$$\left. + 3\eta^2 r_w{}^2 (r''_w)^2 - 36\eta^2 r_w (r'_w)^2 r''_w + 4\eta^2 r_w{}^2 r'_w r'''_w \right] \frac{\partial^2}{\partial \eta^2}$$

$$\frac{1}{r_w{}^2}\left[24\eta r'_w r''_w - \frac{24\eta}{r_w}(r'_w)^3 + \frac{4}{\eta r_w} r'_w - 4\eta r_w r'''_w \right]$$

$$\frac{\partial^2}{\partial z \partial \eta} + \frac{1}{r_w{}^4}\left[- \frac{3}{\eta^3} - \frac{4}{\eta}(r'_w)^2 + 24\eta(r'_w)^4 \right.$$

$$- 36\eta r_w (r'_w)^2 r''_w + 8\eta r_w{}^2 r'_w r'''_w + 6\eta r_w{}^2 (r''_w)^2$$

$$\left. + \frac{2}{\eta} r_w r''_w - \eta r_w{}^3 r_w{}^{(iv)} \right] \frac{\partial}{\partial \eta}$$

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Multicomponent Liquid Phase Adsorption in Fixed Bed

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Although multicomponent, liquid phase adsorption is often encountered in industrial application, most of the studies concerning fixed-bed sorption processes have been dealt primarily with systems containing one adsorbable species. The present work provides a numerical solution to the fixed-bed, multicomponent adsorption problem, taking into account both separately or in combination the effect of liquid and/or solid phase mass transfer resistance and of variation of the assumed governing adsorption isotherm. Numerical solutions of several example problems are presented and compared with results based on equilibrium theory and a simplified method developed by Cooney and co-workers previously (1972).

SCOPE

This work was undertaken in order to establish a rigorous general theoretical model pertaining to fixed-bed adsorption in multicomponent liquid systems. The nonequilibrium theory developed here is capable of accommodating, separately as well as in combination, the effects of liquid and/or solid mass transfer resistances and of variations in the form of the assumed governing adsorption isotherm, and it can therefore be used to estimate the interactive influences of these effects. Furthermore, the present theory can be used to assess the effectiveness of approximations based on the computationally convenient, though physically unrealistic, concepts of equilibrium or single solute lumping. The theory can be extended, in principle, to account for an increasing number of possible adsorbable species, and this makes it particularly apt for wastewater adsorption processes.

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CONCLUSIONS AND SIGNIFICANCE

The results of this study represent a more general, and also more realistic, alternative to most available theoretical analyses on fixed-bed, multicomponent liquid adsorption. The significance of these results resides in their freedom from the equilibrium assumption, their ability to account for the coexistence of various competing adsorbable species, and their flexibility to accommodate varying combinations of liquid or solid mass transfer resistances and assumed forms of the governing adsorption isotherm. Aside from their providing a more faithful description of actual liquid phase adsorption processes, which almost invariably involve many adsorbable species, these results can be used to evaluate the various approximation schemes and the compromises entailed by them. While the results of such evaluations suggest that under certain circumstances the approximation can differ measurably from the exact solution, important methods such as the equilibrium based *h*-transformation procedure, which is computationally convenient and conceptually elegant, would find wider use if their limitations were defined.

Fixed-bed, liquid phase adsorption is not an uncommon procedure in industrial separation and purification processes. Although most processes involve multicomponent systems, the literature in this area pertains in the main to systems comprised of a single adsorbable species. Unlike the single-solute case, multicomponent adsorption is characterized by interactive and competitive effects involving the various adsorbable species. These effects may manifest themselves in two ways: competition in the mass transfer process (within and surrounding the adsorbent), and displacement from the adsorbent of those species possessing lower adsorption affinities in favor of those with higher values. The latter effect is illustrated in Figure 1, which portrays the effluent history for a liquid comprising two adsorbable solutes with different adsorption affinities passing through an adsorption column. It is shown here that the effluent concentration of the species possessing the lower adsorption affinity rises above the inlet value at a certain time, and this result (which could never happen in single-solute adsorption) is a direct consequence of the displacement from the adsorbent of this component by the second solute which has a higher adsorption affinity.

In general, calculations relating to the dynamic behavior of sorptive processes in fixed beds can be classified according to two categories: those based on equilibrium theory and those based on nonequilibrium theory. Among the various studies based on equilibrium theory, the *h*-transformation method for Langmuir types of isotherms proposed by Helfferich (1967, 1968) and by Helfferich and Klein (1970) is the most comprehensive. The application of the *h*-transformation for multicomponent adsorption in fixed bed was recently reexamined and clarified by Tien et al. (1976).* According to the equilibrium theory, local equilibrium is assumed between the fluid and the sorbent phases, and mass transfer effects both within and outside the sorbent are eliminated. Thus it is possible to obtain important information on the performance of the adsorption column using stoichiometric and equilibrium relations without excessive calculation. The convenience obtained entails compromises in accuracy, since the mass transfer effect is one of the most important factors in the design of any mass transfer process.

Useful as they are on a qualitative or even semiquantitative level, the results of the equilibrium theory are not equal to the more stringent requirements of design work. A quantitative prediction model of fixed-bed, multicomponent adsorption requires that the restriction of local equilibrium be relaxed. Efforts to obtain analytical solutions for nonequilibrium multicomponent interactive adsorption in fixed beds have, in the past, met with very limited success. Since the equilibrium isotherms for multicomponent systems are likely to be nonlinear, the need to resort to numerical methods is inevitable. Dranoff and Lapilus (1958) considered the ion exchange problem in batch and fixed-bed systems with two different exchangeable species present in the liquid phase. Solutions were obtained for the case when the ion exchange rate is of second order and the reaction is reversible. It is difficult, however, to extend this scheme to the analysis of adsorption in multicomponent systems, since the second-order rate expression does not always hold true for such processes.

A rather ingenious scheme for dealing with multicomponent adsorption calculations was proposed by Cooney and co-workers (1966, 1972). It represents an extension to multicomponent systems of the asymptotic results for the single-solute case obtained previously by them (Cooney and Lightfoot, 1965). These authors argued that for fixed-bed operation, the saturation curve pertaining to equilibrium theory can be considered to be applicable to the nonequilibrium case, provided the ratio of the mass transfer coefficients of the various species are near unity. For a binary system, Cooney and Strusi (1972) demonstrated that if one assumes that the liquid phase concentrations of the two species are related in accordance with the equilibrium theory, and if this relationship is substituted into the adsorption isotherm for the binary solute system, the generalized Langmuir isotherm can be decomposed into two separate isotherms,

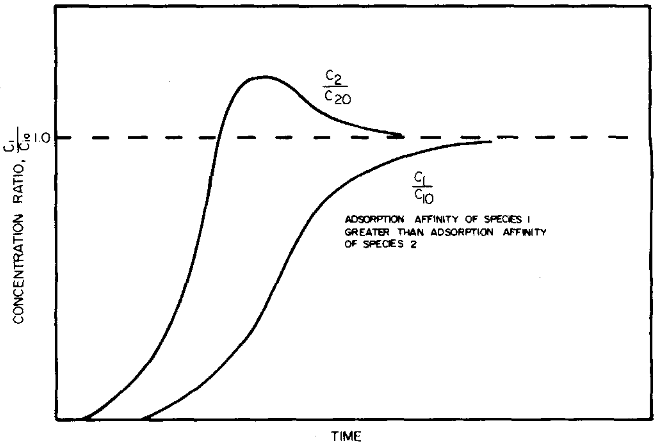

Fig. 1. Breakthrough curve for a two-component system.

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* See also the correspondence with Helfferich in this issue of the Journal.

each of which could be treated as a pseudo single-solute isotherm. The transformation therefore, in effect, reduces the original two-component Langmuir adsorption system into two single-component systems. It is not clear whether this transformation can be enforced if the number of the adsorbable species exceeds two, nor is it clear to what degree the accuracy of the approximation would suffer if the mass transfer coefficients corresponding to the various species are widely different.

In a more recent work directed at establishing a comprehensive method for the design of activated carbon columns for waste treatment, Weber and Crittenden (1975) carried out adsorption calculations pertaining to two adsorbable species. The equilibrium relationship was assumed to follow the modified Langmuir type developed by Jain and Snoeyink (1973), and the rate controlling step was considered to be due to liquid phase diffusion. However, neither the case of particle diffusion (or pore diffusion) control nor the more general case of combined external and particle diffusion were considered.

The aim of the present work is to examine the fixed-bed, multicomponent adsorption problem in a more generalized way and to develop the necessary numerical method for its solution. Comparisons between the present study and the previous ones, including the h-transformation and the asymptotic solution of Cooney, are presented through use of example cases in order that the applicability of the various methods as well as their limitations can be placed in perspective. In addition, procedures are developed for estimating the rate parameters required in the present analysis.

GOVERNING EQUATIONS

For the isothermal, fixed-bed, multicomponent adsorption problem considered here, it is assumed that a fluid stream containing N adsorbable species of known concentrations passes through a bed packed with adsorbents with prescribed initial saturation. If the flow is uniform over any given cross section of the bed (that is, plug flow), and the effect of axial dispersion is insignificant, the macroscopic conservation equations for each adsorbable species can be written as

$$u\left(\frac{\partial c_i}{\partial z}\right) + \epsilon\left(\frac{\partial c_i}{\partial t}\right) + \rho\left(\frac{\partial q_i}{\partial t}\right) = 0 \qquad (1)$$

$$i = 1, 2, 3, \ldots N$$

If one views adsorption as a mass transfer process, the most general rate expression should include effects taking place both within and outside the adsorbent. The rate of adsorption for each species is given by

$$\frac{\partial q_i}{\partial t} = \frac{k_{li}}{\rho}(c_i - c_{si}) = k_{si}(q_{si} - q_i) \qquad (2)$$

$$i = 1, 2, 3, \ldots N$$

which assumes that equilibrium exists at the fluid-particle interface.

The linear driving force approximation is used in describing the diffusion phenomenon within the adsorbent. The use of this approximation greatly simplifies subsequent calculations. The mass transfer coefficients k_l and k_s are assumed to be constant and independent of the transfer rates of the various species. They can be estimated, at least in principle, from empirical correlations or other means. Thus, the interactive and competitive effects characteristic of multicomponent adsorption are accounted for only through the adsorption isotherm which is assumed to be of the Langmuir type, given by

$$q_{si} = \frac{a_i c_{si}}{1 + \sum_{j=1}^{N} b_j c_{sj}} \qquad (3)$$

$$i = 1, 2, 3, \ldots . N$$

The applicability of the present analysis to other kinds of isotherm relationships will be discussed later. In dimensionless form, the above equations reduce to

$$\frac{\partial x_i}{\partial Z} + \rho a_i \frac{\partial y_i}{\partial \theta} = 0 \qquad (4)$$

$$\frac{\partial y_i}{\partial \theta} = \xi_i^l (x_i - x_{si}) = \xi_i^s (y_{si} - y_i) \qquad (5)$$

$$\xi_i^l = \frac{L k_{li}\left(1 + \sum_{j=1}^{N} b_j c_{jo}\right)}{\rho a_i u} \qquad (6)$$

$$\xi_i^s = \frac{L k_{si}}{u} \qquad (7)$$

$$y_{si} = \frac{\left(1 + \sum_{j=1}^{N} b_j c_{jo}\right) x_{si}}{1 + \sum_{j=1}^{N} b_j c_{jo} x_{sj}} \qquad (8)$$

The dimensionless variables used in the above equations are defined by

$$x_i = \frac{c_i}{c_{io}} \qquad (9)$$

$$y_i = \frac{q_i}{q_{io}} \qquad (10)$$

$$Z = \frac{z}{L\left(1 + \sum_{j=1}^{N} b_j c_{jo}\right)} \qquad (11)$$

$$\theta = \frac{u}{L}\left(t - \frac{\epsilon z}{u}\right) \qquad (12)$$

$$q_{i_o} = \frac{a_i c_{io}}{1 + \sum_{j=1}^{N} b_j c_{io}} \qquad (13)$$

If we use the above definitions, the throughput parameter T is $(\theta/\rho Z)\left(\sum_{i=0}^{N} c_{io} \middle/ \sum_{i=1}^{N} a_i c_{io}\right)$.

The most common case in adsorption is the one in which the adsorbent is initially free of adsorbates, and the influent concentration is constant. The corresponding initial and boundary conditions are[*]

$$y_i(Z, 0) = 0 \qquad (14)$$

$$x_i(0, \theta) = 1 \qquad (15)$$

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[*] The numerical method developed can be easily modified to consider more complicated initial and boundary conditions.

NUMERICAL SOLUTION

Development of Computation Algorithms

A third-order method of characteristic algorithms developed previously by Vanier (1970) for the solution of the semilinear hyperbolic equations will be used for the numerical solution of Equations (4) and (5). The computation network is shown in Figure 2. In Vanier's method, the calculation of the dependent variables, x_i's and y_i's at point (j, n) is based on the values of x_i's and y_i's at the neighboring points (k, l) for $k < j$ and $l < n$. First, a set of approximate values of x_i and y_i at point (j, n) are calculated using

$$x_i^{(1)}(j, n) = x_i(j-1, n) + x_i(j, n-1) - x_i(j-1, n-1) + \Delta Z\left[\frac{dx_i(j-1, n)}{dZ} - \frac{dx_i(j-1, n-1)}{dZ}\right] \quad (16)$$

$$y_i^{(1)}(j, n) = y_i(j-1, n) + y_i(j, n-1) - y_i(j-1, n-1) + \Delta\theta\left[\frac{dy_i(j, n-1)}{d\theta} - \frac{dy_i(j-1, n-1)}{d\theta}\right] \quad (17)$$

Next, the second approximations are obtained using the following expressions:

$$x_i^{(2)}(j, n) = x_i^{(1)}(j, n) + \frac{\Delta Z}{2}\left[\frac{dx_i(j, n)}{dZ} + \frac{dx_i(j-1, n-1)}{dZ} - \frac{dx_i(j, n-1)}{dZ} - \frac{dx_i(j-1, n)}{dZ}\right] \quad (18)$$

$$y_i^{(2)}(j, n) = y_i^{(1)}(j, n) + \frac{\Delta\theta}{2}\left[\frac{dy_i(j, n)}{d\theta} + \frac{dy_i(j-1, n-1)}{d\theta} - \frac{dy_i(j, n-1)}{d\theta} - \frac{dy_i(j-1, n)}{d\theta}\right] \quad (19)$$

Vanier (1970) has asserted that the accuracy of the above iteration algorithm may be improved by applying Simpson's rule on alternate steps, which entails the use of the following equations:

$$x_i(j, n) = x_i(j-2, n) + \frac{\Delta Z}{3}\left[\frac{dx_i(j-2, n)}{dZ} + 4\frac{dx_i(j-1, n)}{dZ} + \frac{dx_i(j, n)}{dZ}\right] \quad (20)$$

$$y_i(j, n) = y_i(j, n-2) + \frac{\Delta\theta}{3}\left[\frac{dy_i}{d\theta}(j, n-2) + 4\frac{dy_i}{d\theta}(y, n-1) + \frac{dy_i}{d\theta}(j, n)\right] \quad (21)$$

In using Equations (20) and (21), function evaluations are required not only at immediate neighboring points of point (j, n) but at points $(j-2, n)$ and $(j, n-2)$ as well. The numerical calculations are carried out according to the following steps:

1. The values of $x_i(j, n)$ and $y_i(j, n)$ at $(j = 1, \ldots, k;\ n = 0)$ and $(j = 0;\ n = 1, \ldots, k)$ are obtained from initialization along axis $\theta = 0$ and $Z = 0$.
2. The values of x_i and y_i at (1, 1), (1, 2) and (2, 1) are evaluated from Equations (16) to (19).
3. The values of $x_i(2, 1)$ are recalculated again by applying Simpson's rule [Equation (20)] using the values of x_i at (0., 1), (1, 1) and (2, 1) obtained in step 2.

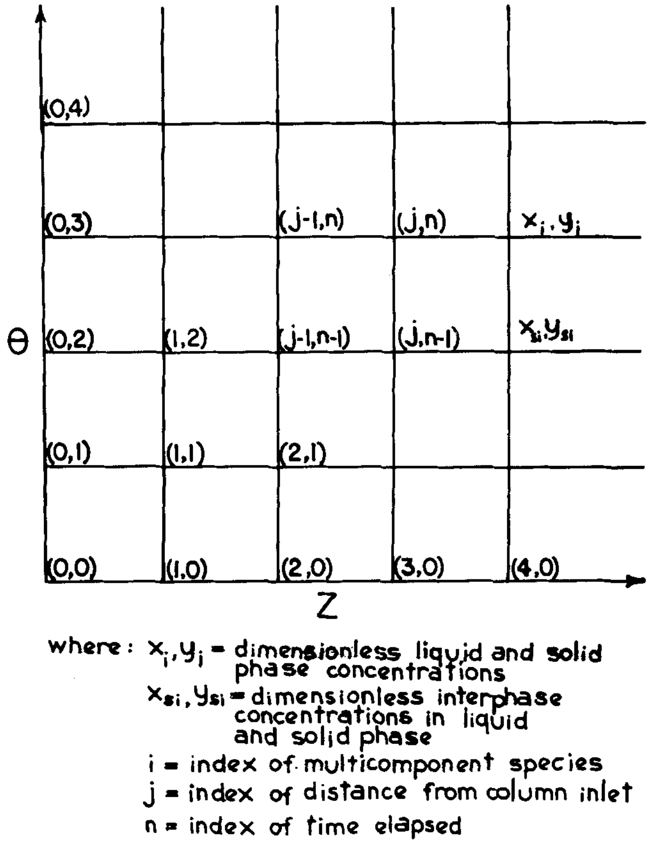

Fig. 2. Computation grids for the numerical integration.

4. The value of $y_i(1, 2)$ is recalculated again by applying Simpson's rule [Equation (21)] using the values of y_i at (1, 0), (1, 1) and (1, 2) obtained in step 2.
5. Now the values of $x_i(2, 2)$ and $y_i(2, 2)$ are evaluated from Equations (16) to (19) using the values of x_i and y_i at (1, 1), (1, 2) and (2, 1).
6. Then the values of $x_i(2, 2)$ and $y_i(2, 2)$ are recalculated again using Simpson's rule [use Equations (20) and (21), respectively].
7. Similarly, for other grid points, $x_i(j, n)$ and $y_i(j, n)$ can be computed. Simpson's rule is only applied to the points x_i and y_i when j (or n) is even.
8. In all, the values of x_i and y_i at point (j, n) (except those on axis $\theta = 0$ and $Z = 0$) are calculated once using Equation (16) to (19).
9. The values of x_i at $(2, n)$, $(4, n)$, $(6, n)$, . . . are evaluated once more by applying Equation (20).
10. The values of y_i at $(j, 2)$, $(j, 4)$, $(j, 6)$, . . . are evaluated once more by applying Equation (21).
11. In other words, the values of both $x_i(j, n)$ and $y_i(j, n)$, at $j = 2, 4, 6 \ldots$ and $n = 2, 4, 6, \ldots$ are reevaluated by applying Simpson's rule [Equation (20) and (21)] in addition to the calculations from Equations (16) to (19).

Evaluation of Interphase Concentrations

The algorithm described in the previous section requires the knowledge of the derivatives, $\partial x_i/\partial Z$ and $\partial y_i/\partial\theta$ for numerical calculation. From the governing equations for the multicomponent adsorption system [Equation (4) and (5)], these derivatives are expressed not only in terms of x_i and y_i, but also in terms of the interphase concentrations (that is, x_{si} and y_{si}) which are related through Equation (8), in which the equilibrium concentration in the particle phase of an individual species is expressed as a function of the equilibrium concentrations in the fluid phase of all species. This represents the major distinguishing feature of multicomponent adsorption. Next we consider procedures for the evaluation of the interphase concentrations from the bulk concentrations.

Liquid Phase Controlling. If external diffusion is considered rate controlling, the concentration gradient within the solid phase is taken to be insignificant, and the liquid interphase concentration x_{si} can be assumed to be in equilibrium with the solid phase average concentration y_i. y_i and x_{si} can, therefore, be related by the adsorption isotherm, or

$$y_i = \frac{\left(1 + \sum_{j=1}^{N} b_j c_{jo}\right) x_{si}}{\left(1 + \sum_{j=1}^{N} b_j c_{jo} x_{sj}\right)} \tag{22}$$

It can be seen from Equation (22) that the ratio of x_{si} to y_i is the same for all $i = 1, 2, 3, \ldots. N$. This ratio is designated by p_l, which is defined as

$$P_l = \frac{x_{si}}{y_i} = \frac{\left(1 + \sum_{j=1}^{N} b_j c_{jo} x_{sj}\right)}{\left(1 + \sum_{j=1}^{N} b_j c_{jo}\right)} \tag{23}$$

Equation (23) gives P_l as a function of the interphase composition x_{sj}. In order to put P_l in a more convenient form for computation purposes, it is desirable to express it in terms of y_i. Therefore, all the x_{sj} in Equation (23) can be replaced by $(P_l y_i)$, where one gets

$$P_l\left(1 + \sum_{j=1}^{N} b_j c_{jo}\right) = \left(1 + \sum_{j=1}^{N} b_j c_{jo} P_l y_j\right) \tag{24}$$

or

$$P_l\left[1 + \sum_{j=1}^{N} b_j c_{jo}(1 - y_j)\right] = 1 \tag{25}$$

that is

$$P_l = \frac{1}{1 + \sum_{j=1}^{N} b_j c_{jo}(1 - y_j)} \tag{26}$$

Thus, the liquid interphase concentration x_{si} is expressed as

$$x_{si} = P_l y_i = \frac{y_i}{1 + \sum_{j=1}^{N} b_j c_{jo}(1 - y_j)} \tag{27}$$

Since P_l is, by definition, always positive, Equation (26) or (27) leads to the following constraint which must be invoked in carrying out the calculations:

$$\sum_{j=1}^{N} b_j c_{jo}(1 - y_j) > -1 \tag{28}$$

The constraint embodied in Equation (28) may at first glance seem redundant, but it is necessary because for a multicomponent adsorption system, an overshoot peak can occur in the breakthrough curves for species with lower adsorption affinities, thus resulting in y_i values exceeding unity. It is conceivable that the use of too large an increment size could lead to negative values of P_l, thereby resulting in physically meaningless solutions. In summary, the governing equations for the multicomponent, nonequilibrium, fixed-bed adsorption with liquid phase controlling can be written as

$$\frac{\partial x_i}{\partial Z} + \rho a_i \frac{\partial y_i}{\partial \theta} = 0 \tag{29}$$

$$\frac{\partial y_i}{\partial \theta} = \xi_i^l \left\{ x_i - \frac{y_i}{1 + \sum_{j=1}^{N} b_j c_{jo}(1 - y_j)} \right\} \tag{30}$$

where

$$\xi_i^l = \frac{L k_{li}\left(1 + \sum_{j=1}^{N} b_j c_{jo}\right)}{\rho a_i u} \tag{31}$$

Equations (29) and (30) can be integrated using the third-order scheme described before.

Solid Phase Controlling. In a similar fashion, if particle diffusion is rate controlling, the solid interphase concentration y_{si} may be considered to be in equilibrium with the liquid phase average concentration x_i. The equilibrium relationship between y_{si} and x_i is

$$y_{si} = \frac{\left(1 + \sum_{j=1}^{N} b_j c_{jo}\right) x_i}{1 + \sum_{j=1}^{N} b_j c_{jo} x_i} \tag{32}$$

It can again be observed from Equation (32) that the ratios of y_{si} to x_i are constant for $i = 1, 2, 3, \ldots N$ which, in this case, is designated as p_s and given by

$$P_s = \frac{y_{si}}{x_i} = \frac{1 + \sum_{j=1}^{N} b_j c_{jo}}{1 + \sum_{j=1}^{N} b_j c_{jo} x_j} \tag{33}$$

which is a function of x_j. The solid interphase concentration y_{si} is given by

$$y_{si} = P_s x_i = \frac{1 + \sum_{j=1}^{N} b_j c_{jo}}{1 + \sum_{j=1}^{N} b_j c_{jo} x_j} x_i \tag{34}$$

In summary, the governing equations for the multicomponent, nonequilibrium, fixed-bed adsorption with solid phase controlling are given by

$$\frac{\partial x_i}{\partial Z} + \rho a_i \frac{\partial y_i}{\partial \theta} = 0 \tag{35}$$

$$\frac{\partial y_i}{\partial \theta} = \xi_i^s \left\{ \frac{1 + \sum_{j=1}^{N} b_j c_{jo}}{1 + \sum_{j=1}^{N} b_j c_{jo} x_j} x_i - y_i \right\} \tag{36}$$

where

$$\xi_i^s = \frac{Lk_{si}}{u} \tag{37}$$

Equations (35) and (36) can be solved readily using the algorithm described previously.

Combined Liquid and Solid Phases Controlling. For the two special cases discussed above, it is possible to eliminate the surface concentration terms from the rate expression (that is, $dy_i/d\theta$). In the general case when mass transfer effects in the solid and liquid phases are of comparable magnitude, however, this is not permissible, since these effects must be considered simultaneously. In the context of the numerical scheme developed in this work, once the dependent variables x_i's and y_i's are determined at a new point (j, n), it is necessary to find the corresponding set of values x_{si}'s and y_{si}'s so that the values of $dy_i/d\theta$ and dx_i/dz at the new point (j, n) can be evaluated. These concentration terms are related by the rate and isotherm expressions

$$x_i - x_{si} = \frac{\xi_i^s}{\xi_i^l}(y_{si} - y_i) = \phi_i(y_{si} - y_i) \tag{38}$$

$$y_{si} = \frac{\left(1 + \sum\limits_{j=1}^{N} b_j c_{jo}\right) x_{si}}{1 + \sum\limits_{j=1}^{N} b_j c_{jo} x_{sj}} \tag{39}$$

$$i = 1, 2, 3, \ldots . N$$

Considerable work was done in developing the recessing iterative procedures which were used to calculate values of x_{si} and y_{si} in terms of x_i and y_i from the above two equations. The detailed description of this part of the work can be found in Hsieh's thesis (1974). The basic elements of the procedure are described here. By combining Equations (38) and (39) and eliminating the liquid phase concentration at the interface, x_{si}, y_{si} can be expressed as

$$y_{si} = \frac{\left(1 + \sum\limits_{j=1}^{N} b_j c_{jo}\right)[x_i - \phi_i(y_{si} - y_i)]}{1 + \sum\limits_{j=1}^{N} b_j c_{jo}[x_j - \phi_j(y_{sj} - y_j)]} \tag{40}$$

After rearrangement, one has

$$b_i c_{io} \phi_i y^2{}_{si} - \left[1 + \sum_{j=1}^{N} b_j c_{jo}(x_j + \phi_j y_j) + \phi_i\left(1 + \sum_{j=1}^{N} b_j c_{jo}\right) - \sum_{j \neq 1}^{N} b_j c_{jo} \phi_j y_{sj}\right] y_{si} + \left(1 + \sum_{j=1}^{N} b_j c_{jo}\right)(x_i + \phi_i y_i) = 0 \tag{41}$$

$$i = 1, 2, 3, \ldots . N$$

For systems containing one adsorbable species, Equation (41) is simplified to

$$b_1 c_{10} \phi_1 y^2{}_{s1} - [1 + b_1 c_{10}(x_1 + \phi_1 y_1) + \phi_1(1 + b_1 c_{10})] y_{s1} + (1 + b_1 c_{10})(x_1 + \phi_1 y_1) = 0 \tag{42}$$

or

$$y_{s1} = \frac{[1 + b_1 c_{10}(x_1 + \phi_1 y_1) + \phi_1(1 + b_1 c_{10})]}{2 b_1 c_{10} \phi_1} \pm \frac{\sqrt{[1 + b_1 c_{10}(x_1 + \phi_1 y_1) + \phi_1(1 + b_1 c_{10})]^2 - 4 b_1 c_{10} \phi_1 (1 + b_1 c_{10})(x_1 + \phi_1 y_1)}}{2 b_1 c_{10} \phi_1} \tag{43}$$

From the pairs of values of y_{si} given above, the one corresponding to the negative sign is physically meaningful as demonstrated in trial calculations (Hsieh, 1974). This is also true for cases with more than one adsorbable species. Equation (41) for $i = 1, i = 2, \ldots ., i = N$ gives

$$b_1 c_{10} \phi_1 y^2{}_{si} s_1 - \left[1 + \sum_{j=1}^{N} b_j c_{jo}(x_j + \phi_j y_j) + \phi_1\left(1 + \sum_{j=1}^{N} b_j c_{jo}\right) - \sum_{j=2}^{N} b_j c_{jo} \phi_j y_{sj}\right] y_{s1} + \left(1 + \sum_{j=1}^{N} b_j c_{jo}\right)(x_1 + \phi_1 y_1) = 0 \tag{44a}$$

$$b_2 c_{20} \phi_2 y^2{}_{s2} - \left[1 + \sum_{j=1}^{N} b_j c_{jo}(x_j + \phi_j y_j) + \phi_2\left(1 + \sum_{j=1}^{N} b_j c_{jo}\right) - \sum_{\substack{j=1 \\ j \neq 2}}^{N} b_j c_{jo} \phi_j y_{sj}\right] y_{s2} + \left(1 + \sum_{j=1}^{N} b_j c_{jo}\right)(x_2 + \phi_2 y_2) = 0 \tag{44b}$$

$$b_N c_{No} \phi_N y^2{}_{sN} - \left[1 + \sum_{j=1}^{N-1} b_j c_{jo}(x_j + \phi_j y_j) + \phi_N\left(1 + \sum_{j=1}^{N-1} b_j c_{jo}\right) - \sum_{j=1}^{N-1} b_j c_{jo} \phi_j y_{sj}\right] y_{sN} + \left(1 + \sum_{j=1}^{N} b_j c_{jo}\right)(x_N + \phi_n y_N) = 0 \tag{44c}$$

To obtain the values of y_{si} from the above equations, a set of values of $y_{s2}^{(1)}, y_{s3}^{(1)}, \ldots ., y_{sN}^{(1)}$ is assumed first. Then the value of $y_{s1}^{(2)}$ can be calculated from Equation (44*a*). The available values of $y_{s1}^{(2)}, y_{s3}^{(1)} \ldots ., y_{sN}^{(1)}$ are used to calculate the $y_{s2}^{(2)}$ from Equation (44*b*). Similarly, $y_{s3}^{(2)}, y_{s4}^{(2)}, \ldots ., y_{s,N-1}^{(2)}$ can be obtained. Finally, the value of $y_{sN}^{(2)}$ is calculated from Equation (44*c*) based on the available values of $y_{s1}^{(2)}, y_{s2}^{(2)}, \ldots ., y_{s,N-1}^{(2)}$. In general, the value of $y_{si}^{(k)}$ is calculated from the values of $y_{s1}^{(k)}, y_{s2}^{(k)}, \ldots ., y_{s,i-1}^{(k)}, y_{s,i+1}^{(k-1)}, \ldots ., y_{sN}^{(k-1)}$. Therefore, $y_{s1}^{(3)}$ is evaluated from the values of $y_{s2}^{(2)}, y_{s3}^{(2)}, \ldots ., y_{s,N}^{(2)}$, and $y_{si}^{(3)}$ is

Table 1. Number of Iteration Required for Computation of Interphase Concentrations

$[x_i - x_{si} = \phi_i(y_{si} - y_i); x_1 = x_2 = 1, y_1 = y_2 = 0]$

$\phi_1 = \frac{\xi_1^s}{\xi_1^l}$	$\phi_2 = \frac{\xi_2^s}{\xi_2^l}$	No. of iteration	x_{s1}	x_{s2}	y_{s1}	y_{s2}
0.9×10^{-3}	0.9×10^{-3}	2	0.99911	0.99913	0.99996	0.99998
0.9×10^{-1}	0.9×10^{-1}	3	0.91160	0.91339	0.99526	0.99722
0.17765	0.17370	4	0.82415	0.82739	0.98988	0.99377
0.26648	0.26055	4	0.73787	0.74221	0.98366	0.98943
0.37307	0.36476	5	0.63636	0.64156	0.97472	0.98268
0.44768	0.43772	5	0.56701	0.57252	0.96718	0.97659
0.49245	0.48149	6	0.52626	0.53187	0.96200	0.97225
0.54169	0.52964	6	0.48235	0.48797	0.95561	0.96675
0.65003	0.63556	7	0.39004	0.39541	0.93835	0.95126
0.72390	0.70779	7	0.33161	0.33662	0.92331	0.93725
0.83611	0.81749	8	0.25261	0.25688	0.89389	0.90902
0.88826	0.86848	8	0.22083	0.22472	0.87719	0.89267
0.98365	0.96176	8	0.17191	0.17514	0.84184	0.85766
1.18038	1.15411	8	0.10618	0.10834	0.75723	0.77260
1.77058	1.73116	5	0.04200	0.04292	0.54106	0.55285
2.65586	2.59674	5	0.02109	0.02155	0.36859	0.37680
5.31172	5.19349	4	0.00836	0.00855	0.18669	0.19090
10.62345	10.38698	3	0.00378	0.00387	0.09378	0.09590
84.98758	83.09580	3	0.00044	0.00045	0.01176	0.01203
339.95033	322.38319	2	0.00011	0.00011	0.00294	0.00301

calculated from the values of $y_{s1}^{(3)}, y_{s2}^{(3)}, \ldots, y_{s,i-1}^{(3)}, y_{s,i+1}^{(2)}, \ldots, y_{sN}^{(2)}$. The value of $y_{sN}^{(3)}$ is calculated from values of $y_{s1}^{(3)}, y_{s2}^{(3)}, \ldots, y_{s,N-1}^{(3)}$. This kind of iteration is carried out repeatedly until the differences of $(y_{s1}^{(m-1)} - y_{s1}^{(m)})$, $(y_{s2}^{(m-1)} - y_{s2}^{(m)}), \ldots, y_{sN}^{(m-1)} - y_{sN}^{(m)})$ are smaller than the preassigned tolerance of error.

The results of an illustrative example of the iteration procedure for a two-component system are listed in Table 1. The important factor in determining the number of iterations is the value of ϕ_i which can be viewed as a measure of the relative resistance to mass transfer in the liquid and solid phases [see Equation (38)]. The number of iterations required increases sharply when the resistances in these two phases become comparable (that is, $\frac{1}{2} < \phi_i < 2$).

When Equations (44*a*) to (44*c*) are used for the iteration algorithm, the y_{si} values are obtained first, and the corresponding x_{si} can be calculated using the rate expression Equation (38). Of course, analogous expressions with x_{si}'s as variables can be obtained by substituting Equation (39) into Equations (44*a*) to (44*c*). The time required, however, was found to be significantly greater, and the method was therefore not used.

Initialization Along Z and θ Axis

To begin the numerical calculation described above, values of x_i's and y_i's (and x_{si}'s and y_{si}'s for the case of combined liquid and solid phase mass transfer) along the Z and θ axis are required. The computation of these values is referred to as initialization.

Liquid Phase Controlling. As mentioned previously, if the rate controlling step is that of liquid phase diffusion, x_{si} is in equilibrium with y_i. Along the Z axis (that is, $\theta = 0$), from Equation (14)

$$y_i = 0 \qquad (14)$$

Equations (29) and (30) become

$$\frac{dx_i}{dZ} = -\rho a_i \frac{\partial y_i}{\partial \theta} = -\rho a_i \xi_i^l x_i$$

and

$$x_i = 1 \quad \text{at} \quad Z = 0$$

or

$$x_i = e^{-\rho a_i \xi_i^l z}$$

$$i = 1, 2, 3, \ldots. N \qquad (45)$$

Equations (14) and (45) give the values of x_i and y_i along the Z axis. Along the θ axis (that is, Z = 0), from Equation (15)

$$x_i = 1 \qquad (15)$$

Equation (30) becomes

$$\frac{dy_i}{d\theta} = \xi_i^l \left\{ 1 - \frac{y_i}{\sum_{j=1}^{N} b_j c_{jo}(1 - y_j)} \right\};$$

$$i = 1, 2, \ldots N \qquad (46a)$$

and

$$y_i = 0 \quad \text{at} \quad \theta = 0 \qquad (46b)$$

Equations (46*a*) and (46*b*) can be solved numerically (Runge-Kutta method) to obtain values of y_i as a function of θ. These, together with Equation (15), complete the initialization along the θ axis.

Solid Phase Controlling. Along the Z axis (that is, θ = 0), Equation (14) gives

$$y_i = 0 \qquad (14)$$

Equations (35) and (36) become

$$\frac{dx_i}{dZ} = -\rho a_i \xi_i^s \left[\frac{1 + \sum_{j=1}^{N} b_j c_{jo}}{1 + \sum_{j=1}^{N} b_j c_{jo} x_j} \right] x_i$$

$$i = 1, 2, 3, \ldots. N \qquad (47a)$$

$$x_i = 1 \quad \text{at} \quad Z = 0 \qquad (47b)$$

Similar to Equations (46*a*) and (46*b*), Equations (47*a*) and (47*b*) can be solved using the Runge-Kutta method to obtain x_i's as functions of Z, which, together with Equation (14), gives values of x_i's and y_i's along the Z axis.

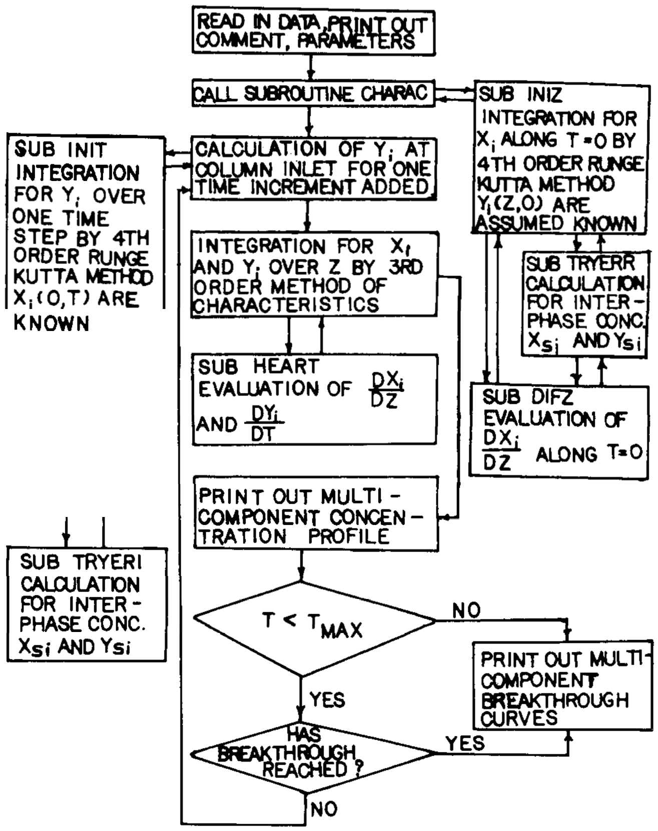

Fig. 3. Flow diagram of computer simulation for multicomponent interactive system.

Along the θ axis, from Equation (15)

$$x_i = 1 \qquad (15)$$

Equation (36) becomes

$$\frac{dy_i}{d\theta} = \xi_i{}^s(1 - y_i); \quad i = 1, 2, \ldots N.$$

and

$$y_i = 0 \quad \text{at} \quad \theta = 0$$

The solution of the previous equation is

$$y_i = 1 - e^{-\xi_i{}^s\theta} \qquad (48)$$

Equations (15) and (48) give the values of x_i and y_i along the θ axis.

Combined Liquid and Solid Phase Controlling. Along the Z axis, one has

$$y_i = 0 \qquad (14)$$

$$\frac{d_{xi}}{dZ} = -\rho a_i \xi_i{}^s(x_i - x_{si}) = -\rho a_i \xi_i{}^s(y_{si})$$

$$i = 1, 2, 3, \ldots . N \qquad (49a)$$

and

$$x_i = 1 \quad \text{at} \quad Z = 0 \qquad (49b)$$

The calculation of x_i, x_{si}, and y_{si} along the Z axis can be effected as follows. Assuming that at point (j, 0) values of x_i are known, one can find the corresponding values of x_{si} and y_{si} based on these values as described before [that is, Equations (44*a*) to (44*c*) and letting $y_i = 0$]. Once the interface concentrations are known, values of dx_i/dZ can be found from Equations (49*a*), which, in turn, permit the calculation of x_i at the next point (j + 1, 0) using the Runge-Kutta method. This process can be repeated to obtain values of x_i, x_{si}, and y_{si} along the Z axis.

Table 2. Breakthrough Curves of Three-Component System with Liquid Phase Control

Time (hr)	$\frac{c_1}{c_{10}}$	$\frac{c_2}{c_{20}}$	$\frac{c_3}{c_{30}}$
20	0.01509	0.03001	0.06125
40	0.02728	0.05250	0.10517
60	0.04370	0.08196	0.16029
80	0.06732	0.12216	0.23087
100	0.09864	0.17328	0.31537
120	0.14040	0.23807	0.41519
140	0.19438	0.31758	0.52874
160	0.26243	0.41245	0.65333
180	0.34479	0.52051	0.78218
200	0.43971	0.63715	0.90649
220	0.54127	0.75253	1.01259
240	0.64184	0.85640	1.09035
260	0.73135	0.93747	1.13229
280	0.80459	0.99275	1.14302
300	0.85900	0.10235	1.13152
320	0.89788	0.10372	1.10988
340	0.92480	0.10401	1.08625

$u = 2.7164 \times 10^{-3}$ m/s (4 gal/min/ft^2)
$L = 0.3429$ m (1.125 ft)
$\rho = 0.39$ g/cm^3
$k_{l1} = 140$ hr^{-1}
$k_{l2} = 120$ hr^{-1},
$k_{l3} = 100$ hr^{-1}
$a_1 = 40$ l/g,
$a_2 = 30$ l/g,
$a_3 = 20$ l/g
$b_1 = 0.05$ l/μmole,
$b_2 = 0.03$ l/μmole,
$b_3 = 0.01$ l/μmole
$c_{10} = 20$ μmole/l,
$c_{20} = 15$ μmole/l,
$c_{30} = 10 \mu$mole/l
$\Delta z = 0.01905$ m (0.0625 ft)
$\Delta t = 4$ hr
CPU time = 60 s

Along the θ axis, one has

$$x_i = 1 \qquad (15)$$

$$\frac{dy_i}{d\theta} = \xi_i{}^l(1 - x_{si}) = \xi_i{}^s(y_{si} - y_i) \qquad (50a)$$

$$y_i = 0 \quad \text{at} \quad \theta = 0 \qquad (50b)$$

The same procedure for the calculation of x_i, x_{si}, and y_{si} along the Z axis described above can be used to calculate y_i, x_{si}, and y_{si} along the θ axis.

PROGRAM STRUCTURE AND NUMERICAL EXAMPLES

In order to carry out the calculations according to the formulation developed above, computer programs for the multicomponent, nonequilibrium, adsorption system have been developed in FORTRAN IV language. A main program and six subroutines are used to perform the numerical integration in either external or internal diffusion control. Two additional subroutines TRYERR and TRYERI are required for the computation of interphase concentrations x_{si} and y_{si} for cases of combined liquid and solid phase diffusion control. The structure of this program is illustrated in Figure 3. Detailed descriptions of the program are given elsewhere (Hsieh, 1974).

A number of numerical examples were calculated to illustrate the interactive breakthrough behavior of multicomponent adsorption. The results of three of them as well as the conditions under which the calculations were made are presented in Tables 2, 3, and 4. These three cases correspond to a three-component system with liquid phase controlling, a four-component system with solid phase controlling, and a two-component system with combined liquid and solid phases controlling, respectively. While the CPU times for the three example problems are quite comparable, the height of bed for the third case (combined liquid and solid phases controlling) is smaller, and clearly the number of adsorbable species is smaller. This, of course, is expected

Table 3. Breakthrough Curves of Four-Component System with Solid Phase Control

Time (hr)	c_1/c_{10}	c_2/c_{20}	c_3/c_{30}	c_4/c_{40}
20	0.0	0.273×10^{-1}	0.407×10^{-1}	0.29314
40	0.0	0.21910	0.26965	0.61545
60	0.0	0.56636	0.62669	0.84609
80	0.0	0.84177	0.88069	0.95885
100	0.0	0.98148	0.99857	1.00531
120	0.0	1.03771	1.04218	1.02388
140	0.0	1.05734	1.05604	1.03164
160	0.0	1.06341	1.05984	1.03514
180	0.0	1.06504	1.06067	1.03682
200	0.0	1.06538	1.06075	1.03765
220	0.0	1.06541	1.06070	1.03806
240	0.902×10^{-10}	1.06538	1.06066	1.03826
260	0.610×10^{-8}	1.06537	1.06064	1.03836
280	0.781×10^{-7}	1.06536	1.06063	1.03840
300	0.674×10^{-6}	1.06535	1.06062	1.03842

$u = 2.7164 \times 10^{-3}$ m/s (4 gal/min/ft^2), $L = 0.762$ m (2.5 ft), $\rho = 0.39$ g/cm^3

$k_{s1} = 0.1103$ hr^{-1}, $k_{s2} = 0.1050$ hr^{-1}, $k_{s3} = 0.1016$ hr^{-1}, $k_{s4} = 0.0563$ hr^{-1}

$a_1 = 45.1$ l/g, $a_2 = 3.4$ l/g, $a_3 = 3.2$ l/g, $a_4 = 2.1$ l/g

$b_1 = 0.280$ l/μmole, $b_2 = 0.007$ l/μmole, $b_3 = 0.003$ l/μmole, $b_4 = 0.002$ l/μmole

$c_{10} = 4.6$ μmole/l. $c_{20} = 41.6$ μmole/l, $c_{30} = 33.3$ μmole/l, $c_{40} = 166.5$ μmole/l

$\Delta z = 0.02987$ m (0.098 ft) $\Delta t = 5$ hr, CPU time = 150 s

because of the additional iterative calculations for the interface concentrations required in the general case.

It is impossible to derive a general criterion for the optimum increment size to be used in the numerical work. For cases with parameters within the ranges used in the example problems, the increment size of $\Delta z = 0.1$ ft and $t = 2.0$ hr can be considered to be adequate. However, when high overshoot peaks occur, the use of smaller increments is necessary to avoid negative values of x_{si}. Also, as the number of species considered is increased, smaller values of increment size should be used to insure the stability of the calculation.

DISCUSSION

Comparison with Cooney's Solutions

The method proposed by Cooney and Strusi (1972) represents an ingenious way of decomposing the multicomponent adsorption problem into pseudo single-solute adsorption problems. The general idea is therefore an important one if it can be shown that this method gives

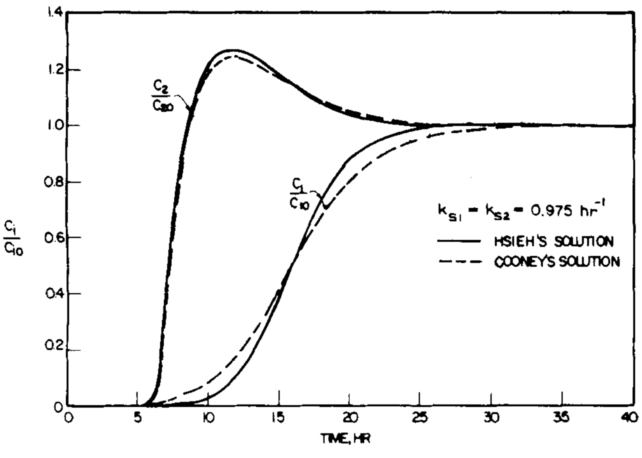

Fig. 4. Comparison between this study and Cooney's solution for two component system with equal mass transfer coefficients.

Table 4. Breakthrough Curves of Two-Component System with Combined Solid and Liquid Phase Resistances

Time (hr)	c_1/c_{10}	c_2/c_{20}
1	0.812×10^{-3}	0.243×10^{-1}
2	0.707×10^{-2}	0.11013
3	0.387×10^{-1}	0.33404
4	0.988×10^{-1}	0.57286
5	0.17002	0.74657
6	0.24296	0.86343
7	0.31354	0.93957
8	0.38016	0.98792
9	0.44197	1.01740
10	0.49864	1.03432
11	0.55083	1.04321
12	0.59869	1.04684
13	0.64213	1.04713
14	0.68158	1.04542
15	0.71730	1.04255
16	0.74945	1.03908
17	0.77848	1.03543
18	0.80448	1.03178
19	0.82769	1.02827
20	0.84846	1.02500

$u = 2.7164 \times 10^{-3}$ m/s (4 gal/min/ft^2) $L = 0.0509$ m (0.167 ft)

$k_{l1} = 2671$ hr^{-1}, $k_{l2} = 1869$ hr^{-1}

$k_{s1} = 0.246$ hr^{-1}, $k_{s2} = 0.405$ hr^{-1}

$a_1 = 198.8$ l/g, $a_2 = 54.3$ l/g

$b_1 = 0.14$ l/μmole, $b_2 = 0.06$ l/μmole

$c_1 = 110$ μmole/l, $c_2 = 300$ μmole/l

$\Delta z = 0.00305$ m (0.01 ft) $\Delta t = 0.1$ hr

$\rho = 0.39$ g/cm^3 CPU time = 120 s

Table 5. Comparison Between Present Work and Cooney's Solution for Two-Component System with Equal Mass Transfer Coefficients

Present work			Cooney's solution		
Time (hr)	c_1/c_{10}	c_2/c_{20}	Time (hr)	c_1/c_{10}	c_2/c_{20}
6.000	0.000	0.016	6.639	0.021	0.130
6.250	0.000	0.049	6.920	0.023	0.259
6.500	0.000	0.121	7.164	0.026	0.389
6.750	0.000	0.231	7.409	0.029	0.518
7.000	0.3×10^{-4}	0.365	7.677	0.032	0.648
7.250	0.9×10^{-4}	0.497	7.986	0.037	0.777
7.500	0.3×10^{-3}	0.624	8.368	0.043	0.907
7.750	0.7×10^{-3}	0.733	8.891	0.053	1.036
8.000	0.1×10^{-2}	0.832	9.762	0.076	1.166
8.250	0.2×10^{-2}	0.913	10.474	0.100	1.235
8.500	0.3×10^{-2}	0.983	12.416	0.200	1.236
8.750	0.5×10^{-2}	1.040	13.768	0.300	1.207
9.000	0.7×10^{-2}	1.089	14.920	0.400	1.177
9.250	0.010	1.113	16.019	0.500	1.148
9.500	0.014	1.161	17.160	0.600	1.118
9.750	0.018	1.186	18.448	0.700	1.089
10.000	0.023	1.208	20.077	0.800	1.059
12.000	0.106	1.267	22.612	0.900	1.030
14.000	0.270	1.218	22.981	0.910	1.027
16.000	0.505	1.147	23.392	0.920	1.024
18.000	0.727	1.082	23.853	0.930	1.021
20.000	0.873	1.038	24.382	0.940	1.018
22.000	0.947	1.016	25.003	0.950	1.015
24.000	0.980	1.006	25.757	0.960	1.012
26.000	0.993	1.002	26.723	0.970	1.009
28.000	0.998	1.001	28.074	0.980	1.005

$u = 6.791 \times 10^{-4}$ m/s (1.0 gal/min/ft^2) $L = 0.305$ m (1.0 ft) $\rho = 0.39$ g/cm^3

$k_{s1} = 0.975$ hr^{-1}, $k_{s2} = 0.975$ hr^{-1}

$a_1 = 3.0$ l/g, $a_2 = 1.0$ l/g

$b_1 = 4.0$ l/μmole, $b_2 = 2.0$ l/μmole

$c_{10} = 1.0$ μmole/l, $c_{20} = 2.0$ μmole/l CPU time = 50 s

$\Delta z = 0.00244$ m (0.008 ft) $\Delta t = 0.25$ hr,

Table 6. Comparison Between Present Work and Cooney's Solution for Two-Component System with Unequal Mass Transfer Coefficients

	Present work		Cooney's solution			
Time (hr)	c_1/c_{10}	c_2/c_{20}	Time (hr)	c_1/c_{10}	Time (hr)	c_2/c_{20}
6.0	0.000	0.4×10^{-3}	8.955	0.010	6.369	0.130
6.5	0.000	0.020	9.990	0.020	6.920	0.259
7.0	0.4×10^{-4}	0.188	10.605	0.030	7.164	0.389
7.5	0.5×10^{-3}	0.548	11.048	0.040	7.409	0.518
8.0	0.2×10^{-2}	0.927	11.396	0.050	7.677	0.648
8.5	0.6×10^{-2}	1.073	11.685	0.060	7.986	0.777
9.0	0.011	1.202	11.933	0.070	8.368	0.907
9.5	0.019	1.232	12.152	0.080	8.891	1.036
10.0	0.028	1.271	12.347	0.090	9.762	1.166
11.0	0.058	1.280	12.525	0.100	10.474	1.235
12.0	0.108	1.269	13.789	0.200	12.416	1.236
13.0	0.181	1.245	14.666	0.300	13.768	1.207
14.0	0.279	1.214	15.415	0.400	14.920	1.177
15.0	0.394	1.177	16.129	0.500	16.019	1.148
16.0	0.515	1.140	16.871	0.600	17.160	1.118
17.0	0.630	1.111	17.708	0.700	18.448	1.089
18.0	0.729	1.079	18.767	0.800	20.077	1.059
19.0	0.808	1.057	20.414	0.900	22.612	1.030
20.0	0.869	1.041	20.655	0.910	22.981	1.027
21.0	0.914	1.029	20.921	0.920	23.392	1.024
22.0	0.946	1.021	21.221	0.930	23.853	1.021
23.0	0.969	1.015	21.565	0 940	24.382	1.018
24 0	0.984	1.012	21.969	0.950	25.003	1.015
25.0	0.995	1.009	22.459	0.960	25.757	1.012

$u = 6.791 \times 10^{-4}$ m/s (1.0 gal/min/ft^2)
$k_{s1} = 1.500$ hr^{-1},
$a_1 = 3.0$ l/g,
$b_1 = 4.0$ l/μmole,
$c_{10} = 1.0$ μmole/l,
$\Delta z = 0.00061$ m (0.002 ft)

$L = 0.305$ m (1.0 ft)
$k_{s2} = 0.975$ hr^{-1}
$a_2 = 1.0$ l/g
$b_2 = 2.0$ l/μmole
$c_{20} = 2.0$ μmole/l
$\Delta t = 0.5$ hr,

$\rho = 0.39$ g/cm^3

CPU time = 90 s

reasonably accurate results. The numerical method developed in this work makes such an assessment possible.

Two examples were worked out to compare the numerical solution with Cooney's solution. For the first example, the two species are assumed to have the same mass transfer coefficients, and the results as well as the values of the operating variables are listed in Table 5 and shown in Figure 4. It can be observed that the breakthrough time from Cooney's solution is approximately 2 hr earlier than that obtained from the present numerical procedure if the breakthrough concentration of $c_1/c_{10} = 0.1$ is chosen. For the second species, the peak height of the concentration history of Cooney's solution is slightly lower than that obtained from the present numerical procedure. In the second example, the mass transfer coefficients are taken to be unequal (but of the same order of magnitude). Two different parameters based on different mass transfer coefficients were calculated and used to obtain the respective breakthrough curves for species 1 and 2 for Cooney's solution. The results are listed in Table 6 and shown in Figure 5. It is clear that the deviation is largest around the overshoot portion of the concentration history for species 2, and there is a somewhat smaller difference in the breakthrough time for species 1 between Cooney's solution and the present numerical procedure. In general, Cooney's method requires less computation and should give satisfactory results for long columns and systems with high mass transfer rates, since the procedure presumes constant pattern behavior and small departures from equilibrium conditions. The numerical procedure developed here, however, can be used for the entire range of nonequilibrium conditions, with more general rate expressions, and is applicable to systems of more than two species. It is obvious that the present numerical procedure has much wider application.

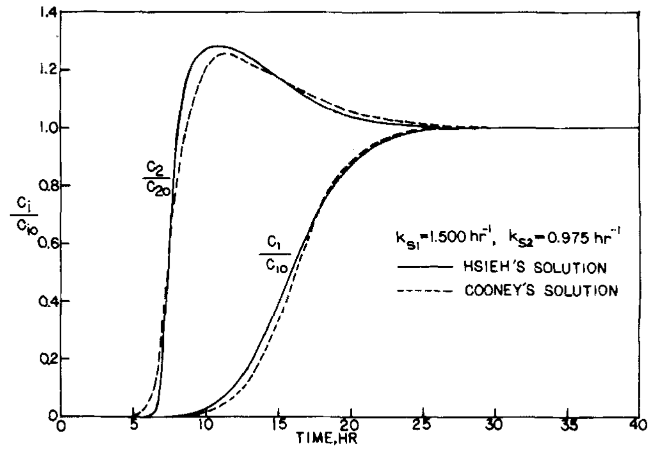

Fig. 5. Comparison between this study and Cooney's solution for two component system with unequal mass transfer coefficients.

Comparison with Equilibrium Solution

In a previous paper, the authors developed procedures for the use of the h-transformation for the solution of multicomponent adsorption in fixed beds under equilibrium conditions. A comparison between the equilibrium solutions and the results of the present work would provide a clear assessment of the effect of mass transfer in multicomponent adsorption.

The particular example which was worked out concerns the adsorption of an aqueous solution containing four adsorbable species (ABS,* D-glucose, DL-valine, and lactic acid) denoted as species 1, 2, 3, and 4, respectively, in a packed bed of granular activated carbon. This system has been used to approximate the secondary treatment effluent of domestic wastewater, and the ad-

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* Alkyl benzene sulfonate.

Table 7. Listed Numerical Values of Concentration Profiles in Mole Fraction of Four-Component Nonequilibrium Calculation in Fixed Bed

T	$1/T$	c_1/c_{10}	c_2/c_{20}	c_3/c_{30}	c_4/c_{40}	c_{overall} (p.p.m.)
0.58781	1.70124	0.0	0.273×10^{-1}	0.407×10^{-1}	0.29314	1.92208
1.17676	0.84979	0.0	0.21910	0.26965	0.61545	4.88930
1.76571	0.56634	0.0	0.56636	0.62669	0.84609	8.02902
2.35467	0.42469	0.0	0.84177	0.88069	0.95885	10.0397
2.94362	0.33972	0.0	0.98148	0.99857	1.00531	10.9734
3.53258	0.28308	0.0	1.03771	1.04218	1.02388	11.3407
4.12153	0.24263	0.0	1.05734	1.05604	1.03164	11.4739
4.71048	0.21229	0.0	1.06341	1.05984	1.03514	11.5207
5.29944	0.18870	0.0	1.06504	1.06067	1.03682	11.5373
5.88839	0.16983	0.0	1.06538	1.06075	1.03765	11.5435
6.47735	0.15438	0.0	1.06541	1.06070	1.03806	11.5460
7.06630	0.14152	0.902×10^{-10}	1.06538	1.06066	1.03826	11.5470
7.65525	0.13063	0.610×10^{-8}	1.06537	1.06064	1.03836	11.5475
8.24421	0.12130	0.781×10^{-7}	1.06536	1.06063	1.03840	11.5477
8.83316	0.11321	0.674×10^{-6}	1.06535	1.06062	1.03842	11.5478

The above breakthrough curves are calculated under the following carbon column specifications:

U (mean superficial flow rate) $= 2.7164 \times 10^{-3}$ m/s $= 4$ gal/min/ft.^{2}

L (total length of column) $= 0.762$ m $= 2.5$ ft.

c_o (overall inlet concentration) $= 12$ p.p.m.

c_{io} (individual inlet concentrations)

$a_1 = 45.08$ l/g	$b_1 = 0.28$ l/μ mole	$c_{10} = 1$ p.p.m.
$a_2 = 3.39$ l/g	$b_2 = 0.00683$ l/μ mole	$c_{20} = 3$ p.p.m.
$a_3 = 3.18$ l/g	$b_3 = 0.00339$ l/μ mole	$c_{30} = 2$ p.p.m.
$a_4 = 2.11$ l/g	$b_4 = 0.00145$ l/μ mole	$c_{40} = 6$ p.p.m.

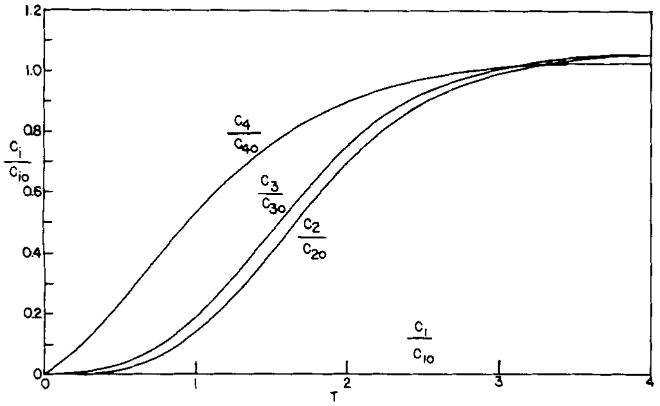

Fig. 6. The breakthrough curves of four-component langmuir adsorption system.

sorption isotherm and the rate parameters have been determined by Hsieh (1974). The experimentally determined isotherm parameters and the conditions pertinent to the example problem are given in Table 7 which also gives the calculated values of effluent concentration as a function of the throughput parameter T, $T = \theta/pZ$ $\left(\sum_{i=1}^{N} c_{io} \Big/ \sum_{i=1}^{N} a_i c_{io} \right)$. from the numerical method developed in this work. The nonequilibrium solutions are also shown in Figure 6. The results of the h-transformation method are given in Figure 7. For comparison of these two solutions, the total effluent concentration as a function of the throughput parameter T is shown in Figure 8. If one takes breakthrough concentration to be 2 p.p.m., the predicted breakthrough time based on the h-transformation method is almost twice as large as that derived by the present analysis. Also, the equilibrium solution predicts an overshoot, whereas the nonequilibrium solution does not (the nonequilibrium solution does, however, predict overshoot for individual species). These discrepancies are entirely in accord with the expectation that predictions based on the equilibrium assumption are only of qualitative or semiquantitative value. For greater precision, the effect of mass transfer must be included.

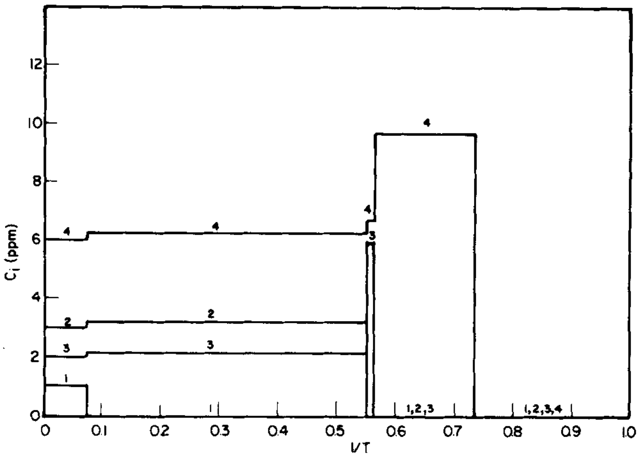

Fig. 7. The concentration profiles of four-component langmuir adsorption system.

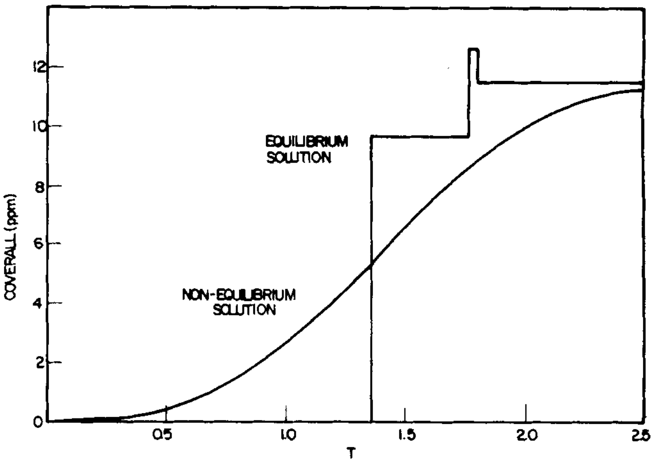

Fig. 8. Comparison between equilibrium and nonequilibrium solution in terms of overall TOC concentration for the four-component langmuir adsorption system.

Estimation of the Transfer Coefficients k_{li} and k_{si}

The analysis developed in this work takes account of the mass transfer effect in the adsorption process through the use of two transfer coefficients k_{l_i} and k_{s_i} [see Equation (21)]. A brief account on how these quantities can be estimated is given below.

For the liquid phase mass transfer coefficient k_{l_i}, Vermeulen et al. (1973) suggested the use of the following expression:

$$k_{l_i} = \frac{2.62\,\rho a_i (D_{f_i} u)^{0.5}}{\left(1 + \sum_{j=1}^{N} b_j c_{jo}\right) \Lambda_i d_p^{1.5}} \tag{51}$$

A particularly important application of adsorption in multicomponent systems is for wastewater treatment. For such an application, the detailed identities of the contaminants is often unknown, and accordingly one does not have the value of D_{f_i}. However, one may obtain the corresponding pore diffusion coefficient for such a contaminant from batch adsorption measurements, and, according to Wheeler (1951, 1955)

$$D_{\text{pore}_i} = \frac{D_{f_i} \chi}{2} \tag{52}$$

where χ is the internal porosity of the adsorbent, k_{l_i} can be estimated as

$$k_{l_i} = \frac{2.62\,\rho a_i \left(\dfrac{2 D_{\text{pore},i} u}{\chi} \right)^{0.5}}{\left(1 + \sum_{j=1}^{N} b_j c_{jo}\right) \Lambda_i d_p^{1.5}} \tag{53}$$

The solid phase mass transfer coefficient can be estimated from either the pore diffusion coefficient or the particle diffusion coefficient. For the pore diffusion case, Vermeulen and Quilici (1970) recommended the use of the following expressions for the rate of diffusion in the particle phase:

$$\frac{dy_i}{dt} = \frac{\chi_{\text{pore}} k_{\text{pore}_i a_p}}{\Lambda_i} \frac{y_{si} - y_i}{\sqrt{1 + (r-1) y_i}} \tag{54}$$

$$k_{\text{pore}_i} a_p = \frac{60 D_{\text{pore}_i} (1 - \epsilon)}{d_p^2} \tag{55}$$

Comparing Equation (5) with Equations (54) and (55), one gets

$$k_{s_i} = \frac{60\, D_{\text{pore}_i} \chi'_{\text{pore}_i} (1 - \epsilon)}{\Lambda_i d_p^2} \tag{56}$$

and χ'_{pore_i} is given by

$$\chi'_{\text{pore}_i} = \frac{0\ 775}{1 - 0.225\, r^{0.4}} \tag{57}$$

A similar but somewhat different expression has been given by Glueckauf and Coates (1947) if the diffusion within the adsorbent is described by the particle diffusion model. This expression is given as

$$k_{s_i} = \frac{60\, D_{si}}{d_p^2} \tag{58}$$

Both D_{pore_i} and D_{s_i} can be obtained directly from the batch adsorption experiments.

Adaptation of the Numerical Method to Other Types of Isotherms

In the present analysis, it was assumed that the generalized Langmuir expression [that is, Equation (3)] could be used to describe the isotherm data of the multicomponent systems. This assumption is supported by limited available data obtained by Hsieh (1974). Other investigators have found, however, that this is not universally true. Thus, modified versions of the Langmuir expression have been proposed recently. Fritz and Schluender (1974) have proposed the following expression for multicomponent isotherm data:

$$q_i = \frac{a_i c_i^{d_{io}}}{1 + \sum_{j=1}^{N} b_j c_j^{d_{ij}}} \tag{59}$$

where d_{io} and d_{ij}'s are empirical constants. Equation (59) reduces to that of Langmuir expression in the special case when $d_{io} = d_{ij} = 1$. Jain and Snoeyink (1973), on the other hand, suggested the following expression for isotherm data of binary adsorbate:

$$q_1 = \frac{a_1 c_1}{1 + b_1 c_1 + b_2 c_2} \left[1 + \frac{\left(1 - \dfrac{a_1 b_2}{b_1 a_2}\right)}{1 + b_1 c_1} b_2 c_2 \right] \tag{60a}$$

$$q_2 = \frac{a_2 c_2}{1 + b_1 c_1 + b_2 c_2} \tag{60b}$$

It is not clear how Equations (60*a*) and (60*b*) can be generalized to the N adsorbate situation when $N > 2$. For this reason, it would be somewhat premature to speculate on how best to adapt the present multicomponent adsorption calculations for this type of isotherm. In the type of situation depicted by Equation (59), however, there should be little difficulty. Equation (3) can be viewed to be equivalent to Equation (59) if the coefficients a_i and b_j's are taken not as constants but as functions of c_i and c_j's. As an approximation, in the numerical calculation one may use the values of c_i's from the preceding point to calculate the necessary coefficients, and all the algorithms developed in this work are then directly applicable. The errors introduced by such an approximation are likely to be insignificant since, experimentally, it was found that the exponents, d_{io} and d_{ij} are fairly close to unity.

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NOTATION

a_i = constant of species i in Langmuir isotherm of species i
a_p = outer surface interfacial area of the sorbent particles per unit volume of contacting system
b_i = constant of species i in Langmuir isotherm
c_i = liquid phase concentration of species i
c_{i0} = column inlet concentration of species i in liquid phase
c_{si} = liquid interphase concentration of species i
D_{fi} = diffusivity in liquid phase of species i
D_{pore_i} = pore diffusion coefficient of species i
D_{s_i} = solid diffusion coefficient of species i
d_p = mean particle diameter
d_{io}, d_{ig} = empirical exponents in adsorption isotherm expression [Equation (59)]
i = index of multicomponent species
j = index of distance from column inlet
k_{l_i} = liquid phase mass transfer coefficient for species i
k_{s_i} = solid phase mass transfer coefficient for species i

L = length of column
M = quantity of adsorbent
N = total number of adsorbable species present in solution
n = index of time elapsed
P_l = defined in Equation (26)
P_s = defined in Equation (33)
q_i = solid phase concentration of species i
q_{i0} = solid phase concentration in equilibrium with c_{i0}
q_{si} = solid interphase concentration of species i
r = separation factor
T = throughput parameter
t = time
u = flow rate
x_i = dimensionless liquid phase concentration
x_{si} = dimensionless liquid interphase concentration for species i
y_i = dimensionless solid phase concentration for species i
y_{si} = dimensionless solid interphase concentration for species i
Z = dimensionless distance variable
z = distance from column inlet

Greek Letters

ϵ = void fraction of fixed bed
θ = dimensionless time variable
Λ_i = partition coefficient of species i
ρ = bulk density of carbon in column
ξ_i^l = dimensionless liquid phase mass transfer coefficient of species i defined in Equation (6)
ξ_i^s = dimensionless solid phase mass transfer coefficient of species i defined in Equation (7)
ϕ_i = parameter defined as ξ_i^s/ξ_i^l
χ = internal porosity of carbon
χ'_{pore_i} = defined by Equation (57)

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Limiting Criteria for Intrinsically Stable Equilibrium in Multiphase, Multicomponent Systems

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Necessary and sufficient conditions for intrinsically stable equilibrium in a multiphase, multicomponent body are developed with interfacial effects taken into full account. There is a limiting criterion for intrinsic stability that must be satisfied within every phase, and there is another limiting criterion that must be satisfied on every phase interface. The limits of intrinsic stability for a multiphase, multicomponent body are defined by the failure either of the first criterion within one of the phases or of the second criterion on one of the phase interfaces.

SCOPE

An equilibrium state is stable if it persists following a disturbance. It is intrinsically stable if it persists following a very small disturbance. The prior literature has been concerned with the necessary and sufficient condi-