Ion Exchange Kinetics for Systems of Nonlinear Equilibrium Relationships

CHI TIEN and GEORGE THODOS

The Technological Institute, Northwestern University, Evanston, Illinois

Mathematical relationships based on material balance and rate equations have been derived for the study of ion exchange kinetics in a fixed-bed operation. Numerical techniques for the solution of the systems possessing equilibrium relationships of the Freundlich-adsorption isotherm type have been developed, and numerical results have been obtained with the use of a digital computer. The resulting numerical solutions have been found to be dependent on parameters involving time, position, and the relative resistances of the liquid and resin phases. The numerical solutions are presented in both tabular and graphical forms.

Ion exchange operations are becoming increasingly important and find considerable utility in processes* associated with the removal of undesirable constituents or the concentration and recovery of valuable components present in trace amounts in solutions. The design of equipment capable of performing a specific separation depends primarily on the prediction of the concentration history of effluent solutions.

The work of Du Domaine, Swain, and Hougen (*3*) presents results which make possible the prediction of the performance of the softening of water through a zeolite bed. Their mathematical analysis has been based on a particular rate-controlling step and therefore proves valuable for the solution of problems limited to this type of mechanism. Hougen and Dodge (*8*) studied the drying of air through a bed of silica gel. A more general case was presented later by Thomas (*12*), who considered a second-order reversible reaction as the rate-controlling step. Subsequent work by Hiester and Vermeulen (*6*) has shown that a certain type of adsorption mechanism can be considered equivalent to that of a second-order chemical reaction. Boyd, Meyers, and Adamson (*1, 2*) considered the rate-controlling mechanism to be the diffusion through the liquid film. Similar work has been carried out by Hagerty (*4*), assuming a Freundlich as well as a Langmuir equilibrium relationship. Later studies by Lapidus and Amundson (*9*) deal with the significance of longitudinal diffusion for the case of a first-order reaction. Perhaps the most rigorous treatment is presented by Rosen (*11*), who considers the resistances of both the liquid and solid phases for systems exhibiting a simple, linear equilibrium relationship.

Since the work of Rosen presents a rather restricted equilibrium relationship, the object of this investigation is to solve the general case for which the equilibrium relationship is of a nonlinear nature. Analytical solutions for this type of problem are quite improbable, and consequently numerical methods have been used. The numerical results to this problem have been made possible through the use of the Univac 1103 and are presented in both tabular and graphical forms.

DEVELOPMENT OF MATHEMATICAL EQUATIONS

The most common ion exchange operation involves the removal of a solute from a solution on solid resins. For a flow system this is accomplished by passing the solution through a bed of resin particles. During the operation the solute is continuously removed until the resin phase reaches equilibrium with the influent stream. For this process the kinetic behavior is determined by the rate-controlling mechanism. Three commonly encountered mechanisms are (1) transfer of solute from solution to resin surface, (2) adsorption of solute at solid surface, and (3) diffusion of adsorbed solute through the resin. Any possible combination of these mechanisms defines the kinetic behavior of the system. In cases when the adsorption step is rapid in comparison with the other steps, it can be disregarded in the subsequent kinetic treatment. Under these condition the kinetics will be controlled by the combination of steps (1) and (3). The transfer of mass across the liquid film and consequent diffusion within the particle are affected by the existence of concentration gradients in the liquid and solid phases. The physical picture is presented diagrammatically in Figure 1.

The following assumptions have been made in this investigation: (1) constant liquid-film resistance during operation, (2) constant diffusion coefficient of solute through resin, (3) insignificant longitudinal diffusion, (4) presence of only linear flow through resin bed, (5) uniform bed porosity, (6) no radial variation of concentration in liquid and solid phases, and (7) perfect spherical particles of uniform size. With these assumptions the equation of continuity can be written as

$$uC\,dt - u\left[C + \frac{\partial C}{\partial z}\,dz\right]dt - \frac{\partial q}{dt}\,\rho\,dz\,dt = \frac{\partial C}{\partial t}\,\varphi\,dz\,dt$$

$$\frac{u}{\varphi}\frac{\partial C}{\partial z} + \frac{\partial C}{\partial t} = -\frac{\rho}{\varphi}\frac{\partial q}{\partial t} \qquad (1)$$

The rate equation considered from the liquid side can be expressed as

$$\frac{\partial q}{\partial t} = k_l[C - C_s] \qquad (2)$$

The adsorption of the solute on the resin establishes a concentration gradient which in turn causes the diffusion of the solute toward the center. Consequently the concentration of solute will vary radially inside the particle. The following expressions will relate q_i, q_s, and q:

$$q(t, z) = \frac{3}{b^3}\int_0^b q_i(t, z, r)r^2\,dr \qquad (3)$$

$$q_s(t, z) = q_i(t, z, b) \qquad (4)$$

At the beginning of the operation q_i, q_s, and q are zero and eventually

---

*Chi Tien is at Assumption University of Windsor, Windsor, Ontario, Canada.

become identical when the particle reaches equilibrium with the influent solution. When this condition prevails, diffusion into the particle ceases.

It is obvious the q_i should be a solution of the following diffusion equation:

$$\frac{\partial q_i}{\partial t} = D\nabla^2 q_i = \frac{D}{r^2}\left[r^2 \frac{\partial q_i}{\partial r}\right] \qquad (5)$$

with the following initial condition:

$$q_i = 0 \quad \text{for} \quad z \geq 0$$

$$0 < r < b \quad \text{when} \quad t \leq (\varphi/u)z$$

where the quantity $(\varphi/u)z$ represents the time required for the liquid front to reach a particular position in the bed, and the following boundary condition:

$$q_i = q_s(z, t) \quad \text{when} \quad r = b$$

The solution of Equation (5) together with its initial and boundary conditions can be obtained by Duhamel's principle (7)

$$q_i = \int_0^\tau q_s(z, \lambda)\, \frac{\partial}{\partial \tau} H(r, \tau - \lambda)\, d\lambda \qquad (6)$$

where

$$\tau = t - \frac{\varphi}{u} z$$

The function $H(r, \tau)$ is the solution of Equations (5) when the surface concentration is unity. For $\tau > 0$, $H(r, \tau)$ can be represented by

$$H(r, \tau) = 1 - 2 \cdot \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{\frac{n\pi}{b} r} e^{-D(n\pi/b)^2\tau} \sin \frac{n\pi}{b} r \qquad (7)$$

Differentiating Equation (7) with respect to τ and substituting into Equation (6) one obtains q_i by integration. This expression is then substituted into Equation (3) to obtain

$$q(z, r) = \frac{6D}{b^2} \cdot \sum_{n=1}^{\infty} \int_0^\tau q_s(z, \lambda)\, e^{-D(n\pi/b)^2(\tau-\lambda)} \cdot d\lambda \qquad (8)$$

When one differentiates Equation (8) with Leibnitz's rule and integrates by parts,

$$\frac{\partial}{\partial \tau} q(z, \tau) = \frac{6D}{b^2} \cdot \sum_{n=1}^{\infty} \int_0^\tau \frac{\partial q_s}{\partial \lambda} e^{-D(n\pi/b)^2(\tau-\lambda)} \cdot d\lambda \qquad (9)$$

Equations (1), (2), and (9) describe the situations existing in the column, the liquid phase, and the resin phase respectively. An additional equation relating the physical picture at the liquid-solid interface is required for the complete description of this problem.

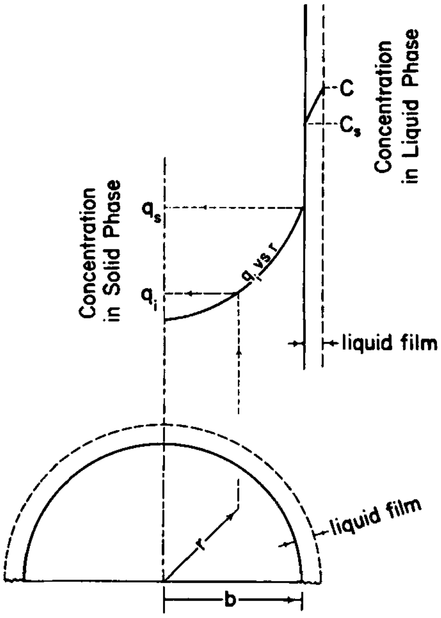

Fig. 1. Concentration gradients around and within a resin particle.

A logical assumption is to consider the existence of equilibrium condition at the interface. For the majority of cases experimental evidence indicates that a Freundlich type of adsorption isotherm could be used to approximate the equilibrium relationship

$$q_s = AC_s^a \qquad (10)$$

With this stipulation and the transformation $\xi = (\rho/u)z$ the fixed-bed operation can be described in terms of the following four equations:

$$\frac{\partial C}{\partial \xi} + \frac{\partial q}{\partial \tau} = 0 \qquad (1)$$

$$\frac{\partial q}{\partial \tau} = k_l[C - C_s] \qquad (2)$$

$$\frac{\partial}{\partial \tau} q(z, \tau) = \frac{6D}{b^2} \cdot \sum_{n=1}^{\infty} \int_0^\tau \frac{\partial q_s}{\partial \lambda} e^{-D(n\pi/b)^2(\tau-\lambda)} \cdot d\lambda \qquad (9)$$

$$q_s = AC_s^a \qquad (10)$$

where $\xi = (\rho/u)z$ and $\tau = t - (\varphi/u)z$

and the following initial and boundary conditions exist:

$$\left.\begin{aligned} C &= 0 \\ q &= 0 \\ C_s &= 0 \\ q_s &= 0 \end{aligned}\right\} \quad \text{for} \quad \xi \geq 0, \qquad \tau < 0$$

$$C = C_0 \quad \text{at} \quad \xi = 0, \qquad \tau \geq 0$$

ADAPTATION OF EQUATIONS FOR NUMERICAL TREATMENT

Equations (1), (2), (9), and (10) contain the four unknown quantities, q, q_s, C, and C_s, the most pertinent being C.

By a process of elimination and substitution a single integral-differential equation containing C alone can be developed to be

$$\frac{\partial C}{\partial \xi} = -\frac{6D}{b^2} \cdot \sum_{n=1}^{\infty} \int_0^\tau aA\left[C + \frac{1}{k_l}\frac{\partial C}{\partial \xi}\right]^{a-1} \cdot \left[\frac{\partial C}{\partial \lambda} + \frac{\partial^2 C}{\partial \lambda \partial \xi}\right] e^{-D(n\pi/b)^2(\tau-\lambda)} \cdot d\lambda \qquad (11)$$

The solution of Equation (11) is the answer to the problem sought in this investigation. However an analytical solution is not available except for the special case $a = 1$, which corresponds to the linear system. In view of this situation, numerical methods must be utilized to obtain the corresponding solutions.

To facilitate the subsequent calculations, it becomes necessary to approximate the infinite series (13), which appears under the integral sign of Equation (9) with the following closed-form expression:

$$\sum_{n=1}^{\infty} e^{-D(n\pi/b)^2(\tau-\lambda)} \approx \frac{b}{2\sqrt{\pi D(\tau - \lambda)}} - \frac{1}{2} \qquad (12)$$

For the simplification of the numerical calculations the following transformations have been introduced:

$$\alpha = \frac{C}{C_0}\left[\frac{C_0 b^2 k_l}{4\pi q_{\max} D}\right]^{1/1-a} \qquad (13)$$

$$\beta = \frac{q}{q_{\max}}\left[\frac{C_0 b^2 k_l}{4\pi q_{\max} D}\right]^{a/1-a} \qquad (14)$$

$$x = k_l \xi = k_l \frac{\rho}{u} z \qquad (15)$$

$$\vartheta = \frac{4\pi D}{b^2}\tau = \frac{4\pi D}{b^2}\left[t - \frac{\varphi}{u} z\right] \qquad (16)$$

and

$$q_{\max} = AC_0^a \qquad (17)$$

Substituting Equations (13,) (14), (15), and (16) into Equations (1), (2), (9), and (10), one gets

$$\frac{\partial \alpha}{\partial x} + \frac{\partial \beta}{\partial \vartheta} = 0 \qquad (18)$$

$$\frac{\partial \beta}{\partial \vartheta} = (\alpha - \alpha_s) \qquad (19)$$

$$\frac{\partial \beta}{\partial \vartheta} = \frac{3}{2\pi} \int_0^\vartheta \frac{\partial \beta_s}{\partial \lambda} \cdot \left[\frac{1}{\sqrt{\vartheta - \lambda}} - \frac{1}{2}\right] d\lambda \qquad (20)$$

$$\beta_s = \alpha_s^a \tag{21}$$

with the following initial and boundary conditions:

$$\left.\begin{aligned} \alpha &= 0 \\ \alpha_s &= 0 \\ \beta &= 0 \\ \beta_s &= 0 \end{aligned}\right\} \quad x \geq 0, \qquad \vartheta < 0$$

$$\alpha = \alpha_0 \quad \text{at} \quad x = 0, \qquad \vartheta \geq 0$$

Approximate solutions of differential equations can be obtained by evaluating the derivatives and integrating numerically by means of the resulting difference equation. To formulate the corresponding difference equations for Equations (18), (19), (20), and (21) a net of mesh-widths of Δx and $\Delta\vartheta$ is established. When the subscript i is used for x and superscript j for ϑ,

$$\frac{\alpha_{i+1}^{\ j} - \alpha_i^{\ j}}{\Delta x} = -\frac{\beta_i^{\ j+1} - \beta_i^{\ j}}{\Delta\vartheta} \tag{22}$$

$$\frac{\beta_i^{\ j+1} - \beta_i^{\ j}}{\Delta\vartheta} = \alpha_i^{\ j} - \alpha_{s_i}^{\ j} \tag{23}$$

$$\frac{\beta_i^{\ j+1} - \beta_i^{\ j}}{\Delta\vartheta} = \frac{3}{2\pi}\int_0^{(j+1)\Delta\vartheta} \frac{\partial\beta_{s_i}}{\partial\lambda} \cdot\left[\frac{1}{\sqrt{(j+1)\,\Delta\vartheta - \lambda}} - \frac{1}{2}\right] d\lambda \tag{24}$$

$$\beta_{s_i}^{\ j} = (\alpha_{s_i}^{\ j})^a \tag{25}$$

There are numerous ways to approximate these derivatives. It is more logical to approximate dy/dx by $(y_{i+1} - y_{i-1})/2\Delta x$. However for this particular case a reiterative type of calculation has to be used if the derivatives are to be approximated in this manner. This procedure would complicate the numerical calculations, and for this reason approximations as expressed in Equations (22) and (23) are used.

Combining Equations (22) and (23) one gets

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

or

$$\alpha_{i+1}^{\ j} = \alpha_i^{\ j} + (\alpha_{s_i}^{\ j} - \alpha_i^{\ j})\,\Delta x \tag{26}$$

The integral of Equation (24) can be rewritten as

$$\begin{aligned} &\int_0^{(j+1)\Delta\vartheta} \frac{\partial\beta_{s_i}}{\partial\lambda} \cdot\left[\frac{1}{\sqrt{(j+1)\,\Delta\vartheta - \lambda}} - \frac{1}{2}\right] d\lambda \\ &= \sum_{k=0}^{j}\left(\frac{\partial\beta_s}{\partial\vartheta}\right)_i^{k+\frac{1}{2}} (2\sqrt{\Delta\vartheta}) \\ &\cdot[\sqrt{(j+1) - k} \\ &- \sqrt{(j+1) - (k+1)}] \\ &- \tfrac{1}{2}\beta_{s_i}^{\ j+1} \end{aligned} \tag{27}$$

When one makes the approximation that

$$\left(\frac{\partial\beta_s}{\partial\vartheta}\right)_i^{k+\frac{1}{2}} \approx \frac{\beta_{s_i}^{\ k+1} - \beta_{s_i}^{\ k}}{\Delta\vartheta}$$

Equation (27) becomes

$$\begin{aligned} &\int_0^{(j+1)\Delta\vartheta} \left(\frac{\partial\beta_s}{\partial\lambda}\right)_i \cdot\left[\frac{1}{\sqrt{(j+1)\,\Delta\vartheta - \lambda}} - \frac{1}{2}\right] d\lambda \\ &= \sum_{k=0}^{j}\left(\frac{\beta_{s_i}^{\ k+1} - \beta_{s_i}^{\ k}}{\Delta\vartheta}\right)(2\sqrt{\Delta\vartheta}) \\ &\cdot[\sqrt{(j+1) - k} - \sqrt{j - k}] \\ &- \tfrac{1}{2}\beta_{s_i}^{\ j+1} \end{aligned} \tag{28}$$

When one rearranges the infinite series, Equation (28) becomes

$$\begin{aligned} &\sum_{k=0}^{j}(\beta_{s_i}^{\ k+1} - \beta_{s_i}^{\ k}) \\ &\cdot[\sqrt{(j+1) - k} - \sqrt{j - k}] \\ &= \beta_{s_i}^{\ j+1} + \sum_{k=1}^{j}\beta_{s_i}^{\ k}\cdot[\sqrt{j - (k-2)} \\ &- 2\sqrt{j - (k-1)} + \sqrt{j - k}] \end{aligned} \tag{29*}$$

The substitution of Equation (29) into Equation (28) produces

$$\begin{aligned} &\int_0^{(j+1)\Delta\vartheta} \frac{\partial\beta_{s_i}}{\partial\lambda} \cdot\left[\frac{1}{\sqrt{(j+1)\,\Delta\vartheta - \lambda}} - \frac{1}{2}\right] d\lambda \\ &= \frac{2}{\sqrt{\Delta\vartheta}}\beta_{s_i}^{\ j+1} + \frac{2}{\sqrt{\Delta\vartheta}} \\ &\cdot\sum_{k=1}^{j}\beta_{s_i}^{\ k}[\sqrt{j - (k-2)} \\ &- 2\sqrt{j - (k-1)} \\ &+ \sqrt{j - k}] - \tfrac{1}{2}\beta_{s_i}^{\ j+1} \end{aligned} \tag{30}$$

Substituting Equation (30) into Equation (24) one obtains

$$\begin{aligned} &\frac{\beta_i^{\ j+1} - \beta_i^{\ j}}{\Delta\vartheta} = \beta_{s_i}^{\ j+1} \\ &\cdot\left(\frac{3}{\pi\sqrt{\Delta\vartheta}} - \frac{3}{4\pi}\right) + \frac{3}{\pi\sqrt{\Delta\vartheta}} \\ &\cdot\sum_{k=1}^{j}\beta_{s_i}^{\ k}[\sqrt{j - (k-2)} \\ &- 2\sqrt{j - (k-1)} + \sqrt{j - k}] \end{aligned} \tag{31}$$

The combination of Equation (31) with Equation (23) yields

$$\begin{aligned} \beta_{s_i}^{\ j+1} &= C_1[(\alpha_i^{\ j} - \alpha_{s_i}^{\ j}) \\ &+ C_2\sum_{k=1}^{j}K_{j-(k-1)}\beta_{s_i}^{\ k}] \end{aligned} \tag{32}$$

$$\frac{1}{C_1} = \left(\frac{3}{\pi\sqrt{\Delta\vartheta}} - \frac{3}{4\pi}\right)$$

$$C_2 \quad \frac{3}{\pi\sqrt{\Delta\vartheta}}$$

and

$$\begin{aligned} K_{j-(k-1)} &= -\sqrt{j - (k-2)} \\ &+ 2\sqrt{j - (k-1)} - \sqrt{j - k} \end{aligned}$$

Equations (32), (26), and (25), together with the proper initial and boundary conditions, constitute the basis for the following numerical calculations:

$$\begin{aligned} \beta_{s_i}^{\ j+1} &= C_1[(\alpha_i^{\ j} - \alpha_{s_i}^{\ j}) \\ &+ C_2\sum_{k=1}^{j}K_{j-(k-1)}\beta_{s_i}^{\ k}] \end{aligned} \tag{32}$$

$$\alpha_{i+1}^{\ j} = \alpha_i^{\ j} + (\alpha_{s_i}^{\ j} - \alpha_i^{\ j})\,\Delta x \tag{26}$$

$$\beta_s = \alpha_s^a \tag{25}$$

$$\left.\begin{aligned} \alpha &= 0 \\ \alpha_s &= 0 \\ \beta_s &= 0 \end{aligned}\right\} \quad \text{at} \quad x \geq 0, \qquad \vartheta \leq 0$$

$$\alpha = \alpha_0 \quad \text{at} \quad x = 0, \qquad \vartheta > 0$$

In accordance with the definition of α, it can be shown that the ratio of the effluent to the influent concentrations C/C_0 is the same as α/α_0. From Equations (32), (26), and (25) it is obvious that for particular values of a, α is a function of x, ϑ, and α_0. The procedure for numerical calculations is summarized as follows:

(1) β_s and α_s are calculated along the ϑ axis for $j = 1, 2, 3, \cdots n$ with Equations (32) and (25).

(2) With the information obtained from step 1, values of α for $x = (i + 1)\Delta x$ and $j = 1, 2, 3, \cdots n$ can be computed through the use of Equation (26).

(3) Values of β_s and α_s are succesively computed by repeating step 1 for $x = (i + 1)\Delta x$ and $j = 1, 2, 3 \cdots n$.

(4) Step 2 is repeated. Values of α are found for $x = (i + 1)\Delta x$ and $j = 1, 2, 3 \cdots n$.

By repeating this procedure, values of α corresponding to particular values of α_0 and a, any value of x and ϑ can be computed.

SELECTION OF INCREMENTS Δx and $\Delta\vartheta$

The accuracy of the numerical calculations is obviously dependent on the magnitude of the increments Δx and $\Delta\vartheta$. The smaller the size of the increments, the more accurate will be the results. However more calculations will be needed to find the value of α for a definite value

---

*Tabular material has been deposited as document No. 5976 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

of x and ϑ. Consequently the selection of these increments becomes a compromise of these opposing factors.

When Equation (26) and the physical situation that $\alpha \geq 0$ are considered, the maximum value of Δx becomes

$$\Delta x < \frac{\alpha_i^{\,j} - \alpha_{i+1}^{\,j}}{\alpha_i^{\,j} - \alpha_{s_i}^{\,j}} < \frac{\alpha_i^{\,j}}{\alpha_i^{\,j} - \alpha_{s_i}^{\,j}} \qquad (33)$$

The value of $\Delta\vartheta$ has to meet the physical reality imposed on this problem. The criterion is developed as follows.

Equation (32) will be considered:

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

$$\text{for} \quad i = 0 \quad \text{and} \quad j = 0$$

$$\beta_{s_0}^{\,1} = C_1[\alpha_0^{\,0} - \alpha_{s_0}^{\,0}]$$

but $\alpha_{s_0}^{\,0} = 0$, and therefore

$$\beta_{s_0}^{\,1} = C_1\alpha_0^{\,0} = C_1\alpha_0$$

However

$$\beta_{s_i}^{\,j} \leq \beta_{\max} = (\alpha_{\max})^a = \alpha_0^{\,a}$$

Therefore

$$C_1\alpha_0 < \alpha_0^{\,a}$$

or

$$C_1 < \frac{1}{\alpha_0^{\,1-a}}$$

since by definition

$$C_1 = \frac{1}{\dfrac{3}{\pi\sqrt{\Delta\vartheta}} - \dfrac{3}{4\pi}} \approx \frac{\pi\sqrt{\Delta\vartheta}}{3}$$

for small values of $\Delta\vartheta$.

This gives

$$\frac{\pi\sqrt{\Delta\vartheta}}{3} < \frac{1}{\alpha_0^{\,1-a}}$$

or

$$\Delta\vartheta < \left(\frac{3}{\pi}\right)^2\left(\frac{1}{\alpha_0^{\,1-a}}\right)^2$$

For example if $a = \frac{1}{2}$ and $\alpha_0 = 1{,}000$

$$\Delta\vartheta < \left(\frac{3}{\pi}\right)^2\left(\frac{1}{1{,}000}\right) = \frac{1}{1{,}097}$$

Another stipulation required by the physical condition of the system is that the numerical value of β_s has to be equal to, or greater than, its preceding value, or that

$$\beta_{s_i}^{\,m+1} \geq \beta_{s_i}^{\,m}$$

or

$$\beta_{s_i}^{\,m+1} - \beta_{s_i}^{\,m} \geq 0$$

and

$$\beta_{s_i}^{\,m} = C_1[(\alpha_i^{\,m-1} - \alpha_{s_i}^{\,m-1}) - C_2(K_1\beta_{s_i}^{\,m-1} + K_2\beta_{s_i}^{\,m-2} + \cdots + K_{m-1}\beta_{s_i}^{\,1})]$$

$$\beta_{s_i}^{\,m+1} = C_1[(\alpha_i^{\,m} - \alpha_{s_i}^{\,m}) - C_2(K_1\beta_{s_i}^{\,m} + K_2\beta_{s_i}^{\,m-1} + \cdots + K_m\beta_{s_i}^{\,1})]$$

TABLE 1. NUMERICAL VALUES OF CONCENTRATION RATIOS FOR SYSTEMS HAVING NONLINEAR EQUILIBRIUM RELATIONSHIPS

for $\alpha_0 = 1{,}000$ and $a = \frac{1}{2}$

where $\alpha_0 = \left[\dfrac{C_0 b^2 k_l}{4\pi q_{\max} D}\right]^{1/1-a}$, $q_{\max} = AC_0^{\,a}$, $x = k_l \dfrac{\rho}{u} z$ and $\vartheta = \dfrac{4\pi D}{b^2}\left[t - \dfrac{\varphi}{u} z\right]$

$\vartheta \times 2^{13}$	C/C_0	$\vartheta \times 2^{13}$	C/C_0	$\vartheta \times 2^{13}$	C/C_0
	$x = 1$		$x = 3$		$x = 5$
1	0.62267	1	0.06727	11	0.00203
11	0.71875	11	0.21612	21	0.02529
21	0.76662	21	0.32565	41	0.13709
41	0.81761	41	0.45978	61	0.24319
81	0.86430	81	0.59273	81	0.32380
161	0.90261	161	0.70603	161	0.50633
321	0.93196	321	0.79419	321	0.65343
641	0.95359	641	0.85952	641	0.76340
821	0.95978	821	0.87824	821	0.79494
	$x = 7$		$x = 9$		$x = 11$
41	0.00128	81	0.00040	161	0.00495
61	0.02632	101	0.00777	181	0.01919
81	0.08579	141	0.07297	221	0.07256
121	0.21088	201	0.19618	301	0.18964
201	0.37606	361	0.40073	441	0.33496
401	0.56465	541	0.51975	581	0.42895
821	0.70959	821	0.62199	821	0.53202
	$x = 13$		$x = 17$		$x = 21$
221	0.00100	421	0.00189	701	0.00747
241	0.00547	441	0.00567	721	0.01316
281	0.03330	481	0.02251	741	0.02049
341	0.10076	541	0.06338	761	0.02914
441	0.20684	601	0.10859	781	0.03873
601	0.32963	701	0.17823	801	0.04886
821	0.43964	821	0.24837	821	0.05957

See footnote page 375

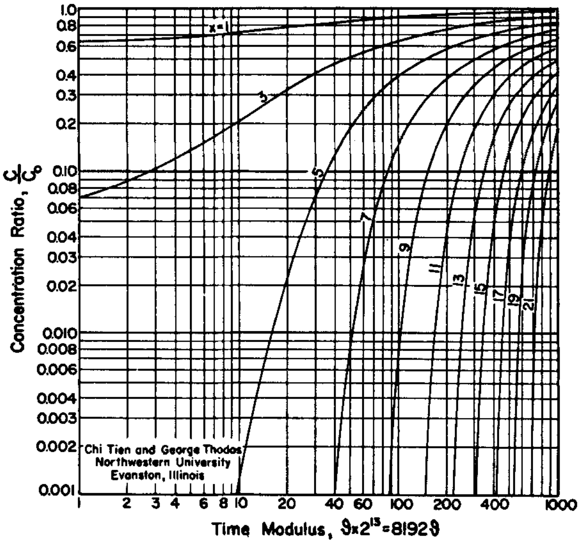

Fig. 2. Concentration- position-time relationship for the case $\alpha_0 = 1{,}000$ and $a = \frac{1}{2}$: $\alpha_0 = \left[\dfrac{C_0 b^2 k_l}{4\pi q_{\max} D}\right]^{1/1-a}$, $q_{\max} = AC_0^{\,a}$, $x = k_l \dfrac{\rho}{u} z$, and $\vartheta = \dfrac{4\pi D}{b^2}\left[t - \dfrac{\varphi}{u} z\right]$.

TABLE 2. NUMERICAL VALUES OF CONCENTRATION RATIOS FOR SYSTEMS HAVING NONLINEAR EQUILIBRIUM RELATIONSHIPS

for $\alpha_0 = 100$ and $a = 1/2$

where $\alpha_0 = \left[\dfrac{C_0 b^2 k_l}{4\pi q_{\max} D}\right]^{1/1-a}$, $q_{\max} = AC_0^a$, $x = k_l \dfrac{\rho}{u} z$ and $\vartheta = \dfrac{4\pi D}{b^2}\left[t - \dfrac{\varphi}{u} z\right]$

$\vartheta \times 2^9$	C/C_0	$\vartheta \times 2^9$	C/C_0	$\vartheta \times 2^9$	C/C_0
	$x = 1$		$x = 3$		$x = 5$
1	0.71036	1	0.20214	1	0.00117
11	0.79039	11	0.38638	11	0.05975
31	0.85409	31	0.56013	21	0.17182
61	0.89398	61	0.67657	41	0.34332
101	0.91968	101	0.75359	101	0.57882
301	0.96151	301	0.88095	301	0.79496
501	0.97524	501	0.92307	501	0.86697
821	0.98578	821	0.95544	821	0.92233
	$x = 7$		$x = 9$		$x = 11$
21	0.00365	41	0.00057	71	0.00037
31	0.03598	51	0.00854	81	0.00421
41	0.09736	61	0.03482	101	0.04252
61	0.22279	81	0.12105	141	0.17521
101	0.39524	121	0.27982	201	0.33414
301	0.70290	301	0.60425	361	0.56462
501	0.80654	501	0.74140	601	0.72384
821	0.88621	821	0.84686	821	0.80407
	$x = 15$		$x = 21$		$x = 29$
161	0.00200	321	0.00125	621	0.01138
181	0.01854	341	0.00905	641	0.02632
201	0.05496	361	0.02792	661	0.04601
301	0.26564	401	0.08565	681	0.06821
441	0.45686	501	0.23354	701	0.09144
641	0.61635	701	0.44291	761	0.16076
821	0.70732	821	0.53073	821	0.22512

See footnote page 375.

This gives the following inequality:

$$-(\alpha_{s_i}^{\ m} - \alpha_{s_i}^{\ m-1}) + (\alpha_i^{\ m} - \alpha_i^{\ m-1}) + C_2[K_1(\beta_{s_i}^{\ m} - \beta_{s_i}^{\ m-1}) + K_2(\beta_{s_i}^{\ m-1} - \beta_{s_i}^{\ m-2}) + \cdots + K_{m-1}(\beta_{s_i}^{\ 2} - \beta_{s_i}^{\ 1}) + K_m\beta_{s_i}^{\ 1}] \geq 0$$

Therefore

$$C_2 \geq \frac{\alpha_{s_i}^{\ m} - \alpha_{s_i}^{\ m-1}}{K_1\Delta_m + K_2\Delta_{m-1} + \cdots + K_m\Delta_1}$$

where

$$\Delta_m = \beta_{s_i}^{\ m} - \beta_{s_i}^{\ m-1}$$

$$\Delta_{m-1} = \beta_{s_i}^{\ m-1} - \beta_{s_i}^{\ m-2}$$

and

$$C_2 = \frac{3}{\pi(\Delta\vartheta)^{\frac{1}{2}}}$$

$$(\Delta\vartheta)^{\frac{1}{2}} \leq \frac{3}{\pi} \cdot \frac{K_1\Delta_m + K_2\Delta_{m-1} + \cdots + K_m\Delta_1}{\alpha_{s_i}^{\ m} - \alpha_{s_i}^{\ m-1}}$$

This requirement would be met, if

$$(\Delta\vartheta)^{\frac{1}{2}} = \frac{3}{\pi}\Delta_m \frac{\sum_{i=1}^{m} K_i}{\alpha_{s_i}^{\ m} - \alpha_{s_i}^{\ m-1}}$$

since

$$\Delta_m \leq \Delta_{m-1} \leq \Delta_{m-2}$$

If m is a relatively large number

$$\sum_{i=1}^{m} K_i \approx 1$$

and the following condition is obtained:

$$(\Delta\vartheta)^{\frac{1}{2}} \leq \frac{3}{\pi}\frac{\Delta_m}{\alpha_{s_i}^{\ m} - \alpha_{s_i}^{\ m-1}} = \frac{3}{\pi}\frac{\beta_{s_i}^{\ m} - \beta_{s_i}^{\ m-1}}{\alpha_{s_i}^{\ m} - \alpha_{s_i}^{\ m-1}} \tag{35}$$

For the case $a = \frac{1}{2}$ and $\alpha_0 = 1{,}000$

$$\beta_s = \alpha_s^{\frac{1}{2}} \quad \text{or} \quad \alpha_s = \beta_s^{\ 2}$$

$$\alpha_{s_i}^{\ m} - \alpha_{s_i}^{\ m-1} = (\beta_{s_i}^{\ m})^2 - (\beta_{s_i}^{\ m-1})^2 = (\beta_{s_i}^{\ m} + \beta_{s_i}^{\ m-1})(\beta_{s_i}^{\ m} - \beta_{s_i}^{\ m-1})$$

When one substitutes into Equation (35)

$$(\Delta\vartheta)^{\frac{1}{2}} \leq \frac{3}{\pi}\frac{1}{\beta_{s_i}^{\ m} + \beta_{s_i}^{\ m-1}} \leq \frac{3}{2\pi\beta_{\max}}$$

$$\Delta\vartheta \leq \left(\frac{3}{2\pi}\right)^2 \frac{1}{\beta_{\max}^{\ 2}} = \left(\frac{3}{2\pi}\right)^2 \frac{1}{\alpha_{\max}} = \left(\frac{3}{2\pi}\right)^2 \frac{1}{\alpha_0} = \left(\frac{3}{2\pi}\right)^2 \frac{1}{1{,}000} = \frac{1}{4{,}410}$$

The latter case is obviously more stringent. At the beginning it was thought that this requirement might be too restrictive. Trial calculations were made with $\Delta\vartheta$ satisfying the first requirement, and the results were compared with those satisfying both requirements. It was found that these numerical values agreed for low values of x, however, as x increased, the resulting values of α

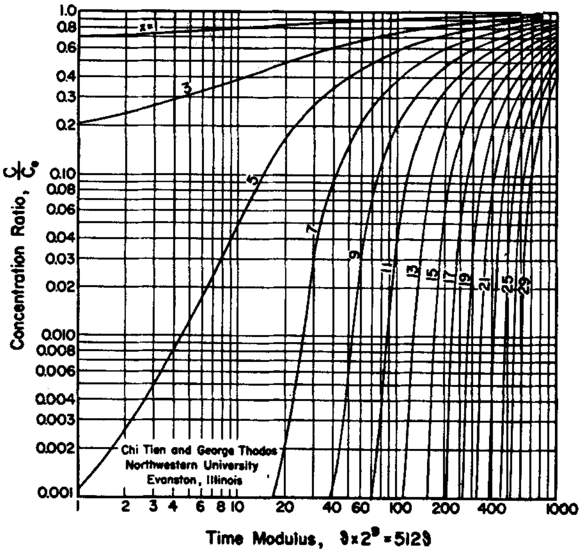

Fig. 3. Concentration-position-time relationships for the case $\alpha_0 = 100$ and $a = \frac{1}{2}$: $\alpha_0 = \left[\dfrac{C_0 b^2 k_l}{4\pi q_{\max} D}\right]^{1/1-a}$, $q_{\max} = AC_0^a$, $x = k_l \dfrac{\rho}{u} z$, and $\vartheta = \dfrac{4\pi D}{b^2}\left[t - \dfrac{\varphi}{u} z\right]$.

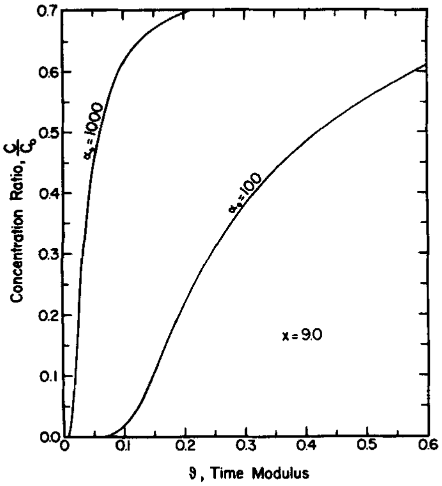

Fig. 4. Effect of α_0 on concentration ratio.

were found to oscillate, a situation similar to that reported by O'Brien (*10*). For this reason the subsequent calculations were restricted to values of $\Delta\vartheta$, satisfying Equation (35).

DISCUSSION OF RESULTS

Numerical calculations were carried out with a digital computer. The coding was based on Equations (32), (26), and (25), and computations were made according to the procedure already outlined. Two cases have been worked for $a = \frac{1}{2}$, one for $\alpha_0 = 1{,}000$ and the other for $\alpha_0 = 100$. The increments used for the case $\alpha_0 = 1{,}000$ are $\Delta\vartheta = 2^{-13}$ and $\Delta x = 1$, whereas for the second case, $\alpha_0 = 100$, the increments are $\Delta\vartheta = 2^{-9}$ and $\Delta x = 1$. All these increments satisfy the requirements of Equations (33) and (35).

The extent of x, which was to be reached for $\alpha_0 = 1{,}000$, was limited to $x = 23$, whereas for $\alpha_0 = 100$, $x = 29$. This restriction was due to the limited storage space on the magnetic core and drum of the computer. It is possible to use the magnetic tape of the machine for additional storage space and thus make it possible to reach higher values of x. This however would reduce the speed of calculation appreciably. Even with the present setup the machine time used for each case was approximately 3 hr.

Numerical values of the concentration ratio C/C_0 for each case are presented both in tabular and graphical form for selected values of x and ϑ. These results appear in Tables 1 and 2 and Figures 2 and 3 for $a = \frac{1}{2}$ and the cases $\alpha_0 = 1{,}000$ and $\alpha_0 = 100$. The accuracy of these computations is accurate to eight decimal places for the case of $\alpha_0 = 1{,}000$ and nine decimal places for $\alpha_0 = 100$. The effect of α_0 is presented in Figure 4, where the concentration ratio C/C_0 is plotted against the time modulus $\vartheta = (4\pi D)/b^2[t - (\varphi/u)z]$ corresponding to the position modulus $x = k_l(\rho/u)z$.

Although the results of this study present solutions for the cases $\alpha_0 = 1{,}000$ and $\alpha_0 = 100$, when both the liquid film resistance and that of diffusion through the solid are significant, it is interesting to point out that $\alpha_0 = 0$ corresponds to the case when the liquid phase is governing and $\alpha_0 = \infty$ for the corresponding case when diffusion through the solid controls.

The plots of Figures 2 and 3 can be used to predict the concentration history of a fluid subjected to ion exchange operations provided that the equilibrium relationship of the system satisfies the Freundlich-adsorption isotherm for the case $a = \frac{1}{2}$. The effect of a and α_0 cannot be stated exactly from the present computational results. Therefore in the absence of further computations it is difficult to state quantitatively that the effect of the exponent a on the breakthrough curve should be generalized beyond $a = \frac{1}{2}$. Further work for different values of a is necessary to clarify this point; this could be conducted by the use of the same basic equations developed in this investigation with slight coding modifications. When results for sufficient cases have been computed, it is very likely that these numerical values could be approximated with some of the known functions in terms of the three parameters and the exponent a. This method has been shown in the resent work of Helfferich and Plesset (*5*).

ACKNOWLEDGMENT

The authors wish to express their gratitude to the Remington-Rand Univac Division of Sperry Rand Corporation, St. Paul, Minnesota, and in particular to L. F. Stutzman and J. W. Tierney for providing the computing facilities that made this work possible.

NOTATION

a = exponent in the equilibrium relationship [Equation (10)]
b = radius of particle, cm.
C = concentration of solution, milliequivalents/cc.
C_0 = concentration of influent solution, milliequivalents/cc.
C_s = concentration of solution at surface of particle, milliequivalents/cc.
D = diffusion coefficient in resin phase, sq. cm./sec.
k_l = mass transfer coefficient for liquid film, milliequivalents/(sec.)(g. of dry resin)(miliequivalents/cc.)
q = average concentration in resin, milliequivalents/g. of dry resin
q_i = point concentration in resin, milliequivalents/g. of dry resin
q_{max} = concentration in resin phase in equilibrium with influent solution, milliequivalents/g. of dry resin
q_s = concentration on resin surface, miliequivalents/g. of dry resin
t = time, sec.
u = superficial velocity of solution, cm./sec.
x = position parameter, $k_l(\rho/u)z$
z = bed height, cm.

Greek Letters

α = concentration parameter for liquid phase,

$$\frac{C}{C_0}\left[\frac{C_0 b^2 k_l}{4\pi q_{max} D}\right]^{1/1-a}$$

α_0 = initial concentration parameter for liquid phase,

$$\left[\frac{C_0 b^2 k_l}{4\pi q_{max} D}\right]^{1/1-a}$$

β = concentration parameter for resin phase [Equation (14)]
ϑ = time parameter, $(4\pi D/b^2)[t - (\varphi/u)z]$
ξ = $(\rho/u)z$
ρ = bulk density of resin, g. of dry resin/cc.
τ = $t - (\varphi/u)z$
φ = porosity of bed, external void volume/total volume, dimensionless

LITERATURE CITED

1. Boyd, G. E., L. S. Meyers, Jr., and A. W. Adamson, *J. Am. Chem. Soc.*, **69**, 2836 (1947).
2. *Ibid.*, 2849.
3. Domaine, John Du, R. L. Swain, and O. A. Hougen, *Ind. Eng. Chem.*, **35**, 546 (1943).
4. Hagerty, P. F., "Numerical Solution for the Non-Linear Transient Behavior of Stationary Beds," N.S.F. Report, Univ. of Pennsylvania, Philadelphia, Penn. (1957).
5. Helfferich, F., and M. S. Plesset, *J. Chem. Phys.*, **28**, 418 (1958).
6. Hiester, N. K., and Theodore Vermeulen, *Chem. Eng. Progr.*, **48**, 506 (1952).
7. Hildebrand, F. D., "Advanced Calculus for Engineers," p. 445, Prentice-Hall, Englewood Cliffs, New Jersey (1948).
8. Hougen, O. A., and F. W. Dodge, "Drying of Gases," prepared for NDRC of OSRD (June 30, 1941); Office of Technical Services, PB 2301, U. S. Department of Commerce (1946).
9. Lapidus, Leon, and N. R. Amundson, *J. Phys. Chem.*, **56**, 948 (1952).
10. O'Brien, G. G., M. A. Hyman, and Sidney Kaplan, *J. Math. Phys.*, **29**, 223 (1951).
11. Rosen, J. B., *J. Chem. Phys.*, **20**, 387 (1952).
12. Thomas, H. C., *J. Am. Chem. Soc.*, **66**, 1664 (1944).
13. Tien, Chi, Ph.D. thesis, Northwestern Univ., Evanston, Ill. (1958).

Manuscript received August 14, 1958; revision received January 9, 1959; paper accepted January 9, 1959. Paper presented at A.I.Ch.E. Cincinnati Meeting.