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Adsorption Kinetics in Fixed Beds with Nonlinear Equilibrium Relationships

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Previous work by the authors on ion exchange kinetics for systems having nonlinear equilibrium relationships has been extended. Computer studies have produced additional concentration—bed length–time relationships for values of α_O = 5, 10, and 50. This information and the results obtained previously for values of α_O = 100 and 1,000 provide an extensive variation of the parameter α_O for design applications. The composite results are represented graphically.

Separation processes in fluid-solid systems have recently become increasingly important. The design of processes conducted in fixed beds requires accurate prediction of the concentration history of the effluent stream.

For the analytical study of the kinetic behavior of a fixed-bed system, the initial task is to express the bed operation mathematically in terms of the continuity equation, the rate of adsorption, and the equilibrium relationship that describes the system. Although the continuity equation is general, the exact form of the rate relationship depends on the individual case. In general, there are two types of such relationships. In the first case the rate is expressed in terms of the fluid concentration and the average concentration within the adsorbent. Here the diffusion resistance in the solid phase is assumed negligible. Most of the investigations reported in the literature are based on this model, notably the comprehensive studies of Goldstein (*1*, *2*), Goldstein and Murray (*3* to *5*), and Vermeulen (*12*). The second type of rate relationship is that in which the solid diffusion resistance is as significant as the resistance in the fluid phase. Rosen (*6*) studied this case for systems having a linear equilibrium relationship. Tien and Thodos (*9*) generalized Rosen's study to include systems having nonlinear equilibrium relationships. The concentration history of the effluent stream expressed in terms of c/c_o was presented as a function of parameters representing time, bed length, and relative resistance.

Although the mathematical treatment of this problem was presented in detail previously (*9*), this study considers the final equations used in the computations and the definitions of the pertinent parameters. The parameters α, α_s, and β are related through the following relationships:

$$\beta_{s_i}^{\,j+1} = C_1 \left[(\alpha_i^{\,j} - \alpha_{s_i}^{\,j}) + C_2 \sum_{k=1}^{j} K_{j-(k-1)} \beta_{s_i}^{\,k} \right] \quad (1)$$

$$\alpha_{i+1}^{\,j} = \alpha_i^{\,j} + (\alpha_{s_i}^{\,j} - \alpha_i^{\,j})\Delta x \quad (2)$$

$$\beta_s = \alpha_s^{\,a} \quad (3)$$

The subscript i and the superscript j refer to x and θ, respectively. The initial and boundary conditions for this problem are

$$\alpha = \alpha_s = \beta_s = 0 \quad \text{for} \quad x \geqq 0 \quad \text{and} \quad \theta \leqq 0 \quad (4)$$

and

$$\alpha = \alpha_o \quad \text{for} \quad x = 0 \quad \text{and} \quad \theta > 0 \quad (5)$$

In Equation (3) the exponent a is a constant dependent upon the appropriate equilibrium relationship. In this study a has been assumed to be 0.5. The constants C_1, C_2, and $K_{j-(k-1)}$ are defined as

$$C_1 = \frac{1}{\dfrac{3}{\pi\sqrt{\Delta\theta}} - \dfrac{3}{4\pi}} \approx \frac{\pi\sqrt{\Delta\theta}}{3} \quad (6)$$

$$C_2 = \frac{3}{\pi\sqrt{\Delta\theta}} \quad (7)$$

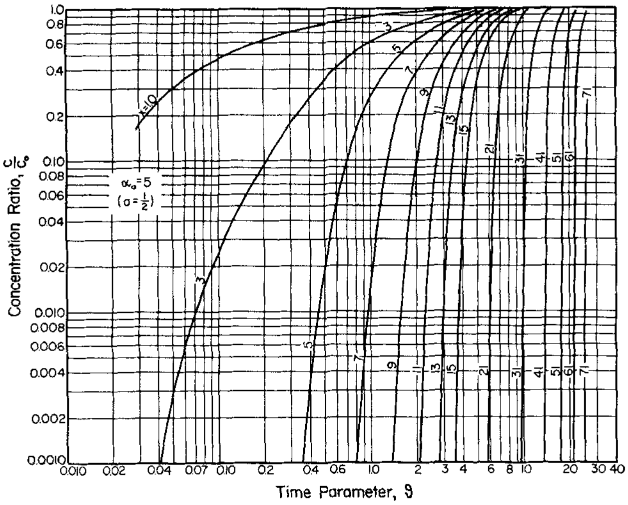

Fig. 1. Concentration—bed length—time relationships for $\alpha_0 = 5$ and $a = ½$.

and

$$K_{j-(k-1)} = -\sqrt{j-(k-2)} + 2\sqrt{j-(k-1)} - \sqrt{j-k} \tag{8}$$

The dimensionless bed-length parameter x in Equation (2) and the dimensionless time parameter θ in Equations (6) and (7) are defined as

$$x = k_l \rho \frac{z}{u} \tag{9}$$

and

$$\theta = \frac{4\pi D}{b^2}\left[t - \phi \frac{z}{u} \right] \tag{10}$$

The fluid- and solid-concentration parameters α and β are defined as follows:

$$\alpha = \frac{c}{c_o}\left[\frac{c_o b^2 k_l}{4\pi q_{\max} D} \right]^{\frac{1}{1-a}} \tag{11}$$

and

$$\beta = \frac{q}{q_{\max}}\left[\frac{c_o b^2 k_l}{4\pi q_{\max} D} \right]^{\frac{a}{1-a}} \tag{12}$$

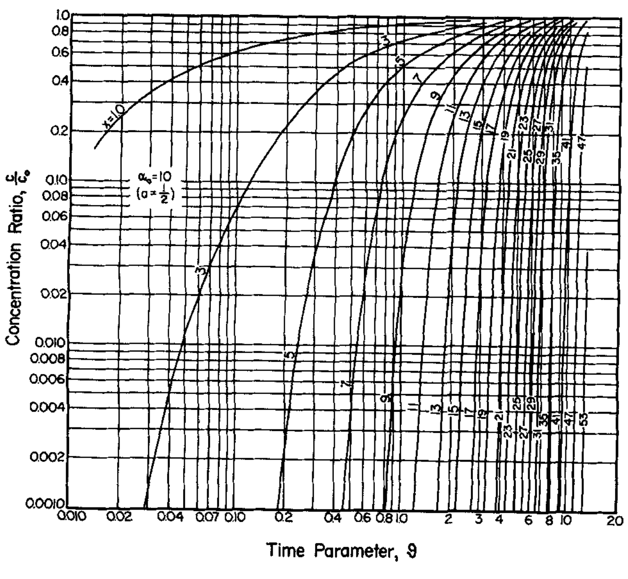

Fig. 2. Concentration—bed length—time relationships for $\alpha_0 = 10$ and $a = ½$.

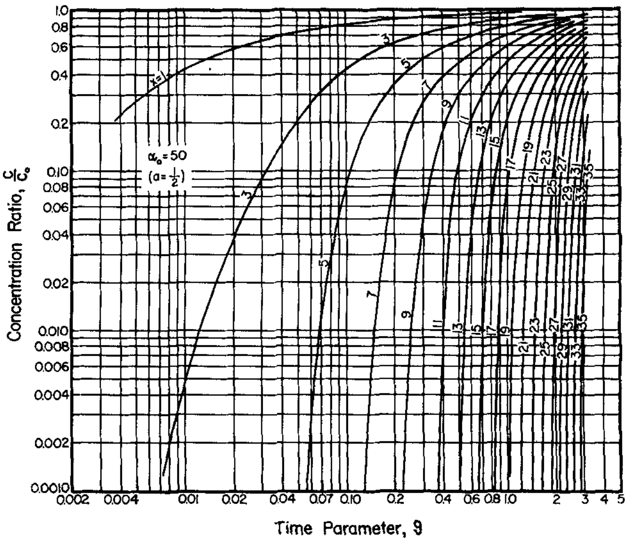

Fig. 3. Concentration—bed length—time relationships for $\alpha_0 = 50$ and $a = ½$.

The concentration ratio c/c_o is equivalent to α/α_o, where

$$\alpha_o = \left[\frac{c_o b^2 k_l}{4\pi q_{\max} D} \right]^{\frac{1}{1-a}} \tag{13}$$

The parameter α_o represents the relative resistance of the solid phase to the fluid phase.

Equations (1) through (13) were used in a digital computer to obtain values of c/c_o vs θ with x as a parameter for a constant value of α_o. The previous study considered the cases of $\alpha_o = 100$ and $\alpha_o = 1{,}000$. In the present study this range has been extended to include the lower values $\alpha_o = 5$, 10, and 50, so that a breakthrough curve may be predicted for cases in which the relative resistance of the fluid becomes more pronounced. Furthermore, for the lower values of α_o the selection of the time increment $\Delta\theta$, which is critical to the convergence of the computation, becomes more relaxed. With the limited memory capacity of the computer this condition permits the calculation of the breakthrough curve for higher values of x, the bed-length parameter. The results

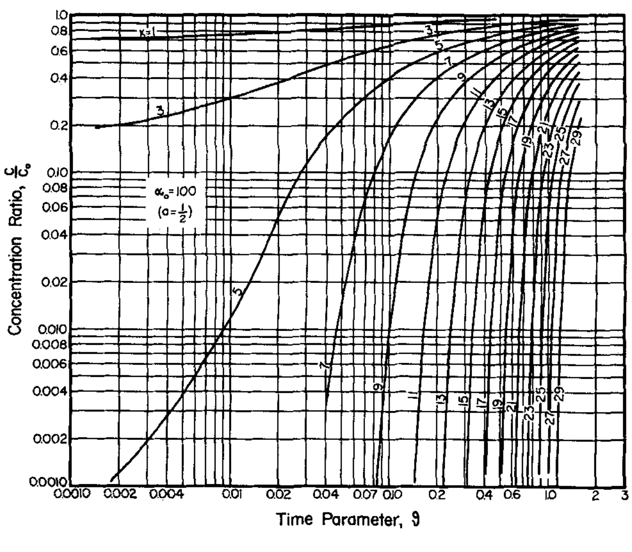

Fig. 4. Concentration—bed length—time relationships for $\alpha_0 = 100$ and $a = ½$.

are presented graphically in Figures 1, 2, and 3. Results for the cases $\alpha_o = 100$ and $\alpha_o = 1{,}000$ were previously presented with the time modulus θ multiplied by 2 raised to the proper powers; in order to simplify the use of these charts and to provide more complete information, the cases of $\alpha_o = 100$ and $\alpha_o = 1{,}000$ are also included in this study, with θ expressed directly as shown in Figures 4 and 5.

DISCUSSION OF RESULTS

The breakthrough curve for any system can be predicted if the operating conditions, particle size, bed length, and physical properties (equilibrium relationship, diffusion coefficient through the solid, density of the particles) are available. The equilibrium relationship can be determined by any of the conventional procedures. The diffusion coefficient for the solid phase can be calculated by the method described by Tien (*8*). (It should be pointed out, however, that in this treatment the solid phase is assumed to be quasihomogeneous.) The liquid-film mass transfer coefficient can be estimated from the *j*-factor correlations for packed beds, or it can be determined experimentally in the manner outlined by Tien and Thodos (*11*).

In the present study the equilibrium relationship is of the following type, with $a = 0.5$:

$$q^* = A(c^*)^a \tag{14}$$

where a is a constant and c^* and q^* represent the equilibrium concentrations in the liquid and solid phases, respectively. In order to apply the results of the present study to cases having the same type of favorable equilibrium relationships but different values of the exponent a, these present results must be interpolated with those for the limiting cases or $a = 0$ and $a = 1$. For the case $a = 0$, the solution was presented by Tien and Thodos (*10*). Rosen (*6, 7*) presented the solution for the case $a = 1$.

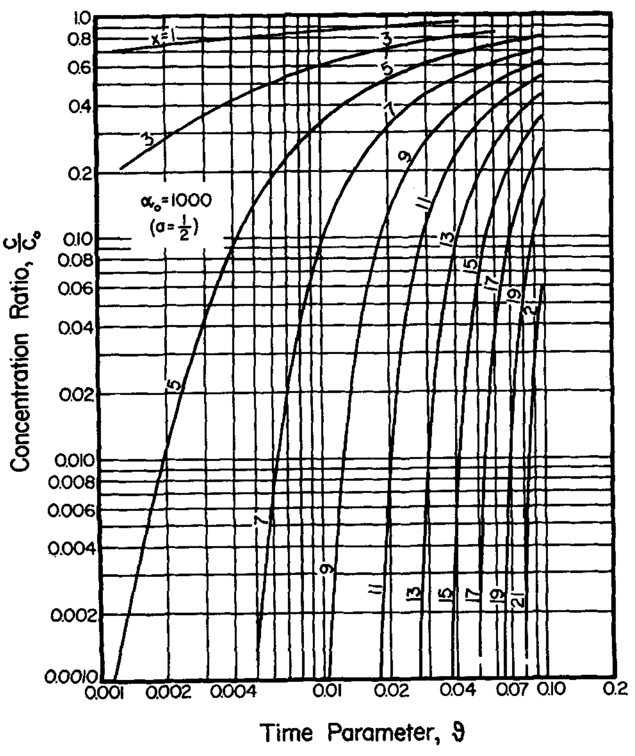

Fig. 5. Concentration—bed length—time relationships for $\alpha_o = 1{,}000$ and $a = ½$.

However, since slightly different parameters were used in his work, it becomes necessary to translate the results of both studies to a common basis. With this information, it becomes possible to predict the breakthrough curve for systems possessing a favorable equilibrium relationship and a rate-controlling mechanism that involves the resistances of both phases.

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NOTATION

a = exponent in the equilibrium relationship, Equation (11)
b = radius of particle, cm.
c = concentration of solution, meq./cc.
c_o = concentration of influent solution, meq./cc.
c^* = concentration of solution at equilibrium, meq./cc.
D = diffusion coefficient in solid phase, sq. cm./sec.
k_l = mass transfer coefficient for liquid film, meq./(sec.)(g. of dry solid)(meq./cc.)
q = average concentration in solid phase, meq./g. of dry solid
q^* = concentration in solid phase at equilibrium, meq./g. of dry resin
q_{max} = concentration in solid phase in equilibrium with influent solution, meq./g. of dry solid
t = time, sec.
u = superficial velocity of solution, cm./sec.
x = bed-length parameter, $k_l(\rho/u)z$
z = bed height, cm.

Greek Letters

α = concentration parameter for liquid phase

$$\frac{c}{c_o}\left[\frac{c_o b^2 k_l}{4\pi q_{max} D}\right]^{\frac{1}{1-a}}$$

α_o = initial concentration parameter for liquid phase

$$\left[\frac{c_o b^2 k_l}{4\pi q_{max} D}\right]^{\frac{1}{1-a}}$$

β = concentration parameter for solid phase

$$\frac{q}{q_{max}}\left[\frac{c_o b^2 k_l}{4\pi q_{max} D}\right]^{\frac{a}{1-a}}$$

θ = time parameter $(4\pi D/b^2)/[t - (\phi/u)z]$
ρ = bulk density of solid phase, g. of dry solid/cc.
ϕ = porosity of bed, external void volume/total volume, dimensionless

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