Analysis of Liquid Phase Adsorption Fractionation in Fixed Beds

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Liquid phase adsorption has been one of the latest unit operations to receive theoretical treatment because of the relative complexity of the mechanisms involved. The purpose of this investigation is to present an improved method for solving problems, especially where intraparticle diffusion is a rate controlling mechanism. Appropriate boundary conditions for liquid phase adsorption and a general nonlinear equilibrium relation are included in deriving a system of partial differential equations describing the process.

The mathematical model consists of a bulk phase material balance, an intraparticle diffusion equation, and a rate for interphase transfer; these equations must be solved simultaneously with the boundary conditions and equilibrium function. A numerical procedure is developed and discussed for use on a high-speed computer.

The results are sets of computed curves for four liquid systems, each requiring a separate computer solution because of changes in feed concentration or equilibrium relationship. It is shown that for three of the four systems tested in this research, experimental data correlate with computed results better than in earlier work. Although the solution of this model has been carried out for particular examples, it should be applicable in the case of other liquid phase systems following the assumed mechanisms.

The mathematics of a comprehensive model of adsorption processes in column operation has until recent times been too complex for exact solution. The development of sophisticated theories of adsorption fractionation processes in a column began in the late 1930's and early 1940's. Some highly complicated mathematical equations were derived; however in many instances they were either overly simplified or not solved for want of a practical means of solution.

In general most authors recognized, at least qualitatively, three rate mechanisms which were thought to influence column operation: surface reaction, intraparticle diffusion, and external diffusion through a film. Most of the work centered on gas-solid systems and with linear isotherms. Some very elegant models were proposed and analytical solutions were found for restricted cases, not only in adsorption, but all of the unit operations, as demonstrated by Marshall and Pigford (*16*). Theoretical investigations began to explain the phenomenon of ion exchange, which is allied in many respects to adsorption. Large-scale commercial applications for newly developed adsorption operations began, as exemplified by the Hypersorb and Arosorb processes for separation of petroleum feed-stocks (*3, 12, 13*).

The actual solution of equations in simple cases for which analytical methods were unavailable or overly complicated began in the early 1950's paralleling the introduction of high-speed, stored-program, electronic computing machines, which could often provide accurate numerical results. An earlier paper dealing with solution of adsorption kinetics problems on the computer was authored by Rose et al. (*20*), in a simple stagewise approach to fractionation of a binary liquid mixture. Instantaneous equilibrium at the particle surface was assumed, neglecting pore diffusion resistances. Schmelzer et al. (*22*) showed qualitatively by a series of interrupted runs that internal diffusion was a significant mechanism.

Amundson and his colleagues (*1, 2, 6, 15*) were among the earliest investigators to attack the problem of internal diffusion quantitatively in overall column operation. They considered the process in terms of an irreversible mechanism where the rate of mass transfer is proportional to fluid stream gas concentration and to the quantity of adsorbate contained in the bed. They also found solutions for the rate where a kinetic theory was assumed, and separately for the case of radial diffusion controlling. Analysis was made of steady state operation in fluidized beds, with a linear isotherm and a kinetic rate mechanism, and with quantitative treatment of internal diffusion.

Rosen (*21*) used a high-speed computer in obtaining a general solution for fixed-bed adsorption kinetics with linear isotherms. Earlier researchers found analytic solutions only in limiting cases.

In subsequent work Tien and Thodos (*23*) presented techniques for solving the kinetics of a fixed-bed ion exchange column having a Freundlich type of equilibrium relationship. In their model the kinetics were controlled by the two mechanisms: transfer of solute to the particle surface, and diffusion within the particle itself.

Johnson (*14*) analyzed liquid phase adsorption fractionation in fixed beds by a complete numerical solution to systems which involved simultaneously the variables of bed depth, time, and concentration. The external film was assumed to control, with instantaneous equilibrium at the interface between adsorbed and nonadsorbed phases. Internal diffusion was neglected, although discussed qualitatively. No restrictions were put on the equilibrium, except that it should not cross the operating line. Particularly interesting was a complete reevaluation of boundary conditions used by past researchers and a resultant modification for use in liquid systems. His work also demonstrated that solutions to certain problems for which no known analytical techniques exist may be found by numerical means on a computer.

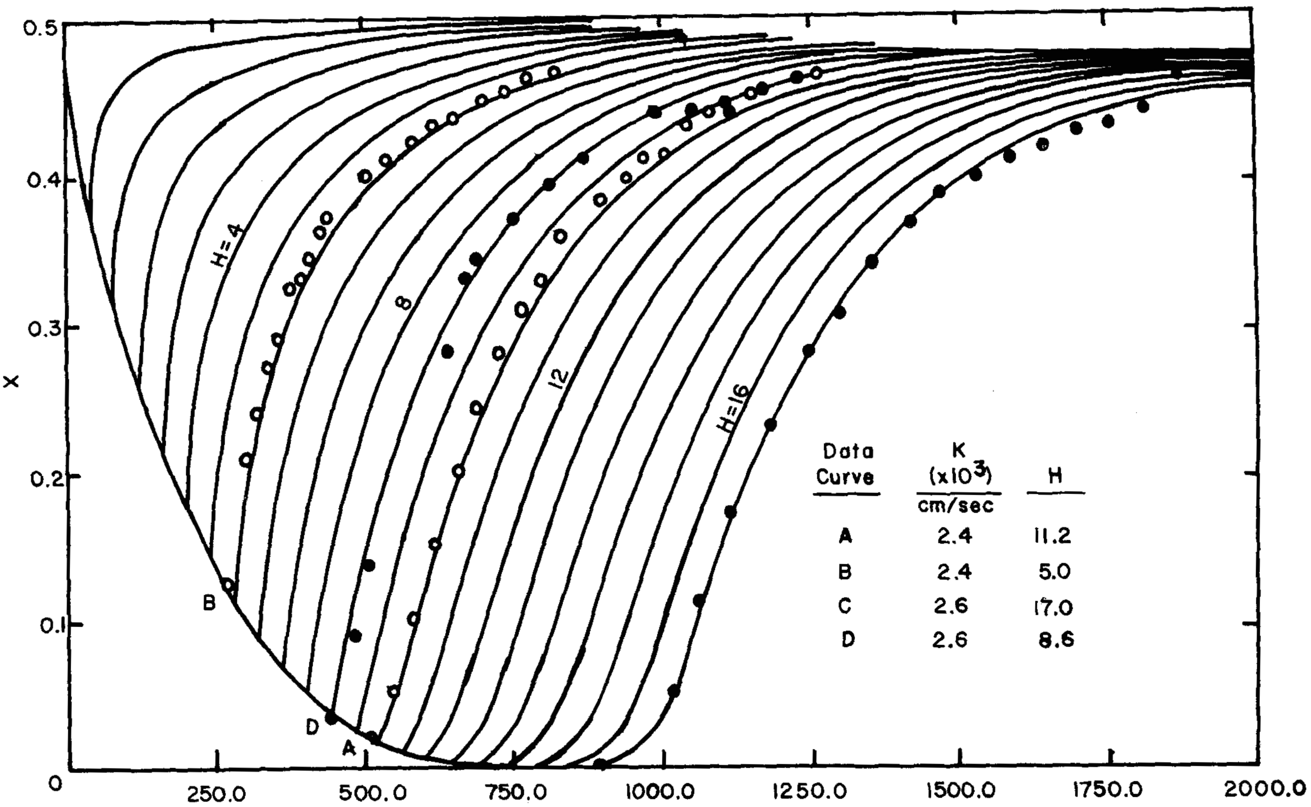


Fig. 1. Methylcyclohexane-toluene on silica gel; $A = 50$.

More recently Masamune and Smith (*17, 18*), also recognizing that the diffusional resistances within the porous bed are of importance, have derived and solved equations relating the variables of concentration, time, level, and particle radius for vapor phase adsorption. Attention was given to the special cases of surface adsorption controlling, pore diffusion controlling, and external diffusion controlling. These investigators assumed equilibria and boundary conditions such that an analytical solution was obtained for each case. With a nitrogen-helium vapor mixture on Vycor particles, the results of experimental tests compared favorably with theory only when the mechanism of pore diffusion was included.

The purpose of this paper is the consideration of liquid phase adsorption in which the variables of time, bed depth, particle size, and concentration are treated simultaneously in a model utilizing a nonlinear equilibrium function and boundary conditions appropriate for liquids.

DESCRIPTION OF EQUATIONS

Given a vertical tower packed with adsorbent material, fed by a binary stream Q of constant composition and feed rate entering at the bottom and flowing upward in pluglike flow, and taking a horizontal slice of thickness dz, one may write an overall bulk phase material balance on the more adsorbed component, in terms of volumetric flow rates, as follows:

$$-Q\left(\frac{\partial x}{\partial z}\right)_{\theta,r} dz + W = f_v\left(\frac{\partial x}{\partial \theta}\right)_{z,r} S\,dz \qquad (1)$$

The quantity W is evaluated by a term expressing mass transfer from the bulk phase across the outer surface of the adsorbent particles and into the interior of the particles, as follows:

1. The volumetric transfer rate of the more adsorbable component per cubic foot of adsorbent is
$$A_s D\left(\frac{\partial y}{\partial r}\right)_{\theta,z,r=a}$$
2. The surface area A_s is the product of the surface area per sphere, the fraction of surface open to the diffusing substance, and the total number of spheres per unit volume of bed:

$$A_s = 4\pi a^2 \cdot \frac{3(1-f_v)}{4\pi a^3} \cdot \frac{V_p\rho_b}{1-f_v}$$

The total diffusion W in a volumetric section Sdz is thus

$$W = \frac{3V_p\rho_b}{a} D\,S\,dz\left(\frac{\partial y}{\partial r}\right)_{\theta,z,r=a} \qquad (2)$$

Substitution of W into Equation (1) gives an overall bulk phase balance:

$$-\frac{Q}{S}\left(\frac{\partial x}{\partial z}\right)_{\theta,r} + \frac{3D(V_p\rho_b)}{a}\left(\frac{\partial y}{\partial r}\right)_{\theta,z,r=a} = f_v\left(\frac{\partial x}{\partial \theta}\right)_{z,r} \qquad (3)$$

Assuming that intraparticle diffusion occurs only in a radial direction, one may write the one-dimensional diffusion equation:

$$D\left[\left(\frac{\partial^2 y}{\partial r^2}\right)_{\theta,z} + \frac{2}{r}\left(\frac{\partial y}{\partial r}\right)_{\theta,z}\right] = \left(\frac{\partial y}{\partial \theta}\right)_{r,z} \qquad (4)$$

At the interface between bulk phase and adsorbent surface, it has been shown that there exist two resistances: a film resistance external to the adsorbent particles as well as the intraparticle resistance itself. The rate of more adsorbable component flowing across the interface between these resistances is

$$K(x - x^*) = D\left(\frac{\partial y}{\partial r}\right)_{\theta,z,r=a} \qquad (5)$$

In order to compute the driving force $x - x^*$, an equilibrium relationship $y = f(x^*)$ is required. The simplest method is to assume linear equilibrium, which may in certain cases provide analytical solutions. However, in some liquid adsorption processes, a substantial curvature is noted in the equilibrium function over the relatively wide concentration ranges involved.

Equations (3), (4), and (5), together with equilibrium relations such as those given in Table 1, simultaneously describe the model of the adsorption process chosen for this investigation. Solution of these equations is best effected by a transformation to dimensionless form:

Introduce three new parameters T, H, and R which are related to the original variables θ, z, and r by these equations:

$$T = \frac{K^2}{D}\left(\theta - \frac{f_v z}{Q/S}\right) = \frac{AK}{a}\left(\theta - \frac{f_v z}{Q/S}\right) \quad (6)$$

$$H = \frac{K V_p \rho_b}{(Q/S) a} \cdot z \quad (7)$$

$$R = r \cdot \frac{K}{D}, \text{ or if } r = a,\ A = a \cdot \frac{K}{D} \quad (8)$$

Substitution of Equations (6), (7), and (8) into Equations (3), (4), and (5) will result in the following transformed equations:

$$\left(\frac{\partial x}{\partial H}\right)_{T,R} = -3\left(\frac{\partial y}{\partial R}\right)_{H,T,R=A} \quad (9)$$

$$\left[\frac{\partial^2 y}{\partial R^2} + \frac{2}{R}\frac{\partial y}{\partial R}\right]_{H,T} = \left(\frac{\partial y}{\partial T}\right)_{H,R} \quad (10)$$

$$x - x^* = \left(\frac{\partial y}{\partial R}\right)_{H,T,R=A} \quad (11)$$

BOUNDARY CONDITIONS

One of the major areas of difficulty in solving such models as derived in the last section is that of deriving the proper boundary conditions. In vapor phase work the assumption is generally made that, at the start, the bed is filled with fluid having concentration y_o for all levels. As the feed stream enters and displaces this original fluid the pore concentration in contact with feed is always y_o. Mathematically this condition is given (in terms of the dimensionless parameters) by the following statement:

$$\text{at } T = 0,\ y = y_o, \text{ for all } H$$

In liquid phase adsorption, it is more reasonable to state that the bed initially contains no fluid, that is, that the bed is completely dry. Actually there is some gaseous fluid in the bed at the start, but liquid is assumed to fill the pore space as well as the void volume almost instantaneously and therefore the bulk stream is now in contact with the pore fluid of the same composition as that of the feed. This condition holds for the front of liquid as it moves up the bed. Therefore at the liquid front, $x = y$. Johnson (*14*) found that the wave front was definable mathematically by the equation $H = T$. However, when the additional variable, particle radius, is introduced, it can be shown that this boundary equation is no longer applicable. It may still be assumed that the pores at the liquid front are filled with liquid of bulk composition x, that is, $y = x$ at the wave front (for all r). To find the correct equation describing the wave front in terms of the new dimensionless parameters, an equation describing the time lapsed when the bed is filled to depth z is stated by

$$\theta = \frac{z}{Q/S}(f_v + V_p \rho_b) \quad (12)$$

The term $(f_v + V_p \rho b)$ gives the total space occupied by liquid per volume of bed depth. Rearranging Equation (12) and multiplying through by K^2/D, we obtain

$$\frac{K^2}{D}\theta - \frac{K^2}{D}\cdot\frac{f_v}{(Q/S)}z = \frac{V_p \rho_b}{Q/S}\cdot\frac{K^2}{D}z$$

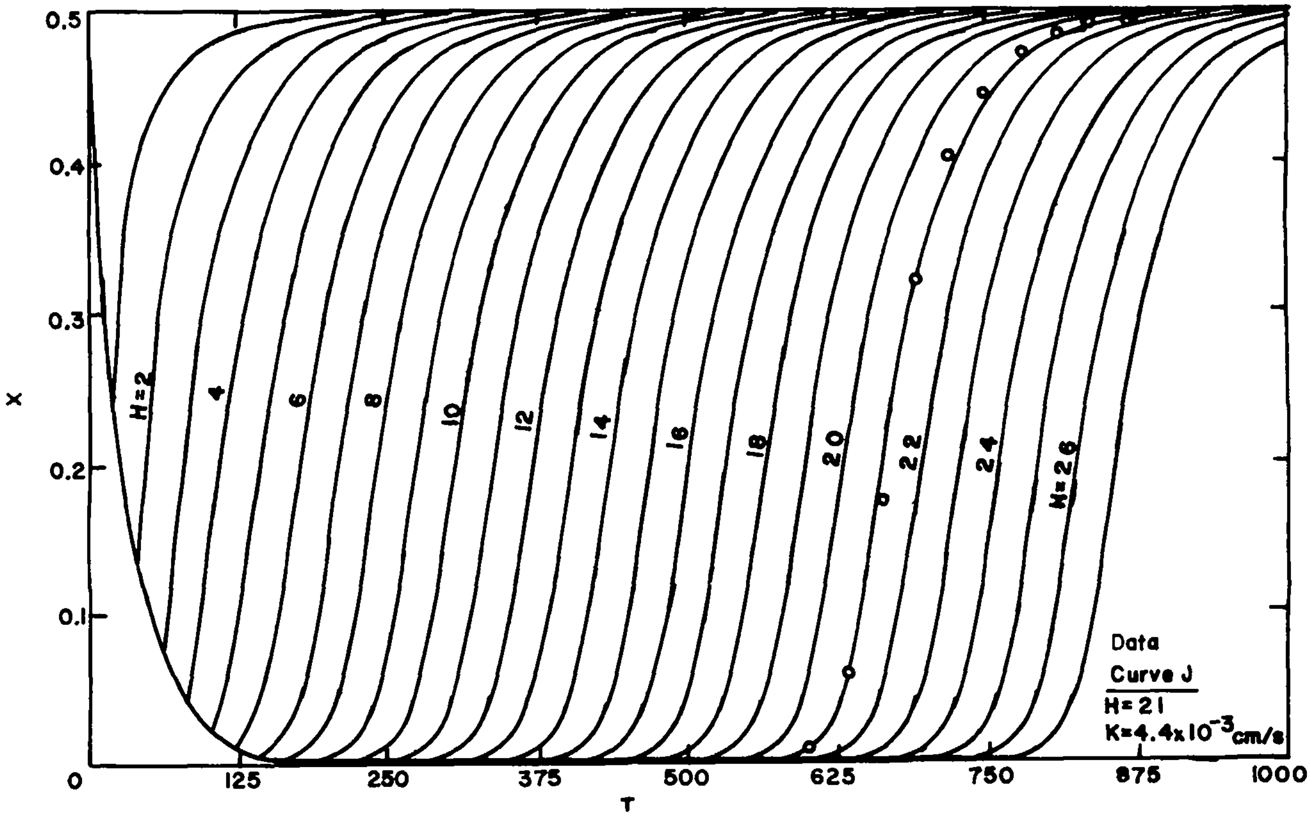


Fig. 2. Benzene—*n*-hexane on silica gel; $A = 20$.

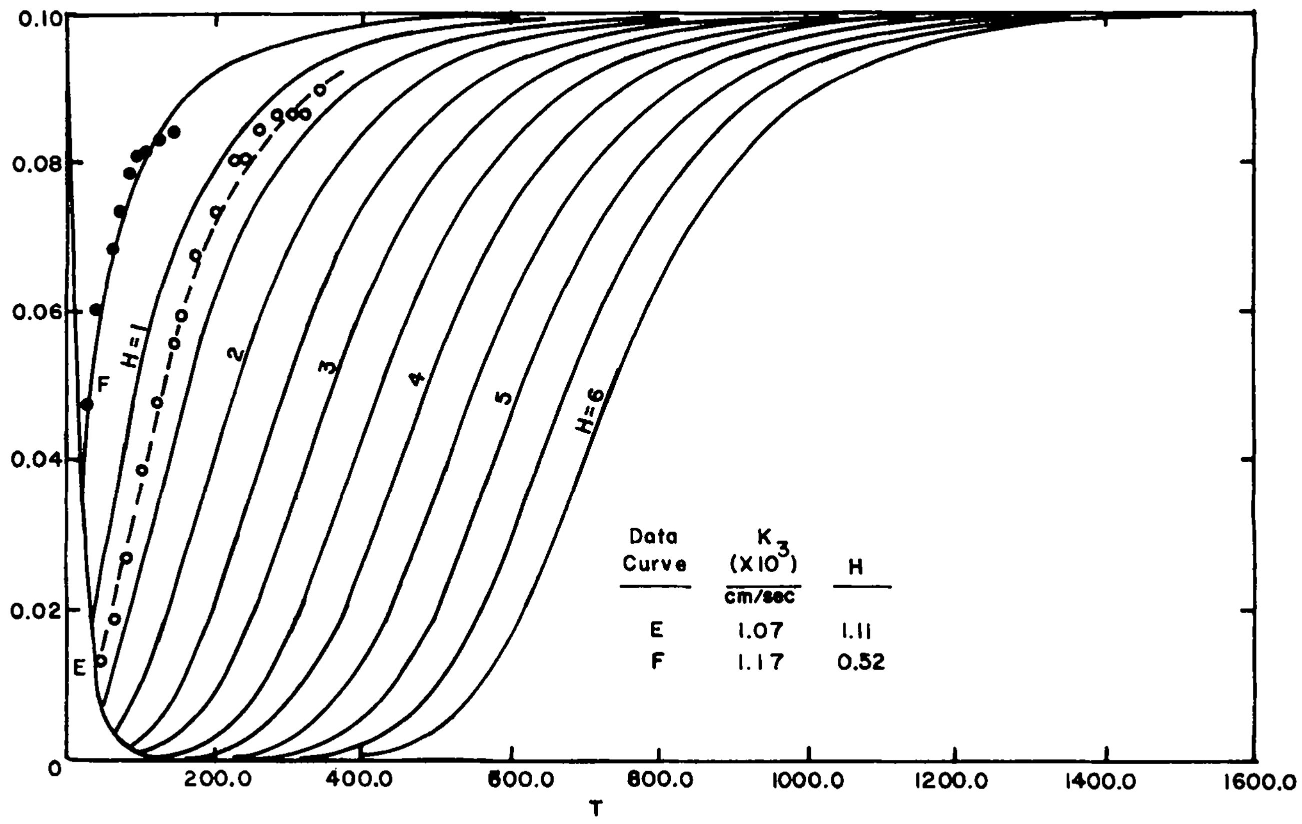


Fig. 3. Methylcyclohexane-toluene on silica gel; $A = 30$.

The left-hand side of this equation is readily seen to be the dimensionless parameter T and the right-hand side can be written as $H(aK/D)$, or HA. Then

$$T = HA \qquad (13)$$

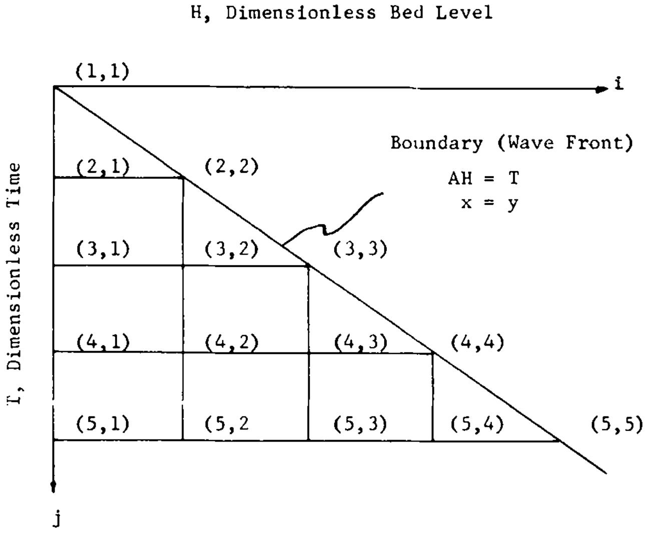
Equation (13) is a statement of the wave front in the dimensionless variables along with the boundary condition: at $T = HA$, $x = y$ for all R.

The other boundary condition, at the feed inlet is straightforward: at $z = 0$, $x = x_F$ for all $\theta \geqq 0$, or in terms of the variables T and H: at $H = 0$, $x = x_F$ for all $T \geqq 0$.

SOLUTION OF ADSORPTION MODEL BY NUMERICAL METHODS

In this work the solution, represented by a set of curves relating the dimensionless parameters, A, H, and T, to liquid concentration, was effected by taking advantage, in part, of certain well-established techniques for linear equations. The criteria ensuring convergence and stability for linear equations cannot usually be guaranteed for a nonlinear system such as that encountered here. However, it can be reasonably expected that in those problems representing physical processes a sufficiently accurate solution will have been reached if the variation of increment size and precision over a considerable range results in essentially the same answer (19).

The desired complete solution is a value of x, liquid phase concentration, for all possible values of the dimensionless variables, A, H, and T. In this case a three-dimensional grid is necessary. In practice it is necessary to consider only one value of the radius parameter A at a time, and for this particular value compute a complete set of curves for various H and T. At a given A, the resulting two-dimensional grid can be shown to have a triangular shape, due to the nature of the boundary conditions (14). To illustrate this a sketch of a partial grid at some constant A is given.



The position of the line representing the liquid front as it rises through the adsorption column depends upon the value of A. All area to the right of the boundary line represents unfilled adsorbent ahead of the liquid front.

Although the bulk phase concentration is of primary interest, it is necessary at each stage of computation to compute a solution for the adsorbed phase concentration. The purpose of the adsorbed phase solution is to provide a value of y, in equilibrium with x, at the interface. The equilibrium relation gives a value of x^* which is necessary in the bulk phase equation.

Solution of Adsorbed Phase (Diffusion) Equation

The most widely used approach to the numerical solution of the diffusion equation is the selection of a suitable finite-difference equation. The procedure selected for this study is an implicit finite-difference method, which is both convergent and stable (4, 7), and the computational aspects are relatively simple. The boundary conditons for this equation require special treatment at the pore opening and at the center of the sphere.

For an *interior* point along the pore radius the difference equations are

$$y_K = \frac{m(1 - 1/K)\, y_{K-1} + m(1 + 1/K)\, y_{K+1} + y_K'}{(2m + 1)}; \qquad K = 1, \ldots, n - 1 \quad (14)$$

The corresponding difference equation for the center of a sphere (at $R = 0, K = 0$) is

$$y_o = \frac{6my_1 + y_o'}{1 + 6m} \quad (15)$$

The boundary point involves the concentration gradient at the entrance to the pore and can be shown to be

$$y_n = \frac{2my_{K-1} + y_n' + 2(x - x^*)(1 + 1/n)m\Delta R}{(1 + 2m)} \quad (16)$$

To solve the diffusion equation it is necessary to obtain a set of values, $y_o, y_1, \ldots, y_{n-1}, y_n$, along the pore radius. Actually the only point of interest is the value of y_n at the pore surface, as well as the gradient at the surface $(\partial y/\partial R)_{R=A}$. This point is used to obtain x^* from an equilibrium relation, which gives the driving potential $x - x^*$ needed in the solution of the bulk phase equation. Solution of the set of $n + 1$ simultaneous equations which were derived for the pore is relatively straightforward, except that a value of x must be assumed. As will be shown later, this procedure involves considerable iteration at every grid point, in which the set of pore equations must be resolved several times.

Solution of Bulk Phase Equation

The final solution for a given parameter A is obtained from the overall bulk phase material balance equation. A numerical solution may be considered complete when the adsorption wave reaches steady state; however, comparison of experimental results with computed results does not require the complete solution if the actual experiment does not reach steady state. In the work of Johnson (*14*) data were obtained before steady state was reached. Other experimenters allowed the system to reach steady state (*1*, *2*, *8* to *11*).

The procedures for solving the bulk phase equation are explained briefly in Appendix I. Points along the diagonal $AH = T$ and along columns one and two of the triangular grid require a modification of the general methods used or an interior grid point.

Discussion of Computational Problems

One of the most critical values affecting the rate of convergence is the damping factor used to adjust the estimated value of y for iteration purposes. It has been found that for some values of this factor, an excessive number of iterations is required, and even in some cases divergence was observed. It is mostly a matter of trial-and-error to find an optimum factor, which if too small, could increase the number of iterations, and if too large cause divergence. Generally a factor between 0.2 and 1.0 was sufficient to produce relatively rapid convergences. However, in the region of most rapid mass transfer (along the straightest and steepest portions of the adsorption wave) between ten and thirty iterations were usually required. In addition to the damping factor, the number of iterations is affected to some extent by the closeness of estimate required for both x and y at each grid point.

Although the maximum error bounds for linear systems (*7*) are stated, they are assumed to be valid for this particular adsorption model. That the method is stable and convergent can be presumed, since the results behaved as expected, as well as the fact that the solution converged as the increments ΔH, ΔR, and ΔT were decreased. It is conceivable that some very wide variation in parameters or unusual equilibrium could make the process

TABLE 1. SUMMARY OF ADSORPTION SYSTEMS INVESTIGATED

System and reference	Curve ident. (Fig. 1–4)	Feed fraction x_f	Column diam., cm.	Bed wt., g.	Liquid rate, cc./sec.	Bed density, g./cc.	Pore vol., cc./g.	Fraction voids	M.T. Coeff. $K(\times 10^3)$ cm./sec.	Dimensionless parameter A (best for system)	K_{avg} $(\times 10^3)$, cm./sec.
1. MCH-toluene on	*A*	0.5	2.47	195	0.0786	0.679	0.402	0.293	2.42		
6-12 mesh	*B*	0.5	2.47	95	0.0786	0.679	0.402	0.293	2.43	50	2.54
silica gel (*14*)	*C*	0.5	2.47	191	0.050	0.679	0.402	0.293	2.61		
(feed fraction = 0.5)	*D*	0.5	2.47	95	0.050	0.679	0.402	0.293	2.70		
2. MCH-toluene on 6-12 mesh	*E*	0.1	2.47	96	0.174	0.679	0.402	0.293	1.07	30	1.12
silica gel (*14*)	*F*	0.1	2.47	45	0.174	0.679	0.402	0.293	1.17		
(feed fraction = 0.5)	G	0.5	2.47	268	0.0625	0.883	0.189	0.425	0.816		
3. MCH-toluene on 8-14 mesh	*H*	0.5	2.47	130	0.0625	0.883	0.189	0.425	0.711	3	0.741
alumina (*14*)	*I*	0.5	2.47	63	0.0625	0.883	0.189	0.425	0.697		
4. Benzene–*n*-Hexane on thru-200-mesh silica gel (*20*)	*J*	0.5	1.9	20	0.00406	0.712	0.357	0.528	0.0442	20	0.0442

Equilibrium relations (*14*): Systems 1 and 2: $y = x/0.203;\ x < 0.030$

$y = [x/0.1705\ (1 - x)]^{0.689}/\{1 + [x/0.1705\ (1 - x)]^{0.689}\};\ x \geqq 0.030$

3: $y = 2.718\ [x/(1 - x)]^{0.76}$

4: $y = \dfrac{x}{1.315x + 0.103};\ x \leqq 0.226$

$y = \dfrac{x}{0.9398x + 0.147};\ x > 0.226$

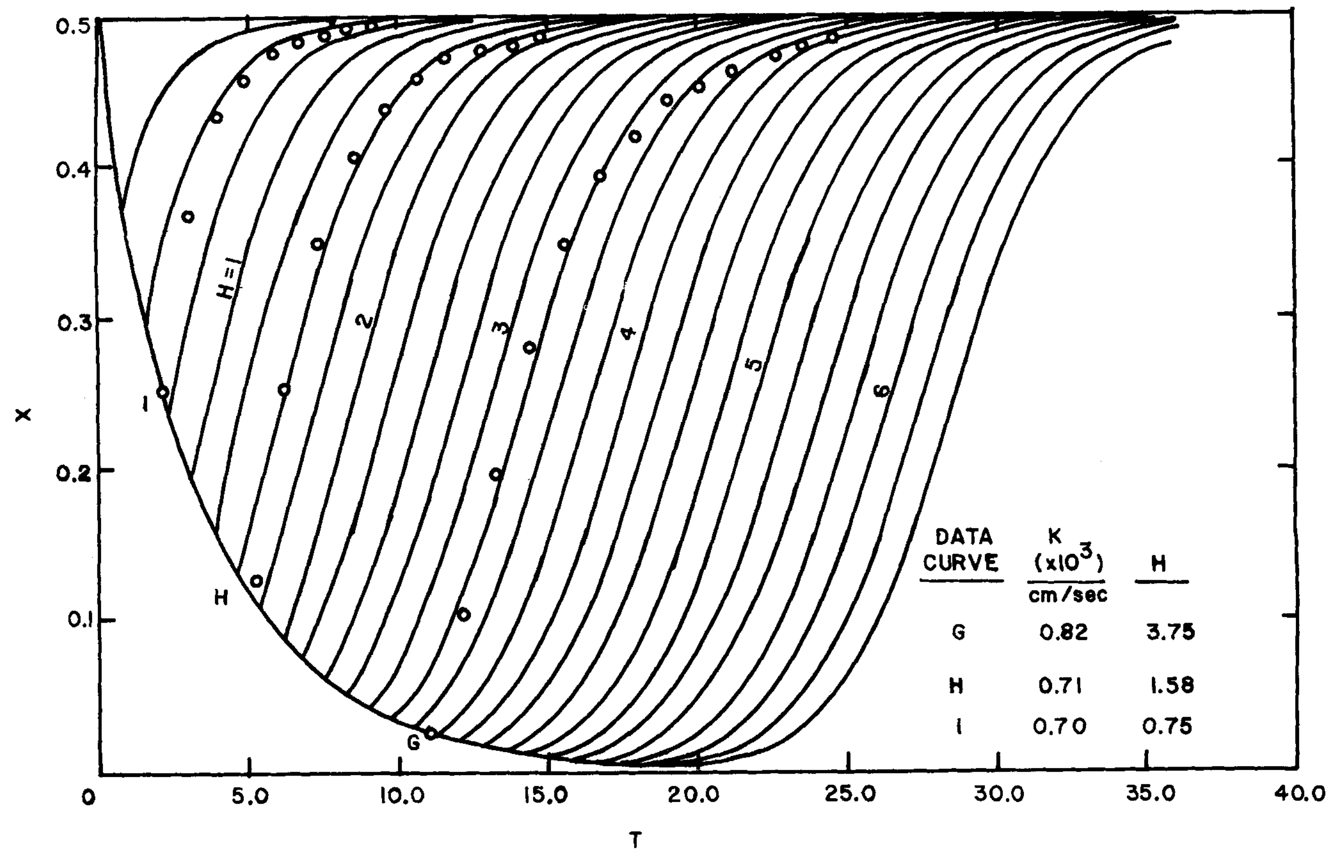


Fig. 4. Methylcyclohexane-toluene on alumina; $A = 3.0$.

unstable, although such was not the case for any of the runs made in this study, provided a suitable damping factor was used.

Computation times for each setting of the parameters averaged approximately 2 hr. on an IBM 7040 computer. The shortest runs lasted about 20 min. and at the other extreme, some of the slower converging cases ran up to 8 hr.

DISCUSSION OF RESULTS

Presentation of Calculations

The solutions are given as a set of curves in Figures 1 through 4. Table 1 summarizes the characteristics of each system studied. Data for these systems were taken from results by Johnson (*14*).

The object of this work is a satisfactory comparison between theoretical and experimental curves without covering necessarily a wide range of parameters. The curves presented in these figures reflect the optimum solution found after a number of trial runs were made. In Figures 1 through 4, the computer solutions are solid lines, while real data, converted to dimensionless form for the corresponding system, are plotted as points for comparative purposes.

Comparison of Computed and Experimental Curves

The theoretical solutions involve the parameters A, H, and T, as defined previously. Conversion of these results into the terms of actual time, particle radius, and bed depth requires knowledge of the mass transfer coefficient K and the effective internal diffusion constant D. Johnson (*14*) showed that the value of K may be determined in a trial-and-error procedure of matching experimental with theoretical curves. To do this a value of K was selected so that a curve of T *vs.* X could be converted into θ *vs.* x by means of the transformation equation.

In practice Johnson (*14*) discovered that no exact match of the actual with theoretical curves could be found. In general, the experimental curves which gave the best fit were somewhat flatter than the theoretical curves. It was because of this fact that Johnson concluded intraparticle diffusion affected those adsorption systems which he investigated and further recommended that additional theoretical treatment involving this mechanism was necessary.

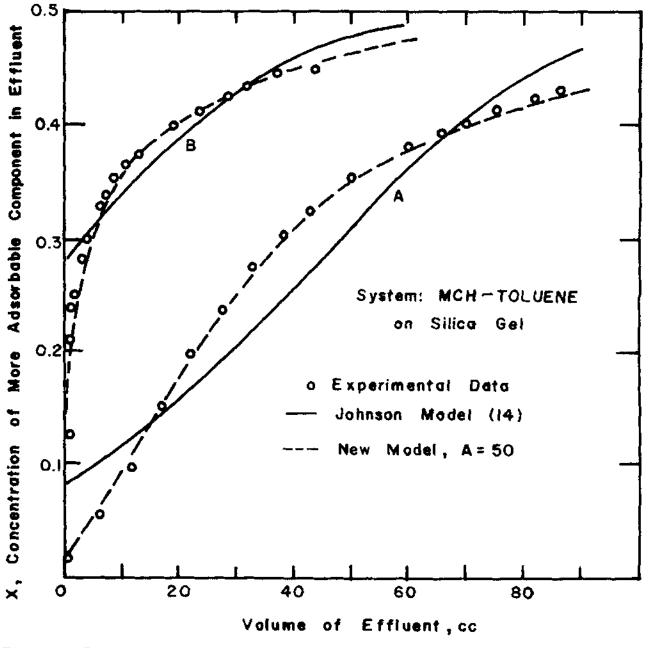


Fig. 5. Comparison of Johnson's model with the proposed model (curves *A* and *B*)

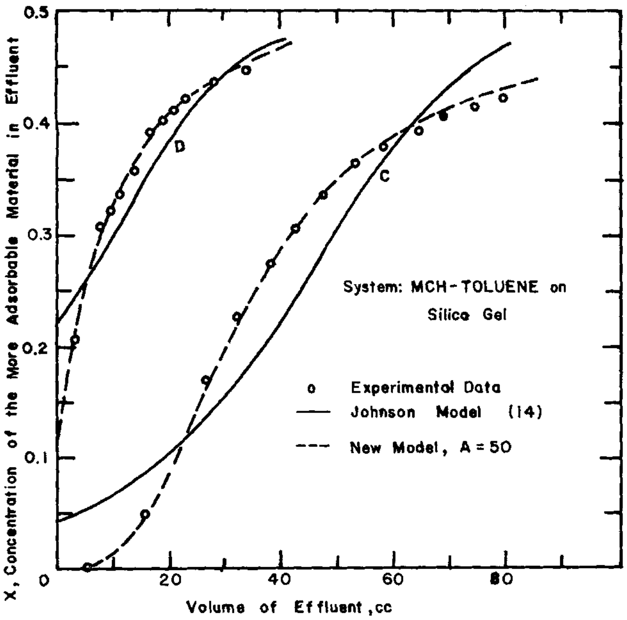


Fig. 6. Comparison of Johnson's model with the proposed model (curves C and D).

When intraparticle diffusion is considered, a similar matching procedure can be employed, but it is considerably more involved because of the added parameter A. Stated briefly, the procedure involves finding the best match, not only on one set of curves, but from all curves with *any* combination of H, T, and A. The problem becomes essentially three-dimensional in scope.

For the case of methylcyclohexane-toluene on silica gel at 0.5 feed concentration, the best match was found to be near $A = 50$, with $K = 2.4 \times 10^{-3}$ cm./sec., as shown in Figure 1. Substantial improvement in matching actual data with a model is seen by comparing Figure 1 ($A = 50$) with Figures 5 and 6, obtained from Johnson's work (*14*).

Of particular interest is the constancy of K with a change in bed height and feed rates. Additional experimental runs at different bed levels and feed rates demonstrated that it is possible to obtain approximately the same K through a similar matching procedure (curve B in Figure 1), at least over the range of variables studied. An experiment of this type tends to support the assumption that neglects longitudinal (axial) diffusion, at least between the two bed heights illustrated, and for the system considered.

The film coefficients obtained in this study may be compared with those calculated from rate data given by Eagle and Scott (*5*). Although direct comparisons for identical systems are not available, it may be seen that the results compare within an order of magnitude. For instance in the adsorption of toluene-octane on 10-14 mesh silica gel, values of K are noted to be in the range 1.27 to 1.69×10^{-4} cm./sec., with the data of Eagle and Scott, which compare with the values of 2.5×10^{-3} and 1.12×10^{-3} obtained in this study with methylcyclohexane-toluene on silica gel. Although the two figures differ by a factor of about 10, this is not totally unexpected because of the methods used and the difference in systems. Similar comparisons are made for adsorption on alumina. Data obtained from Eagle and Scott yield a value of $K = 0.85 \times 10^{-4}$ for the adsorption of toluene-octane, compared with 0.74×10^{-3} in this study for methylcyclohexane-toluene on alumina. The only system in which a good correlation between experimental data and computed curves is not obtained is that of methylcyclohexane-toluene on alumina (system 3 in Table 1).

NOTATION

a = effective particle radius, ft.
A = dimensionless particle radius, defined by Equation (8)
A_s = surface area across which diffusion occurs on the surface of the spherical particles, sq.ft./cu.ft. bed
D = effective intraparticle diffusivity, sq.ft./hr.
f_v = fraction voids within adsorbent bed
H = dimensionless bed level parameter, defined by Equation (7)
i, j = subscripts denoting column and row number of triangular grid
K = mass transfer coefficient for external surface film, ft./sec.
m = ratio of ΔT to $(\Delta R)^2$ in finite-difference equation for internal diffusion
Q = total liquid feed flow rate, cu.ft./hr.
r = particle radius variable, ft.
R = dimensionless particle radius variable, defined by Equation (8)
S = cross-sectional area of adsorbent column, sq.ft.
T = dimensionless time variable, defined by Equation (6)
V_p = pore volume, cu.ft./lb. adsorbent
W = rate of transfer of more adsorbable component from bulk phase to adsorbed phase in differential section dz, cu.ft./hr.
x = volumetric concentration of more adsorbable component in nonadsorbed phase, cu.ft./cu.ft.
x_f = volumetric feed concentration of more adsorbable component, cu. ft./cu.ft.
x^* = volumetric concentration of more adsorbable component on bulk-phase side of interface in equilibrium with the adsorbed phase interfacial concentration, cu.ft./cu.ft.
y = volumetric concentration of more adsorbable component in adsorbed phase, cu.ft./cu.ft.
y^* = volumetric concentration of more adsorbable component in adsorbed phase, cu.ft./cu.ft.
z = bed height variable, ft.
θ = real time elapsed since initial contact of feed with adsorbent, hr.
ρ_b = bed density, lb./cu.ft.

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APPENDIX I: PROCEDURE FOR NUMERICAL SOLUTION OF MODEL

Referring to the triangular grid described in developing this model, the following basically outlines the steps involved in a computer solution.

In column one of the triangular grid, which corresponds to feed entering the adsorption bed, the values of bulk concentration are known: $x_{j,1} = x_f$. However, it is necessary to have the concentration y_n at the surface of the particle in order to obtain the solution at the next level, that is, at $i = 2$. The procedure for obtaining y_n at the feed inlet for all later time values can be summarized as follows:

1. Assume initial estimate of surface concentration $y_n^{(o)}$.
2. Calculate x^* from equilibrium function: $x^* = f(y_n^{(o)})$, from which the term $x_f - x^*$ may be computed.
3. Solve diffusion equation to obtain a new estimate $y_n^{(1)}$ of surface concentration.
4. If the new surface concentration $(y_n^{(1)})$ varies significantly from $y_n^{(o)}$; adjust the estimate of y_n by a convergence factor q:

$$y_n^{(2)} = y_n^{(o)} + (y_n^{(o)} - y_n^{(1)})q \tag{17}$$

Repeat the computations from step 2, replacing $y_n^{(o)}$ by $y_n^{(2)}$.

At the completion of the above approximation for y_n (at point j,1, the entire procedure must be repeated for y_n (at point $j + 1$, 1) which corresponds to the next time level. In order to calculate y_n at any later time step it is necessary to save the entire diffusion curve (as a sequence of points) from the preceding time level, as each of these values is necessary in solving the diffusion equation. As will be seen later, it is also necessary to save the quantities x and x^* for use at higher bed levels. The extent to which the solution steps are carried out along the T axis depends upon the nature of the system being studied. The computer program was so designed to discontinue the above procedure after y_n approached its equilibrium value with x_f at any given dimensionless bed level, H, within a predetermined tolerance.

It is possible next to estimate the bulk phase concentration along column two of the triangular grid. This corresponds to the second dimensionless bed level over a range of time starting with $T = \Delta T$. The procedure for evaluating $x_{2,2}$ is also iterative, but slightly different from the preceding discussion for the first bed level. First an estimate of $x_{2,2}$ is made by fitting a first-order equation over the interval from $H = 0$ to $H = \Delta H$, with error bound of magnitude $(\Delta H)^2$. This estimate is obtained from the bulk phase material balance:

$$\left(\frac{\partial x}{\partial H}\right)_{T,R} = -3\left(\frac{\partial y}{\partial R}\right)_{H,T,R=A} \tag{18}$$

The right-hand term is equal to $3(x^* - x)$. The first-order approximation is thus

$$\overset{(o)}{x}_{2,2} = x_{2,1} + 3(x - x^*)_{2,1}\,\Delta H \tag{19}$$

Using $\overset{(o)}{x}_{2,2}$ we can obtain a better estimate, $\overset{(1)}{x}_{2,2}$, by means of a second-order formula with error of order $(\Delta H)^3$. This formula can be applied repeatedly until $x_{2,2}$ is determined within a specified tolerance. The second-order equation requires a value of $\partial x/\partial H$ at both grid points (2,1) and (2,2). With the estimated $x_{2,2}$ from the first-order equation used, an estimate of $x^*_{2,2}$ is made since it is known that $x_{2,2} = y_{2,2}$ from the model, and that $x^*_{2,2} = f(y_{2,2})$ from equilibrium data. Now it is possible to get a new estimate of $x_{2,2}$:

$$\overset{(o)}{x}_{2,2} = x_{2,1} + \frac{3}{2}\left[\left(\frac{\partial y}{\partial R}\right)_{2,1} + \left(\frac{\partial y}{\partial R_{2,2}}\right)\right]\Delta H \tag{20}$$

or

$$\overset{(2)}{x}_{2,2} = x_{2,1} + 1.5\,[x^* - x)_{2,1} + (x^* - x)^{(1)}_{2,2}]\,\Delta H \tag{21}$$

The new estimate of $x_{2,2}$ may be used to refine the term $(x^* - x)_{2,2}$ and to repeat calculations until no further improvement in $x_{2,2}$ occurs. During this stage it is not necessary to solve the diffusion equation as the initial distribution of concentration is equal to x at that point. In order to compute a distribution at the next step (time level 3), the initial distribution within the pore mus be defined: $y_k = x_{2,2}$.

The remaining grid points of column two of the triangular grid may be solved by a procedure which turns out to be double trial and error. This happens because two unknowns, $x_{j,2}$ and $y_{j,2}$ must be determined. Both $x_{j,2}$ and $y_{j,2}$ are estimated. For the estimated $y_{j,2}$, the corresponding $x_{j,2}$ is computed by essentially the same means as for point (2,2). This value of $x_{j,2}$ is then used in solving the diffusion equation to obtain a better estimate of $y_{j,2}$ as was done for column one, which in turn refines $x_{j,2}$. After both $x_{j,2}$ and $y_{j,2}$ compare favorably with previous estimates, the procedure is repeated for point (j + 1,2), and carried out for successive j's until y is sufficiently close to y^*, in equilibrium with x_f. At each higher time level, the preceding adsorbed phase distribution must be saved for at least one additional time level. Likewise, the term $x - x^*$ for each point along column one must have been previously saved. As calculations progress columnwise, older terms in computer storage may be replaced by newer ones as needed.

The calculation of remaining grid points, including the diagonal elements, follows a general procedure described briefly below. The diagonals are obtained by a method similar to that for point (2,2), except that from now on a third-order method is used, with error of order $(\Delta H)^4$. Use of a third-order integration formula requires that x and x^* from two preceding columns must have been retained in computer storage. The third-order integration formula used was (where $3 \leq i$)

$$\overset{(1)}{x}_{i\ \,i} = x_{i,i-1} - 3\,\Delta H\left[\frac{5}{12}\left(\frac{\partial y}{\partial R}\right)_{i,i} + \frac{8}{12}\left(\frac{\partial y}{\partial R}\right)_{i,i-1} - \frac{1}{12}\left(\frac{\partial y}{\partial R}\right)_{i,i-2}\right] \tag{22}$$

which becomes, after substitution of Equation (13)

$$\overset{(i)}{x}_{i\,,\,i} = x_{i,i-1} + \frac{\Delta H}{4}\,[5(x^* - x)^{(o)}_{i\,,\,i} + 8(x^* - x)_{i,i-1} - (x^* - x)_{i,i-2}] \tag{23}$$

In Equation (23) it is necessary to guess $\overset{(o)}{x}_{i\,,\,i}$, get $(x^* - x)_{i,i}$ from equilibrium relations, and then compute $\overset{(1)}{x}_{i\,,\,i}$. This value may be employed in turn on the right-hand side until the desired balance is reached. As in the case of grid point (2,2) the pore phase distribution is constant at the diagonal: $x_{i,i} = y_k$ ($k = 0,1,2,\ldots, n$).

The remaining points along column three and all higher numbered columns are solved by double trial-and-error in a manner similar to that described for column two. The only difference is that a third-order integration formula is applied, requiring the terms $(x^* - x)$ from two preceding columns.

The overall solution, with the above-described methods used, is obtained columnwise; that is, the entire history of the bed at a given dimensionless bed level is computed.

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