should be noted that Do and Mayfield's approximation [8] assumes a step change in the surface concentration for the purpose of determining E as a function of τ. This method, therefore, leads to significant error in cases where the surface saturates gradually (see Fig. 4). To overcome this limitation, we now develop an improved approximation which incorporates into E an explicit dependence on the rate at which the surface concentration is changing, analogous to the dependency in Glueckauf's equation (A) [6]. It should be noted that for all of the approximation methods, the surface concentration (i.e. $A_{i,\delta}$) is calculated as a by-product; thus, $\mathrm{d}A_{i,\delta}/\mathrm{d}\tau$ makes a convenient correlation variable for use in determining E. As an additional improvement, τ can be replaced by $A_{i,\text{ave}}$ in the determination of E since this is generally more convenient for practical applications.

The average concentration and the interfacial flux are related by

$$\frac{\mathrm{d}A_{i,\text{ave}}}{\mathrm{d}\tau} = \frac{3RN_{i,\delta}}{D_i\rho_\text{p}\Delta q_{i,\text{total}}}. \tag{A4}$$

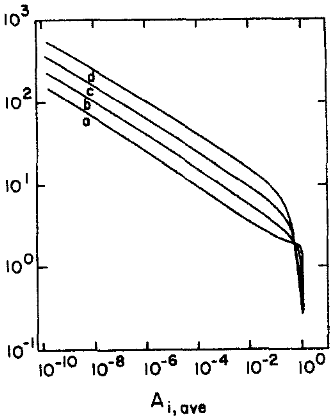

FIG. 9. Values of E as a function of dimensionless time when a constant-diffusivity binary system is subjected to a gradual rise in surface concentration prescribed by a Gaussian function. (a) $b = 0.1$; (b) $b = 1.0$; (c) $b = 10$; (d) $b = 100$.

Combination of equations (A3) and (A4) yields an explicit expression for E

$$E = \frac{RN_{i,\delta}}{D_i\rho_\text{p}\Delta q_{i,\text{total}}(A_{i,\delta} - A_{i,\text{ave}})} - 3. \tag{A5}$$

In order to develop a method for predicting E, exact solutions of equations (1) and (2) must be generated. For this purpose the surface concentration is assumed to be given by a single-sided Gaussian function

$$A_{i,\delta} = 1 - \exp(-b\tau^2) \tag{A6}$$

where b is an adjustable parameter. This choice makes the resulting method particularly suitable for fixed bed sorption processes where 'S' shaped concentration profiles are generally produced. Nevertheless, the method yields acceptable accuracy under a variety of other conditions such as when the surface concentration has an exponential dependence, as in Figs. 1–8. Numerical results using equation (A6) are illustrated in Fig. 9 which shows the functional relation between E and $A_{i,\text{ave}}$ for various values of b.

Consider the two variables defined as

$$G = -1.199 - 0.754\ln(A_{i,\text{ave}}) + 1.8383\ln\left(\frac{\mathrm{d}A_{i,\delta}}{\mathrm{d}\tau}\right) \tag{A7}$$

$$H = -1.69 - 1.2\tan^{-1}(50G). \tag{A8}$$

The curves in Fig. 9 can be empirically represented as follows: if

$$A_{i,\text{ave}} < 0.544\exp\left(\frac{0.2076G - 0.3738}{H}\right) \tag{A9}$$

then

$$\ln(E) = -0.1966\ln(A_{i,\text{ave}}) + 0.2076G + 0.1997 \tag{A10}$$

otherwise

$$\ln(E) = (H - 0.1966)\ln(A_{i,\text{ave}}) + 0.6086H + 0.5735. \tag{A11}$$

This approximation method is readily applied to multicomponent systems using procedures described in Section 2. Note that for multicomponent systems, $\tilde{A}_i$ is defined as

$$\tilde{A}_i = \frac{\tilde{q}_i - \tilde{q}_{i,\text{initial}}}{\tilde{q}_{i,\text{final}} - \tilde{q}_{i,\text{initial}}}. \tag{A12}$$

As an example of the application of these equations, consider mass transfer from a fluid to a porous particle with transport resistances in both phases. If a simple Euler integration technique is used, the method involves the following steps: (i) select a large value for E to begin the calculation (e.g. $E = e^{10}$); (ii) determine the value of the concentrations at the particle–fluid interface by solving simultaneously the equilibrium relation at the interface and the flux equations for both fluid and intraparticle mass transfer; (iii) determine $\Delta A_{i,\mathrm{ave}}$ for the time step $\Delta\tau$ using equation (A4); (iv) determine $\Delta A_{i,\delta}/\Delta\tau$ for the time step by repeating step (ii); (iv) calculate E using equations (A7)–(A11); (v) return to step (iii).

CALCUL MATRICIEL DE LA DIFFUSION VARIABLE DE PLUSIEURS COMPOSANTS DANS DES MILIEUX POREUX

Résumé—La théorie linéarisée du transfert de masse décrite par Stewart et alii est employée pour développer des méthodes générales matricielles qui étendent les approximations pour la diffusion binaire variable dans les milieux poreux aux cas des interactions entre plusieurs composants. La précision de ces approximations élargies et leur adéquation comme méthode simple, efficace pour simuler les mécanismes de sorption sont étudiées pour le transfert de masse par échanges d'ions. On développe une nouvelle approximation de la diffusion binaire intraparticulaire et on l'évalue.

BERECHNUNG DER TRANSIENTEN DIFFUSION MEHRERER KOMPONENTEN IN PORÖSEN ABSORBENTEN

Zusammenfassung—Die von Stewart u.a. beschriebene linearisierte Theorie des Stofftransports wird angewandt, um mit Hilfe allgemeiner Matrix-Methoden die Näherungen für die instationäre Zweistoff-Diffusion in porösen Absorbenten auf Fälle mit Wechselwirkungen mehrerer Komponenten zu erweitern. Die Genauigkeit dieser erweiterten Näherungen und ihre Eignung als einfache effiziente Methode für die Beschreibung der Diffusion von Partikeln mehrerer Komponenten bei Sorptionsprozessen wurde für den Stofftransport durch Ionen-Austausch untersucht. Außerdem wurde eine neue Näherungsmethode für Zweistoff-Diffusion entwickelt und ausgewertet.

МАТРИЧНЫЙ РАСЧЕТ МНОГОКОМПОНЕНТНОЙ НЕСТАЦИОНАРНОЙ ДИФФУЗИИ В ПОРИСТЫХ СОРБЕНТАХ

Аннотация—С использованием описанной Стюартом и его соавторами линеаризованной теории массопереноса разработаны общие матричные методы, позволяющие применить приближения для нестационарной бинарной диффузии в пористых сорбентах к случаям с многокомпонентными взаимодействиями. Исследована точность таких обобщенных приближений и их применимость в качестве простого эффективного метода учета многокомпонентной диффузии внутри частиц для моделирования процессов сорбции при массопереносе с ионным обменом. Предложено новое приближение для бинарной диффузии внутри частиц и дана его оценка.