n = fitted exponent in Eq. 3
TDH = transport disengaging height
U = superficial gas velocity
U_{mf} = superficial gas velocity corresponding to minimum fluidization conditions
w_i = weight of particles in the i^{th} size fraction
X = dimensionless distance, x/x'
x = distance from mean expanded bed surface position to top of tube
x' = value of x at which $(h - h_\infty)/(h_b - h_\infty)$ reaches 0.025

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Numerical Solution of Liquid-Phase Multicomponent Adsorption in Fixed Beds

A generalized mathematical model is developed to describe the process of multicomponent adsorption on activated carbon in fixed beds. Numerical, finite difference, solutions for the adsorption of binary, and ternary organic mixtures are shown to satisfactorily match previously published experimental data.

AWADH MANSOUR,
D. U. von ROSENBERG,
and N. D. SYLVESTER

Department of Chemical Engineering
University of Tulsa
Tulsa, OK 74104

SCOPE

The removal of pollutants from aqueous waste streams by adsorption onto activated carbon in fixed beds is an important wastewater treatment process. Design and analysis of such systems requires consideration of multicomponent, nonlinear adsorption phenomena in conjunction with intraparticle and interparticle mass transport in a flow system. The objective of this study was to develop a comprehensive mathematical model for multicomponent, liquid phase adsorption in fixed beds and the necessary numerical solution method. Although many investigators have presented models for multicomponent liquid phase adsorption in fixed beds (Tables 1 and 2), the model developed herein is the most comprehensive. It accounts for intraparticle, interparticle and interphase mass transport, non-equilibrium conditions and non-linear multicomponent adsorption. The numerical solution developed permits detailed design and analysis of liquid phase multicomponent adsorption in fixed beds under both steady and unsteady state operation and should be especially useful to pollutant removal from aqueous waste streams.

Correspondence concerning this paper should be addressed to N. D. Sylvester.

A. Mansour is currently in the Chemical Engineering department at the University of Yarmouk; D. U. von Rosenberg, with Mobile Research in Dallas, TX.

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CONCLUSIONS AND SIGNIFICANCE

A comprehensive mathematical model and numerical solution of multicomponent liquid phase adsorption in fixed beds has been developed. It is applicable to both equilibrium and non-equilibrium adsorption, and any number of sorbates. The model, consisting of $4N$ partial differential equations (where N is the number of sorbates), takes into account intraparticle, interparticle and interphase mass transport and nonlinear adsorption. The numerical, finite difference solution method is shown to accurately predict experimental fixed bed adsorption data for both binary and ternary systems. The observed chromatographic peaks of the less strongly adsorbed species and the effect of adsorber length on breakthrough times and peak heights were also accurately predicted. The model developed will be most useful in the design and analysis of fixed bed activated carbon adsorbers treating multicomponent aqueous wastes. In addition, it can be readily extended to multicolumn and/or unsteady state process operation.

INTRODUCTION AND LITERATURE REVIEW

Adsorption is one of the most important processes used in industry for the separation of solutes from a fluid stream onto a solid surface and especially important in advanced wastewater treatment processes. Many investigators have presented models for multicomponent liquid phase adsorption in fixed beds as shown in Tables 1 and 2. None of these models has accounted for all of the factors listed below for multicomponent systems.

TABLE 1. HOMOGENEOUS LIQUID PHASE—SOLID DIFFUSION MODEL (FIXED BED)

Investigator	Film Resistance	Axial Diffusion	Micro System (Inside Particles)	Mathematical Treatment
		Linear Isotherm		
Rosen (1952, 1954)	Yes	No	No	Analytical and Numerical
Tien and Thodos (1960)	Yes	No	No	Analytical
Colwell and Dranoff (1966)	Yes	No	No	Rosen's Solution (1952, 1954)
Liaw et al. (1979)	Yes	No	No	Analytical
		Nonlinear Isotherm		
Tien and Thodos (1959, 1965)	Yes	No	No	Numerical
Cooney and Lightfoot (1966)	Yes*	No	No	Analytical and Experimental
Hall et al. (1966)	Yes	No	No	Analytical and Numerical
Kostecki et al. (1967)	Yes	No	No	Experimental
Morton and Murrill (1967)	Yes	No	No	Numerical
Chen et al. (1968)	No	No	No	Numerical
Colwell and Dranoff (1969, 1971)	Yes	No	No	Numerical
Cooney and Strusi (1972)	No	Yes	No	Analytical**
Usinowics ((1972)	Yes	No	No	Numerical and Experimental
Gariepy and Zwiebel (1975)	Yes	No	No	Numerical
Tien et al. (1976)	Yes	No	No	Analytical
Klaus et al. (1977)	Yes	No	No	Numerical
Hsieh et al. (1977)	Yes	No	No	Numerical
von Rosenberg et al. (1977)	Yes	No	No	Numerical
Balzli et al. (1978)	No	No	No	Numerical
Sung et al. (1979)	Yes	No	No	Numerical
Reis et al. (1979)	No	Yes	No	Analytical

* Only asymptotic solution was obtained.
** Pseudo-binary isotherms were used.

TABLE 2. PORE DIFFUSION MODEL

Investigator	Film Resistance	Axial Diffusion	Micro System (Inside Particles)	Mathematical Treatment
		Linear Isotherm		
Kasten et al. (1952)	Yes	No	No	Analytical
Lapidus and Amundson (1952)	No	Yes	No	Analytical
Szirmay (1978)	Yes	No	No	Experimental
		Nonlinear Isotherm		
Hall et al. (1966)	Yes	No	No	Numerical and Analytical
Rolke and Wilhelm (1969)	Yes	Yes	Yes*	Numerical
Ranjit and Weber (1975)	Yes	Yes	Yes*	Numerical and Experimental
Liapis and Rippin (1977)	Yes	No	Yes**	Numerical
Ozil and Bennetain (1977)	Yes	Yes	No	Analytical and Experimental
Crittenden et al. (1978)	Yes	No	No	Numerical
Balzli et al. (1978)	Yes	Yes	Yes	Experimental
Wilson (1979)	Yes	Yes	No	Numerical***

* One-component system was considered.
** Only two-component equilibrium model was solved.
*** One-component system was considered.

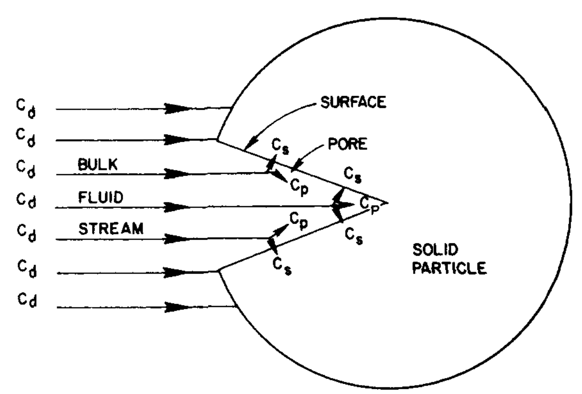

Figure 1. Diffusion of adsorbate into pores and adsorption onto solid surface.

1. (1) Intraparticle diffusional resistance
2. (2) Interparticle diffusional resistance
3. (3) Nonequilibrium conditions
4. (4) Nonlinear equilibrium relationship
5. (5) Interphase film resistance.

In this study, all of these factors are taken into account in the model developed.

MATHEMATICAL ANALYSIS

Physical Model

This study is concerned with the removal of sorbates from an aqueous stream entering a bed packed with spherical sorbent particles. Liquid containing one or more (1,2,3,. . .) sorbates is flowed through at constant velocity in plug flow. Sorbates, as shown in Figure 1, are transferred from the flowing stream to the pore liquid at the outer surface of the particles by the mechanism, $K_f(C_d - C_p|_{r=R})$. Inside the particles sorbates diffuse in the pore liquid by the mechanism $(-\epsilon_p D_p \partial C_p/\partial r)$. Also, they are adsorbed onto the internal surface through the mechanism $K_1(C_s - C_s^*)$, where C_s^* is the surface concentration in equilibrium with pore concentration, C_p. Sorbates also may diffuse into the particle by surface diffusion given by $(-D_s \partial C_s/\partial r)$. Thus, the transport processes (steps) can be summarized as follows:

1. Mass transport from bulk liquid to pore liquid at the particle surface
2. Diffusion into the porous solid
3. Adsorption onto the solid surface

In the packed-bed adsorption process, the radial concentration distribution of the adsorbates inside the particles as well as the longitudinal concentration profiles along the bed are to be determined as functions of time.

Mathematical Model

For each sorbate, two differential equations are needed to define the pore and surface concentrations inside the particles (*micro system*) as functions of particle radius, r, and time, t. These result from balances on the mass of the sorbate in the pore liquid and on the adsorbent surface. The equations are:

$$\epsilon_p D_p \left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C_p}{\partial r}\right)\right] - K_1 (C_s^* - C_s) = \epsilon_p \frac{\partial C_p}{\partial t} \qquad (1)$$

$$D_s \left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C_s}{\partial r}\right)\right] + K_1 (C_s^* - C_s) = \frac{\partial C_s}{\partial t} \qquad (2)$$

Since a pair of such equations is written for each sorbate, the variables C_p, C_s and C_s^* and the parameters D_p, D_S, and K_1 should be further subscripted with an index i which then takes on values from 1 to n, where n is the total number of sorbates in the system.

Equations 1 and 2 contain three dependent variables for each sorbate, since C_s^* is also unknown. C_s^* is expressed in terms of C_p by an equilibrium relation. After testing a number of well known relationships for multicomponent adsorption equilibria, it was concluded (Fritz and Schluender, 1974) that none of them was adequate to represent the adsorption of organic mixtures from aqueous solution on activated carbon and the general empirical equation, shown in Eq. 3 was used.

$$C_{si}^* = \frac{a_{i0}\, C_{pi}^{b_{i0}}}{C_i + \sum_{i=1}^{n} a_{ij}\, C_{pi}^{b_{ij}}} = f_i(C_{p^1},C_{p^2},\ldots,C_{pn}) \qquad (3)$$

In Eq. 3, C_{si}^* is the amount of solute i adsorbed per unit volume of the particle at equilibrium with a liquid-phase concentration C_{pi}, in a solution containing n solutes.

The Langmuir and Freundlich and other well known isotherms are special cases of Eq. 3. This equation has been used to fit experimental data of two and three solutes with satisfactory results (Fritz and Schleunder, 1974; and Balzli, 1978). The equilibrium isotherms determined for the binary system used in this study have the following form (Balzli, 1978):

$$C_{s1}^* = \frac{1.06\, C_{p1}^{1.217}}{C_{p1}^{0.812} + 0.626\, C_{p2}^{0.764}} \qquad (3A)$$

$$C_{s2}^* = \frac{1.07\, C_{p2}^{1.254}}{C_{p2}^{0.906} + 0.045\, C_{p1}^{0.634}} \qquad (3B)$$

where butanol-2 is taken as component 1 and t-amyl alcohol as component 2. For the ternary system the equilibrium relationships are:

$$C_{s1}^* = \frac{1.05\, C_{p1}^{1.134}}{C_{p1}^{0.73} + 1.44\, C_{p2}^{0.793} + 0.53\, C_{p3}^{0.467}} \qquad (3C)$$

$$C_{s2}^* = \frac{1.09\, C_{p2}^{1.182}}{C_{p2}^{0.831} + 0.52\, C_{p1}^{0.884} + 0.30\, C_{p3}^{0.536}} \qquad (3D)$$

$$C_{s3}^* = \frac{0.79\, C_{p3}^{0.224}}{C_{p3}^{0.002} + 1.07\, C_{p1}^{0.286} + 0.79\, C_{p2}^{0.235}} \qquad (3E)$$

where components 1 and 2 are as above and phenol is taken as component 3.

The initial and boundary conditions needed to complete the definition of the mico system are:

$$@t = 0,\ C_p = C_s = 0 \text{ for all } x \text{ and } r$$

$$@r = 0,\ \frac{\partial C_p}{\partial r} = \frac{\partial C_s}{\partial r} = 0 \text{ for all t}$$

$$@r = R,\ \frac{\partial C_s}{\partial r} = 0,\ \epsilon_p D_p \frac{\partial C_p}{\partial r} = K_f(C_d - C_p) \text{ for all } t$$

A material balance applied to the adsorbate carried by the flowing fluid stream (*the macro system*) gives the following equation:

$$\frac{\partial C_d}{\partial t} + \left(\frac{1-\epsilon_B}{\epsilon_B}\right)\left(\frac{3K_f}{R}\right)(C_d - C_p)_{r=R} + \frac{V}{\epsilon_B}\frac{\partial C_d}{\partial x} = D_L \frac{\partial^2 C_d}{\partial x^2} \qquad (4)$$

For $Z \gg d_p$, $\mathrm{Pe}_p > 1$, and $\mathrm{Re}_p \geq 10$, axial dispersion is unlikely to be significant, since

$$\frac{d_p}{Z}\left(\frac{1}{Pe_p}\right)\frac{\partial^2 C_d}{\partial x'^2} \ll \frac{\partial C_d}{\partial x'} \ (\text{for } x' = x/Z)$$

(Szekely et al., 1976; Gottschlich, 1963; Crittenden and Weber, 1978; and Lapidus and Amundson, 1952). In a recent paper, Farkas and Byleveld (1979) have found by experiment that axial dispersion is insignificant even when $\mathrm{Re}_p < 10$ and Pe_p is in the range of 0.02 to 0.22. In the present study, the values of Re_p and Pe_p will be respectively about 2.0 and 0.3. Therefore the neglect of axial dispersion will be reasonable especially when the adsorber is relatively long. Moreover the findings of Farkas and Byleveld (1979) indicate that axial dispersion does not contribute significantly to the shapes of the breakthrough curves. In the present model, axial dispersion is neglected because to consider it would increase tremendously the difficulty of obtaining the numerical solution of the resulting equations. Thus, Eq. 4 is simplified to the following form:

$$\frac{\partial C_d}{\partial t} + \left(\frac{1-\epsilon_B}{\epsilon_B}\right)\left(\frac{3K_f}{R}\right)(C_d - C_p)_{r=R} + \frac{V}{\epsilon_B}\frac{\partial C_d}{\partial x} = 0 \quad (4A)$$

A set of equations (Eqs. 1–3) is written for each sorbate. Equations 1 and 2 are coupled in C_p and C_s for a given sorbate through the interphase adsorption term, $K_1(C_s^* - C_s)$. The pairs for the various sorbates are also coupled through the equilibrium relation of Eq. 3. In addition, each pair for a specific sorbate is coupled with Eq. 4A through the term $K_f(C_d - C_p)_{r=R}$. Each set of equations may be solved simultaneously or sequentially. Since the equations are highly nonlinear, an iterative sequential numerical procedure was followed.

METHOD OF NUMERICAL SOLUTION

Micro-System

The governing equations of the micro-system are nonlinear partial differential equations, second order with respect to r and first order with respect to t. An iterative procedure for the finite difference equations is required to eliminate the nonlinearity arising from the term C_s^*. The denominator of this expression is evaluated with values obtained from the previous iteration. The form $C_s^* = C_pF(C_{pA})$ is linear in C_p since C_{pA} is the value of C_p obtained from the previous iteration. At the end of each iteration, the value of C_p is checked to determine whether it equals C_{pA} within a set tolerance. If it does not match, the computed values for C_p are used as C_{pA}, and another iteration is performed.

Finite Difference Equations

This system, i.e., Eqs. 1 and 2 for any component i, may be solved by either backward or the Crank-Nicolson methods (von Rosenberg, 1977; and Carnahan et al., 1969). Both of these methods are recommended because they are unconditionally stable (von Rosenberg, 1977; and Carnahan et al., 1969). Also, the same system has been solved by Mansour (1979) and shown to be unconditionally stable. Therefore the backward method was used in this study. The finite difference equations for the micro-system are described in detail by Mansour (1980).

Macro-System

This system is described by the hyperbolic partial differential Eq. 4A. This type of equation can be solved numerically by using the central difference technique (von Rosenberg, 1977). The finite difference grid used to set up the numerical analogs for the micro-macro system is shown in Figure 2. Both the hyperbolic and the parabolic equations are written at the + point; however, the grid for each variable is staggered. The grid alternates with values of C_d at the O's and $C_p|_{r=R}$ at the X's. The finite difference equations for the macro-system are given by Mansour (1980).

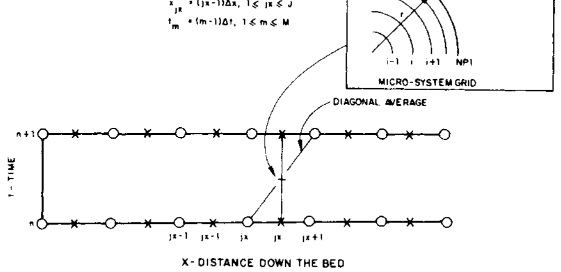

Figure 2. Finite-difference grid for micro-macro system.

Scheme of Numerical Solution

Equations 1 and 2 (the micro-system) form a bi-tridiagonal system, with $i = 1, 2, \ldots NR, NP1$. This system is solved by the algorithm for bi-tridiagonal matrices (von Rosenberg, 1977). The procedure of calculation is as follows: The first half of the algorithm is solved, i.e., all the coefficients A1(I), B1(I), . . . , etc., and all parameters β's, λ's, δ's and γ's are computed. The second half is solved back, i.e., the variables C_s's and C_p's are computed. This algorithm is used to solve the finite difference equations during each iteration at a given time step. After convergence is obtained, the coefficients are updated, and the procedure is repeated for the next time step.

RESULTS AND DISCUSSION

Parametric Analysis

The purpose of this analysis is to study the effects of different parameters on the performance of fixed-bed adsorbers. A summary of the ranges of values of the important parameters used by other investigators is shown in Table 3. Some of the parameters were held constant at their average values, while other parameters were varied over their ranges. The values of fixed parameters, K_f, V, ϵ_p, ϵ_B, C_o and Z were taken respectively as: 1×10^{-3} cm•s^{-1}, 0.2 cm•s^{-1}, 0.8, 0.45, 10^{-5} g•cm^{-3} and 100 cm. The varied parameters were the adsorption rate constant, K_1, the pore diffusion coefficient, D_p, and the particle size, R. Their variation is also shown in Table 3.

Effect of Adsorption Rate Constant on Breakthrough Curves. The effect of adsorption rate constant, K_1, is illustrated in Figure 3 for the three runs in which the only variable was K_1. Referring to the curves in Figure 3 at early times the effluent concentration is highest for $K_1 = 10^{-4}$s^{-1} and decreases as K_1 increases. To interpret the physics behind this phenomenon Figure 4 is used to

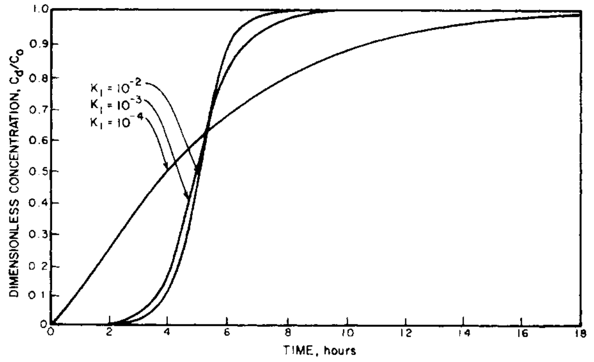

Figure 3. Effect of K_1 on predicted breakthrough curves.

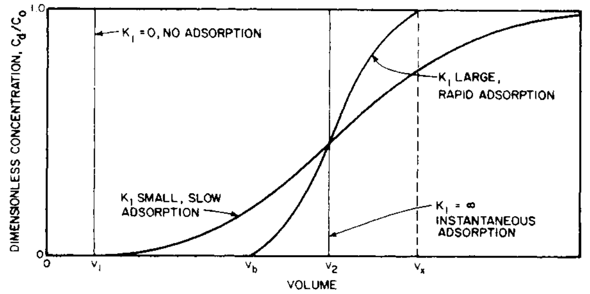

Figure 4. Dependence of breakthrough on adsorption rate constant (ideal breakthrough curves).

TABLE 3. PARAMETERS IN LITERATURE

Investigator	K_1, s^{-1}	K_f, cm·s^{-1}	V, cm·s^{-1}	D_p, cm^2·s^{-1}	ϵ_p	ϵ_B	C_o, g·cm^{-3}	Z, cm	R, cm
Klaus et al. (1977)*	—	0.0712	0.22	9×10^{-6}	0.79	0.5	6×10^{-5}	101	0.062
Wilde (1979)*	—	—	0.272	7×10^{-6}	0.60	0.4	$10^{-5}-10^{-4}$	200	0.05
Hsieh et al. (1977)**	$1.56–41.7 \times 10^{-4}$	—	0.272	—	—	—	$1-6 \times 10^{-6}$	76.2	—
Chakrovorti and Weber (1975)**	—	$0.711–1.1 \times 10^{-3}$	1.09 − 8.08	$2.5–8.3 \times 10^{-6}$	—	—	$2.4–5.4 \times 10^{-6}$	183	0.069–0.1248
Crittenden and Weber (1978)**	—	2.35×10^{-3}	0.736–1.54	9.64×10^{-6}	0.85	0.45–0.43	$6.5–5.3 \times 10^{-6}$	30.5–88.6	0.0155–0.0765
Balzli et al. (1978)**	$3.28–5.3 \times 10^{-4}$	$1.68–2.11 \times 10^{-3}$	0.14	$7.4–13 \times 10^{-6}$	0.94	0.45	$1-2 \times 10^{-3}$	41 −287	0.05
Martin and Al-Bahrani (1977, 1978)**	—	—	0.144	—	—	—	$0.125–5.3 \times 10^{-5}$	8–22.5	0.045–0.055
Range of variation	$10^{-4}–10^{-1}$	1×10^{-3}	0.2	$10^{-6}–10^{-5}$	0.8	0.45	10^{-5}	100	0.05–0.125

* Numerical Work
** Experimental Work

represent idealized breakthrough curves. For $K_1 = \infty$, any resistance to mass transfer will not slow down the rate of adsorption and equilibrium between solid and liquid phases is established at all points in the bed, or in symbols $C_s = C_s^* = f(C_{p1}, C_{p2} \ldots C_{pn})$. For small values of K_1, the resistance to mass transfer is relatively large and the rate of adsorption will be slower and the breakthrough less sharp. For all curves, except $K_1 = 0$, the amount of sorbates to saturate all sorbent should be the same and is equal to the integral $\int_{V_1}^{\infty} (1 - C_d/C_o) dV$. This integration can be evaluated either numerically or graphically after changing the limits of integration to give the expression:

$$\text{Amount required for saturation} = \int_0^1 \left(1 - \frac{C_d}{C_0}\right) d\left(\frac{V - V_b}{V_x - V_b}\right)$$

where

V_b = break-point effluent volume
V_x = an arbitrary selected volume where the sorbent is considered to be essentially exhausted or C_x, closely approaching C_o

The three curves, in Figure 3, must eventually cross since the area above the breakthrough curves is related to the total adsorption capacity of the bed. Since the bed in each case contains the same mass of particles and the particles have essentially the same capacities, the total capacity in each case is about the same.

Effect of Pore-Diffusion Coefficient on Breakthrough Curves. Almost the same effect is observed when one increases the pore-diffusion constant of the sorbate into the pores, as shown in Figure 5. For $D_p = 10^{-7}$ cm^2·s^{-1}, the breakthrough at early times is highest and decreases as D_p increases. This behavior is expected since at constant values of mass transfer coefficient, K_f and particle size, R, Sherwood number, Sh_p, for the least value of D_p will be the highest, which means that intraparticle diffusion is the significant mass transfer resistance exhibited by the system and this will result in earlier breakthrough and sharper wave front. Moreover, it has been shown by many investigators (e.g., Hsieh et al., 1977) that for a constant particle size the adsorption rate constant is a direct linear function of D_p and therefore they both have similar effects on the predicted breakthrough curves.

It should be noted that the K_1 value used (i.e., $K_1 = 10^{-4}$) was for the case of a slow rate of adsorption. Thus a relatively large effect of D_p is noted in Figure 5. If $K_1 = 10^{-2}$ were used a much smaller effect of D_p would be found.

Effect of Particle Size on Breakthrough Curves. The effect of particle size is shown in Figure 6. It is obvious that a strong influence occurs at early breakthrough times which is seen to be highest for $R = 0.125$ cm and decreases as the particle size decreases. Two factors contribute to this (e.g., Chakravorti and Weber, 1975). The first is the mass transfer coefficient and the outside surface per unit volume. When particles are first contacted by liquid containing sorbate, the rate of mass transfer is controlled by the outside film resistance. Each of the runs has the same inlet concentration, so the effect of this factor is the same in all three of the cases. Therefore, the rate of mass transfer is proportional to the product of the mass transfer coefficient and the outside area of the particles per unit volume. Since this product for the 0.125 cm particle is smallest, the mass transfer rate is initially slower for them. The second factor that causes earliest breakthrough for the largest particles is that for a given particle, as time proceeds, the diffusional resistance becomes increasingly significant. Since the largest particles have the longest diffusional paths, they would be expected to have the earliest breakthrough. The three curves should intersect, since the area under the breakthrough curves is related to ultimate holdup of the bed. Since the bed in each case contained the same mass of particles and the particles had essentially the same capacities, the holdup in each case was about the same. Nevertheless, the effect of the particle size is much less than that of K_1 and D_p.

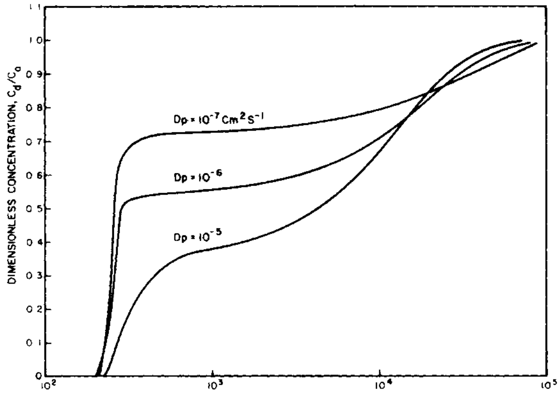

Figure 5. Effect of pore diffusion coefficient on predicted breakthrough curves.

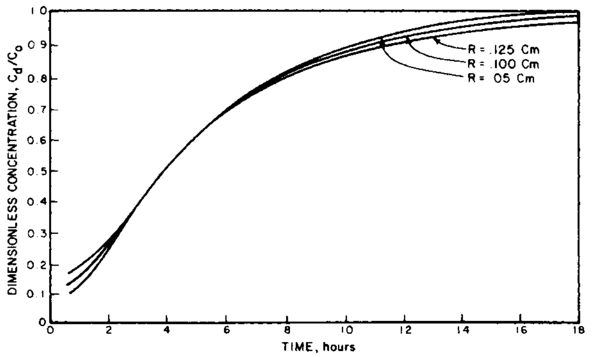

Figure 6. Effect of particle size on predicted breakthrough curves.

Effect of Time Step Size on Breakthrough Curves. Runs with several time-step sizes (from 0.8 to 30 seconds) were carried out to check stability and truncation error. No fluctuations were encountered and smooth regular behavior for all breakthrough curves was obtained. A time-step as large as 26.54 seconds was used in all computer programs and the results, to the third digit, were as accurate as the ones found when $\Delta t = 0.82958$ s. Moreover, for single, binary and ternary systems, two or three iterations were enough to achieve convergence in the micro-system. Typical CPU times were 57 s for the binary system and 82 seconds for the ternary on the Honeywell Sigma-6.

Results for a 41-cm Adsorber

Results for the Two-Component System. The parameter values used for this case were as follows: $\epsilon_p = 0.94$, $\epsilon_B = 0.45$, $V = 0.139$ cm·s^{-1}, $Z = 41$ cm, $C_{o1} = 0.001$ g·cm^{-3}, $C_{o2} = 0.001015$ g·cm^{-3}, $K_{f1} = 2.115 \times 10^{-3}$ cm·s^{-1}, $K_{f2} = 1.68 \times 10^{-3}$ cm·s^{-1}, $K_{1,1} = 0.0005333$ s^{-1} and $K_{1,2} = 0.004917$ s^{-1}. The coefficients in the isotherms were given above. These values of constants and parameters were used in the experiments that Balzli (1977) performed and to which the results are compared.

Excellent agreement between the theoretical results and the experimental data has been achieved as shown in Figure 7. In Figure 7, the effluent concentration profile shows a peak, indicating a concentration higher than the feed concentration ($C_{d1}/C_{o1} > 1$). Similar observations were reported by Helfferich and Klein (1970) and have been found by others including Zwiebel et al. (1974), Hsieh et al. (1977), Klaus et al. (1977), Balzli et al. (1978), and Sung et al. (1979). In order to explain this phenomena let us define the components in a multicomponent system according to the degree of adsorption affinity or the degree of nonlinearity in their equilibrium isotherms. The component having the most nonlinear isotherm is defined as the key component ($i = 2$) while the other is defined as nonkey component ($i = 1$). The behavior of breakthrough profiles in a two-component system is entirely different from that of the one-component system. The peak in Figure 7 (Zwiebel et al., 1974; Balzli et al., 1978; and Sung et al., 1979) arises from competitive adsorption between the two sorbates. In earlier stages of adsorption, both butanol (C_1) and t-amyl alcohol (C_2) are adsorbed on the activated carbon. Later, since the key component (C_2) has the stronger affinity, it replaces the non-key component (C_1), which then appears in the effluent as a concentration peak. It will be shown later that the height of the peak is a function of both the relative affinities and the length of the column. In conclusion, it can be said that the more nonlinear the non-key equilibrium curve the more delayed its breakthrough.

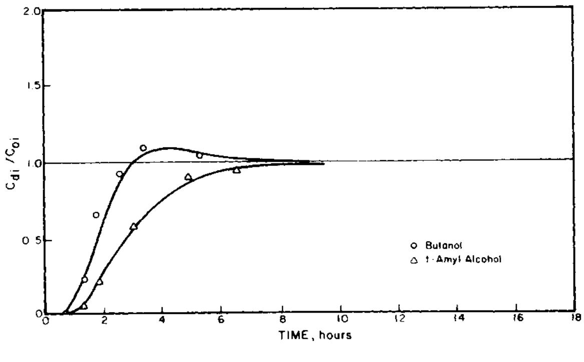

Figure 7. Simultaneous adsorption of butanol and *t*-amyl alcohol.

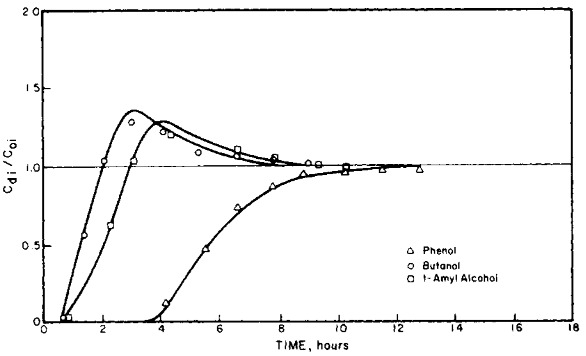

Figure 8. Simultaneous adsorption of butanol, *t*-amyl alcohol and phenol in a 41cm bed.

Results for the Three-Component System. The values of parameters for this model were also used experimentally by Balzli (1977) where butanol is taken as component 1 (C_1), *t*-amyl alcohol as component 2 (C_2), and phenol as component 3 (C_3). These values are: $\epsilon_p = 0.94$; $\epsilon_B = 0.45$; $V = 0.139$ cm·s^{-1}; $Z = 41$ cm; $C_{o1} = 9.15 \times 10^{-4}$ g·cm^{-3}; $C_{o2} = 9.12 \times 10^{-4}$ g·cm^{-3}; $C_{o3} = 9.97 \times 10^{-4}$ g·cm^{-3}; $K_{f1} = 2.12 \times 10^{-3}$ cm·s^{-1}; $K_{f2} = 1.95 \times 10^{-3}$ cm·s^{-1}; $K_{f3} = 2.17 \times 10^{-3}$ cm·s^{-1}; $K_{1,1} = 0.0005333$ s^{-1}; $K_{1,2} = 0.0004917$ s^{-1}; and $K_{1,3} = 0.0003278$ s^{-1}. Coefficients in the isotherms were given above.

Figure 8 shows excellent agreement between the theoretical predictions of this study and experimental data obtained by Balzli (1977). What has been said about the results of the two-component system can also be said here and the only difference between the two cases is that phenol (C_3) is taken as the key component while butanol and *t*-amyl alcohol are taken as the nonkey components. Similar behavior of effluent concentration curves is observed in Figure 8 for the three component system. The wave fronts of the nonkey components (C_1 and C_2) appear at about the same time and are crowded together because the values of their physical parameters are close to one another. Likewise, concentration peaks occur only for the nonkey components (C_1 and C_2), which were at first adsorbed into the activated carbon in the bed. Since phenol has the strongest adsorption affinity, it appears in the effluent only after a very long time.

Results for the Three-Component System in an 82-cm Adsorber

All parameter values used here are the same as above except for $Z = 82$ cm.

Figure 9 shows an excellent agreement with experimental data. In addition it can be seen that the bed length affects the breakthough times and peak heights. It was found that when the length of bed was doubled an increase of 25% and 23.5% in the peak heights of component C_1 and C_2, respectively, occurred. Also it can be noticed that the breakthough curves were delayed by 1.5, 2 and 5.5 hours for component 1, 2 and 3 respectively. Similar observations have been reported by Zwiebel et al. (1974), Klaus et al. (1977), Balzli et al. (1978) and Sung et al. (1979). It is believed that the height of the peak is a function of the length of the column; because, the longer the bed the larger the total amount of the nonkey component displaced. Also as peaks increase the breakthrough time increases. Also, the separation between the fronts

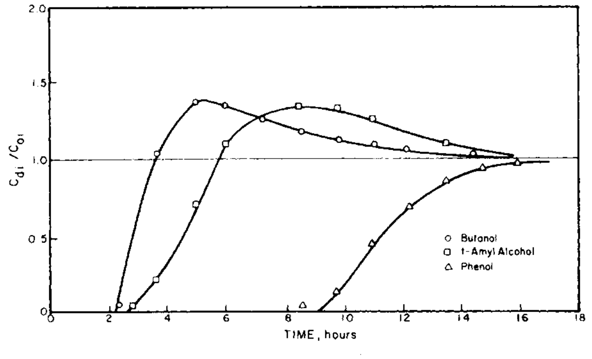

Figure 9. Simultaneous adsorption of butanol, *t*-amyl alcohol and phenol in a 82cm bed.

increases in the longer beds. Thus, there is a critical bed length (Zwiebel et al., 1974) beyond which the extra amount of nonkey component displaced can no longer catch up with the front and add to the peak height; instead, it will only contribute to the tail end, or descending portion, of the breakthrough curve.

NOTATION

a_{i0}, a_{ij} = coefficients in Eq. 3
b_{i0}, b_{ij} = exponents in Eq. 3
C_d = concentration of solute in fluid phase of the bed, g/cc
C_0 = value of C_d at the entrance of bed
C_p = concentration of solute in pore fluid phase, g/cc
C_s = concentration of solute in solid phase (per unit volume of particles), g/cc
D_L = longitudinal diffusivity, cm^2/s
D_p = effective diffusivity in pore fluid, cm^2/s
d_p = particle diameter, cm
D_s = effective diffusivity in particle solid phase, cm^2/s
K_f = mass transfer coefficient for liquid-particle transfer, cm/s
K_1 = adsorption rate coefficient, s^{-1}
Pe_p = particle Peclet number $(d_p V/D_L)$, dimensionless
r = radial distance in particle, cm
R = radius of particle, cm
Re_p = particle Reynolds number $(\rho V d_p/\mu)$, dimensionless
Sh_p = particle Sherwood number $(d_p K_f/D_p \epsilon_p)$, dimensionless
t = time, s
V = fluid velocity, cm/s
x = distance along bed, cm
Z = length of adsorber, cm

Greek Letters

ρ = fluid density, g/cc
μ = fluid viscosity, g/cm·s
ϵ_B = bed void fraction
ϵ_p = particle void fraction

Superscripts

$*$ = equilibrium value

Subscripts

i = integer value
j = integer value
p = pore
s = solid

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Diffusivity of Urea in Concentrated, Saturated and Supersaturated Solutions

A relatively simple and extremely versatile optical method of obtaining diffusion coefficient data known as Gouy interferometry was employed to measure diffusion coefficients in undersaturated and supersaturated aqueous urea solutions at 25°C. The use of laser light as a monochromatic light source in the interferometer greatly simplified the procedure for obtaining diffusivity data from the interferometer. A novel design of a real image camera was employed to record the interferometric data. Values obtained from the interferometric data for low concentration (0–4 molar) aqueous urea solutions were within ±5% of literature values.

The diffusion coefficient was found to decrease linearly with increasing concentration up to the saturation point of the aqueous urea solutions, and to decrease drastically with increasing concentration in the supersaturated region. This behavior is similar to that observed in liquid-liquid systems near the consolute point (Cussler, 1980). It is speculated that this phenomenon is a result of molecular aggregation of the urea molecules in supersaturated aqueous solutions. Very little experimental data have previously been obtained in the supersaturated region due to crystallization problems. Supersaturated diffusion coefficient data are important in the study and design of crystallization processes.

The solid-solute-liquid solvent binary systems urea-water and sucrose-water were modeled as a saturated solution solute-liquid solvent system in order to test various concentration dependent diffusion relationships. Two of these relationships, the Vignes and Leffler-Cullinan equations, showed improved correlation with experimentally determined diffusivity data for aqueous urea and aqueous sucrose solutions at undersaturated conditions.

L. S. SORELL and
A. S. MYERSON

School of Chemical Engineering
Georgia Institute of Technology
Atlanta, GA 30332

SCOPE

The measurement of diffusion coefficients in supersaturated solutions is of fundamental importance in further understanding the mechanism of diffusion. In particular, diffusion data in the supersaturated range are necessary for the rational design of crystallization processes. Virtually no data of this kind exists, however, resulting in the use of values obtained through the extrapolation of lower concentration data to the supersaturated region. Diffusion coefficients obtained through this extrapolation could be seriously in error as a result of molecular aggregation postulated to occur in supersaturated solutions. In addition, the prediction of diffusion coefficients in concentrated solid solute-liquid solvent systems are limited by the fact that many of the widely used equations employed in the prediction of concentration dependent diffusion coefficients were designed for use with liquid-liquid systems. The purpose of this study is as follows: (1) the experimental measurement of diffusion coefficients in concentrated, saturated and supersaturated solutions of nonelectrolytes (2) comparison of results obtained in the supersaturated region with those predicted by existing correlations and by extrapolation of data in the undersaturated region, and (3) comparison of results obtained in both the undersaturated and supersaturated region with modifications of predictive equations normally used in liquid-liquid systems.

L. S. Sorell is presently at the Texaco Research Laboratory, Beacon, N.Y.
Correspondence concerning this paper should be sent to A. S. Myerson.
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