Staged Approach of Percolation Processes

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Sorption processes in a perfectly mixed reactor are analyzed by using two models: the equilibrium model and a kinetic model which considers the effect of the external mass transfer resistance. In both cases, a general nonlinear equilibrium isotherm is considered.

The influence of the different model parameters on the response of the perfectly mixed sorber and their effect on a design parameter (the breakthrough time) are discussed.

A criterium is derived in order to predict when the equilibrium model is valid.

Part I. Sorption Processes in a Perfectly Mixed Reactor: Influence of Nonlinear Equilibrium Isotherm and External Mass Transfer Resistance

SCOPE

This work was undertaken in order to treat percolation processes by using the methodology of chemical engineering science. The modeling of these processes, viewed as the key of simulation, extrapolation, and optimization operations, was the first objective of the project. Then we chose the philosophy of modeling, synthetized as follows: to start with simple models (equilibrium model) and to add successively mass transfer resistances (nonequilibrium model).

In this work, a class of models which uses the staged approach of percolation processes was investigated. These models consider the column as a series of J cells; J is only a measure of the axial dispersion. They are different from the plate model of Martin and Synge (1941), in which a plate includes all deviations from equilibrium. Also, the Martin and Synge model is limited to linear equilibrium.

The staged approach we used is currently employed in chemical reactor theory; it is a form of writing conservation equations which leads to a system of differential equations. The stiff nature of these equations explains why staged models were not widely used to describe percolation processes. According to the methodology mentioned above, we studied first the cell of the staged model, that is, the perfectly mixed sorber, before modeling the column. In this context, we used some knowledge about perfectly mixed sorber behavior resulting from a simple equilibrium model (Rodrigues, 1973) in order to attempt a simple design procedure. When the objective of the sorption operation is the removal of solutes to obtain a good effluent quality, a design criterium could be the breakthrough time θ_{Bp}; so the simple design procedure is based on a plot of θ_{Bp} as a function of the model parameters (equilibrium constant K and capacity parameter ξ).

Then, a nonequilibrium model, which considers an external mass transfer resistance, is analyzed in order to find answers to questions such as: how is the design parameter modified by the mass transfer resistance? When can we use the simple equilibrium model for design purposes?

Briefly, we considered a nonlinear equilibrium case, and we tried to separate the different contributions to dispersive phenomena (axial dispersion, mass transfer resistances) instead of putting together all effects in a term $\mathcal{R}$ (global rate of sorption) which fits experimental data. It follows that we not consider the validity of a model as a straightforward result of a good fitting, but instead of that the model parameters should be measured by independent experiments and compared with the best fitted values in order to test their physical meaning.

In further work, this methodology will be applied to a series of sorbers. This model can accommodate several mass transfer resistances, any type of equilibrium isotherm, and the cyclic regime of operation.

CONCLUSIONS AND SIGNIFICANCE

In the present study, a methodological approach is used to analyze the influence of mass transfer resistances on the behavior of a perfectly mixed sorber. We developed equilibrium and nonequilibrium models for sorption in a perfectly mixed sorber in the general nonlinear equilibrium isotherm case. From these models, we obtained a simple design procedure based on the breakthrough time approach.

The analysis of the perfectly mixed sorber, first based on an equilibrium model (Rodrigues, 1973) was summarized by plotting a design parameter (breakthrough time θ_{Bp}) as a function of the model parameters (capacity factor ξ and equilibrium constant K). This plot can be useful for the design of stirred sorbers, and a sample procedure is presented. We also note that the increase of ξ and/or K favors the removal of solute; however, over a certain value of ξ, its influence is unimportant. Then, a nonequilibrium model was investigated, including film mass transfer resistance.

The model parameters are now ξ, K, and N_f, a number measuring the film resistance to mass transfer (high N_f means low mass transfer resistance). When this mass transfer resistance is important, the effluent concentration in-

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creases fast to a plateau concentration mainly dependent on the N_f value. In terms of driving force for mass transfer, we can observe that it decreases during most of the time of the operation until a point where the equilibrium is approached; this point is also related to the values of the parameters. Then, by comparing the equilibrium and nonequilibrium models, we can see how the mass transfer parameter N_f modifies the breakthrough curves and the design parameter θ_{Bp} (breakthrough time). Resulting from this analysis, a sample procedure for designing perfectly mixed sorbers is given when the controlling step is the external mass transfer resistance. We have also been able to propose a criterion defining the range of validity of the equilibrium model.

Percolation processes are a wide class of chemical engineering operations. They include adsorption (both liquid and gas adsorption), ion exchange, deep-bed filtration, chromatography, leaching, etc., namely, all the processes in which a fluid passes through a fixed bed of some kind of support (particles, fibers, membranes).

The aim of these operations may be the removal of toxic solutes, the recovery of valuable substances, or the fractionation of mixtures for analysis (laboratory chromatography) or industrial production (large scale chromatography). For this last reason, these separation processes are sometimes called chromatographic processes.

The mathematical formulation of these operations involves, as any other chemical engineering problem (Le Goff, 1972), the statement of conservation equations (mass, energy, momentum), equilibrium law at the interface fluid solid, kinetic laws of transport and reaction processes, and initial and boundary conditions.

If we intend to design a percolation column, we should be able to predict the effluent concentrations as a function of time (history of concentrations or breakthrough curves). To do this, we build a model of the column, the complexity of the model being related to the objectives. The basic features of percolation column behavior were first derived by de Vault (1943) from a simple equilibrium model. He was able to obtain the important notions of compressive and dispersive fronts. Since the pioneer work of de Vault, a number of important contributions to the theory of chromatography (equilibrium and nonequilibrium cases) have been made, namely, by Rhee (1968), Tondeur (1969), Helfferich and Klein (1970), and Aris and Amundson (1973).

During the last two decades, a lot of papers dealing with modeling of percolation columns appeared using either analytical or numerical methods. Two different approaches have been used. The differential approach leads to a PDE (distributed system), and the staged approach leads to a system of ODE (lumped system). The frequent use of staged models in chemical reaction engineering suggests that it might be interesting to apply them to percolation processes.

A choice about the philosophy of modeling must be made. One possibility is to put together all kinetic effects in a term R (global rate of sorption) which fits the experimental points (Farkas and Himsley, 1975). A second point of view is to try to separate the different contributions of dispersive phenomena (axial dispersion, external mass transfer, pore diffusion). This approach implies the ability to measure independently the model parameters.

We have chosen this last approach in order to predict the importance of dispersive phenomena on the design parameters. To do this, we begin with the equilibrium model, and then we introduce an external mass transfer resistance. In this paper we study the elementary cell of the model, that is, sorption in a perfectly mixed reactor. The approach we used is different from that of Martin and Synge (1941) which considers all deviations from equilibrium lumped in an empirical parameter, EHTP (equivalent height theoretical plate). The Martin and Synge model is limited to linear equilibrium, and the EHTP can not be predicted, which is not convenient.

The aims of the paper, apart from a didatic view of the subject, are the development of equilibrium and nonequilibrium models for sorption in a perfectly mixed sorber (nonlinear equilibrium case), the formulation of a design procedure based on the breakthrough time approach, and the statement of a criterion which determines when external mass transfer resistance can be neglected.

SORPTION PROCESSES IN A PERFECTLY MIXED REACTOR EQUILIBRIUM MODEL

Sorption operations can be performed in a perfectly mixed reactor; this mode of operation is especially interesting when swelling of solid occurs or suspended materials lead to mechanical problems with increase of pressure drop and clogging of packed beds (Prout, 1961).

Let us write the mathematical equations for the sorption of a single solute in a solid phase contained in a perfectly mixed reactor (Figure 1) in order to predict the evolution of effluent concentration as a function of time (breakthrough curves, history of concentrations).

Assuming instantaneous equilibrium between fluid and solid phases (equilibrium model) and complete mixing within the reactor, we get

1. Unsteady state material balance. The mass balance for a solute over the perfectly mixed reactor is

$$Uc_0 = Uc_1 + v_s \frac{dc_1}{dt} + v_R \frac{dq_1}{dt} \qquad (1)$$

Several authors have improperly omitted the transient term relative to the accumulation in the fluid phase (Slater, 1975; Marchello and Davis, 1963).

2. Equilibrium law at the interface. In order to analyze the influence of the nonlinearity of the equilibrium

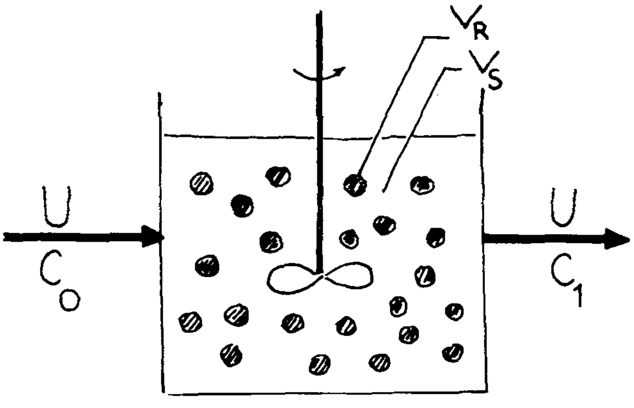

Fig. 1. The perfectly mixed sorber.

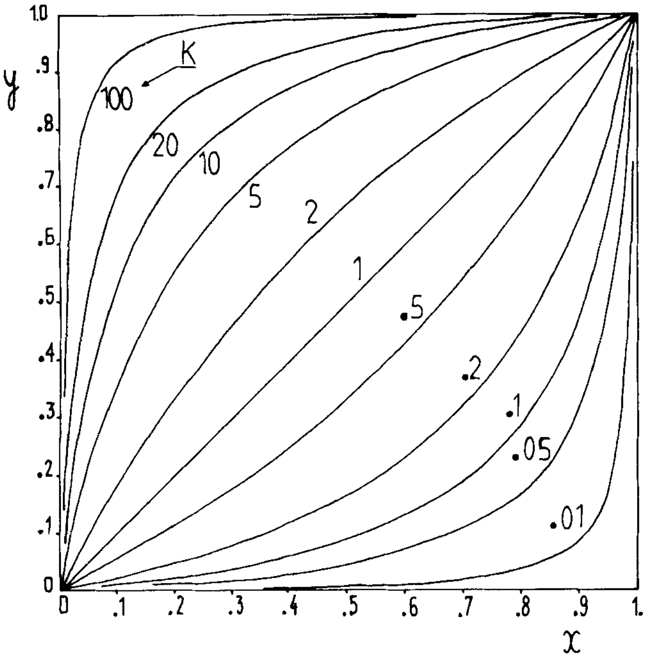

Fig. 2. Sorption equilibrium isotherms for various separation factors K.

isotherm, we assume a constant separation factor

$$K = \frac{q_1\,(c_0 - c_1^*)}{(Q - q_1)c_1^*}$$

which may also be written as

$$q_1 = \frac{K\,Q\,c_1^*}{c_0 + c_1^*(K-1)} \tag{2}$$

3. Kinetic law. In the case of equilibrium theory, there are no mass transfer resistances to the transport of a molecule from the bulk of fluid to the sites on the solid phase; then

$$c_1 = c_1^* \tag{3}$$

4. Initial and boundary conditions. We assume that the solid has no solute sorbed at time $t = 0$ and that the input is a step function of concentration $c_E = c_0\,H(t)$, where $H(t)$ is the Heaviside function

$$t = 0, \quad c_1 = q_1 = 0 \tag{4a}$$

$$c = c_0\,H(t)\ \forall\ t \quad \text{at the inlet} \tag{4b}$$

Introducing dimensionless variables

$$y_1 = \frac{q_1}{Q}, \quad x_1 = \frac{c_1}{c_0}, \quad \theta = \frac{t}{t_{st}}$$

and taking into account that

$\frac{v_s}{U} = \tau$ (space time)

$\frac{v_r}{U} = \frac{1-\epsilon}{\epsilon}\tau$ (ϵ is the porosity or the fraction of the reactor volume occupied by the fluid)

$\xi = \frac{1-\epsilon}{\epsilon}\,\frac{Q}{c_0}$ (capacity parameter)

$t_{st} = \tau(1+\xi)$ (stoichiometric time)

we get from Equations (1) and (2)

$$\frac{dx_1}{d\theta} = \frac{1 - x_1}{f(x_1)} \tag{5}$$

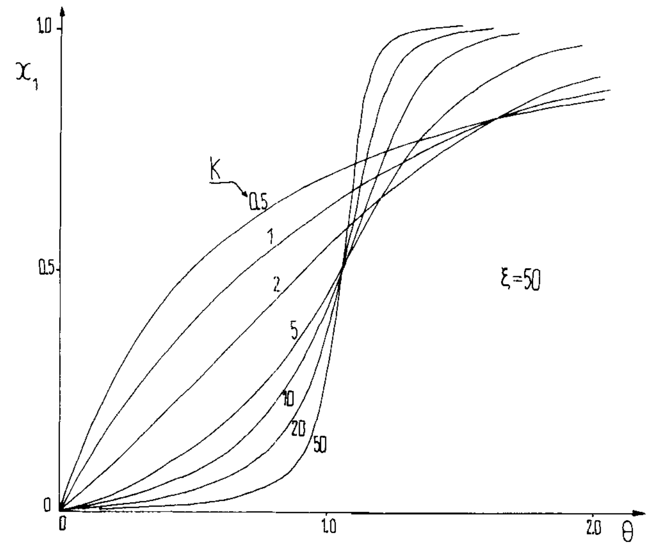

Fig. 3. Influence of the equilibrium constant K on the effluent concentration x_1 (θ). Equilibrium model.

where

$$f(x_1) = \frac{1}{1+\xi}\left\{1 + \frac{\xi K}{[1 + x_1\,(K-1)]^2}\right\}$$

Generally, this equation is a nonlinear ODE (for $K = 1$ it becomes linear).

The response of a perfectly mixed sorber to a step change of concentration at the inlet, that is, $x_1(\theta)$, can be obtained analytically (Rodrigues, 1973; Rodrigues and Tondeur, 1975):

$$\frac{(1-x_1)\,\{(1-x_1)/[1 + x_1\,(K-1)]\}^{\xi/K}}{\exp\{\xi\,(K-1)\,x_1/[1 + x_1\,(K-1)]\}} = \exp[-\,(1+\xi)\theta] \tag{6}$$

The effluent concentration $x_1(\theta)$ depends on two parameters: ξ, the capacity parameter, takes into account the feed concentration, sorbent capacity, and void fraction; K, the equilibrium constant, gives the importance of the nonlinearity of the isotherm.

Curves $x_1(\theta)$ were calculated for different equilibrium isotherms represented in Figure 2. Several conclusions can be drawn:

1. If the isotherm is linear ($K = 1$), the normalized

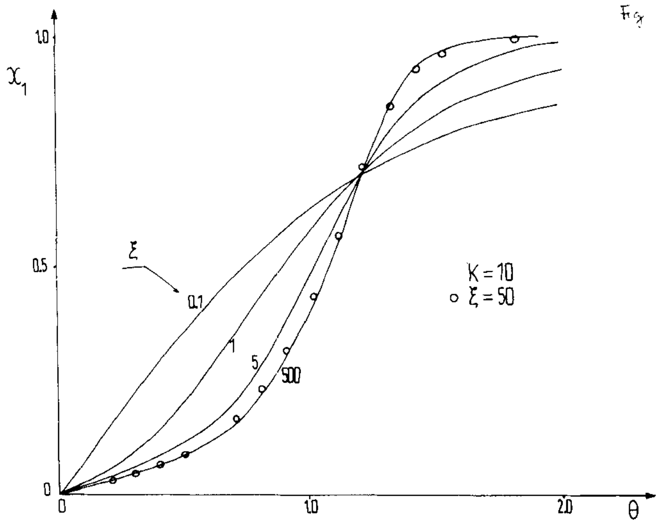

Fig. 4. Influence of the capacity parameter ξ on the effluent concentration x_1 (θ). Equilibrium model.

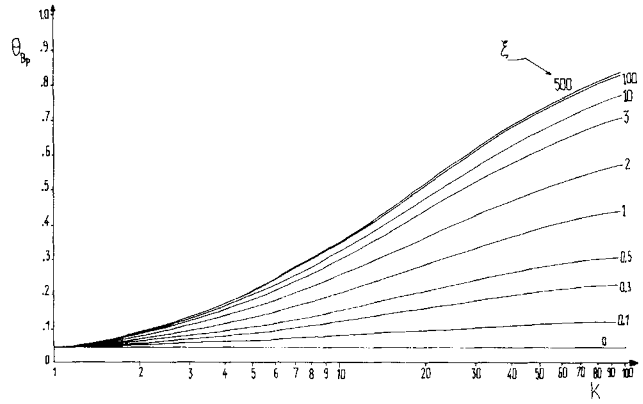

Fig. 5. Breakthrough time θ_{Bp} vs. equilibrium constant K, with ξ as a parameter. Equilibrium model.

response of a perfectly mixed sorber in terms of x_1 as a function of θ is a unique curve, independent of ξ.

2. The influence of K and ξ is in the same direction; that is, an increase of K (or ξ) gives an increase of the quantity of solute retained by the solid phase. However, the effect of ξ is less important than that of K, and above a certain value of ξ its effect is unimportant (Figures 3 and 4).

3. If the equilibrium is irreversible ($K = \infty$), it can be shown (Rodrigues, 1973) that, after linearization of Equation (2), we obtain

$$x_1 = [1 - \exp\{-(\theta - \theta_0)(1 + \xi)\}]\, H(\theta - \theta_0)$$

where

$$\theta_0 = \frac{\xi}{1 + \xi}$$

For design purposes, it is convenient to plot a design parameter: breakthrough time θ_{Bp} (time at which $x_1 = 0.05$, for instance) as a function of K with ξ as a parameter. This graph (Figure 5) shows that the influence of ξ is more important at higher K; the asymptotic expression for $\xi \to \infty$ is

$$\theta = \frac{x_1(K-1)}{1 + x_1(K-1)} - \ln\left[\frac{1 - x_1}{1 + x_1(K-1)}\right]^{1/K}$$

with $x_1 = 0.05$.

A sample procedure can be developed in order to use this plot for the design of perfectly mixed sorbers. Let us suppose that we have to treat a feed containing a pollutant at concentration c_0 in order to obtain an effluent quality $x_1 < 0.05$ during a time t_1 with a flow rate U. The adsorbent to be used has a maximum capacity Q at the concentration c_0.

The volume of adsorbent v_s or the volume of the perfectly mixed reactor ($V = v_s/\epsilon$) is calculated as follows:

1. From a laboratory experiment, determine the equilibrium isotherm, that is, K.
2. Choose ϵ, so ξ is fixed.
3. Using Figure 5 read, θ_{Bp} for given values of K and ξ.
4. The time of operation being fixed t_1, we deduce from the θ_{Bp} calculated before a value $\tau_1 = t_1/\theta_{Bp}(1 + \xi)$ and then the volume of adsorbent.

NONEQUILIBRIUM MODEL (EXTERNAL MASS TRANSFER RESISTANCE)

Now that the results from the equilibrium theory are established, we follow a systematic approach by introducing one resistance to mass transfer (the external mass transfer resistance) due to a stagnant film of fluid around the particles. In practice, this is the controlling mechanism when we use dilute solutions, low particle size, and low flow rates.

This approach is quite different from that used by Farkas and Himsley (1975). Chen et al. (1965, 1972) and Belter et al. (1964) present the material balance in a correct form; Belter et al. (1973) obtain the solution for a Freundlich isotherm using an overall mass transfer coefficient depending on the solid load.

Our objective is to observe what happens to the breakthrough curves when this nonequilibrium model (with external mass transfer resistance) is considered, how the design parameter is modified, and finally to define a criterion which determines the conditions of validity of the equilibrium model. The mathematical formulation follows the previous one.

The equations are still the mass balance, Equation (1); the equilibrium isotherm, Equation (2); and the initial and boundary conditions, Equations (4*a*) and (4*b*). The kinetic law of transport is now

$$\frac{dq_1}{dt} = K_f\, a_p\, (c_1 - c_1^*) \qquad (7)$$

In dimensionless form, the system of Equations (1), (2), and (7) can be written as

$$\frac{dx_1}{d\theta} = f_1(x_1, y_1) \qquad (8a)$$

$$\frac{dy_1}{d\theta} = f_2(x_1, y_1) \qquad (8b)$$

where

$$f_1(x_1, y_1) = (1 + \xi)\left\{1 - (1 + N_f)x_1 + \frac{N_f\, y_1}{y_1 + K(1 - y_1)}\right\}$$

$$f_2(x_1, y_1) = \frac{1 + \xi}{\xi} N_f \left\{x_1 - \frac{y_1}{y_1 + K(1 - y_1)}\right\}$$

and $N_f = 1 - \epsilon/\epsilon\ K_f\, a_p\, \tau$ is a measure of the mass transfer conductance by film diffusion.

NUMERICAL SOLUTION OF THE SYSTEM OF EQUATIONS (8*a*) AND (8*b*)

This system of nonlinear ODE can be solved numerically. Explicit methods such as fourth-order Runge-Kutta or Hamming predictor-corrector are time consuming, even using a variable step of integration. This is especially important for a cascade of reactors, as we will see in a following paper (this is perhaps the justification for the little use of these staged models in percolation processes). The reason for that is the stiff character of the system of Equations (8*a*) and (8*b*).

Lapidus and Seinfeld (1971) define a system as stiff when the Jacobian has at least one eigenvalue which does not contribute significantly to the solution in the whole integration domain. The stiffness conditions are, in general, $Re(\lambda_i) < 0$ and $S(x) >> 0$, where $S(x)$ is the local stiffness ratio defined as $S(x) = \text{Max}\, Re(-\lambda_i)/\text{Min}\, Re(-\lambda_i)$, where Re means the real part of the eigenvalue.

The Jacobian of the system of Equations (8*a*) and (8*b*) is

$$J = \begin{bmatrix} \dfrac{\partial f_1}{\partial x_1} & \dfrac{\partial f_1}{\partial x_2} \\ \dfrac{\partial f_2}{\partial x_1} & \dfrac{\partial f_2}{\partial x_2} \end{bmatrix} =$$

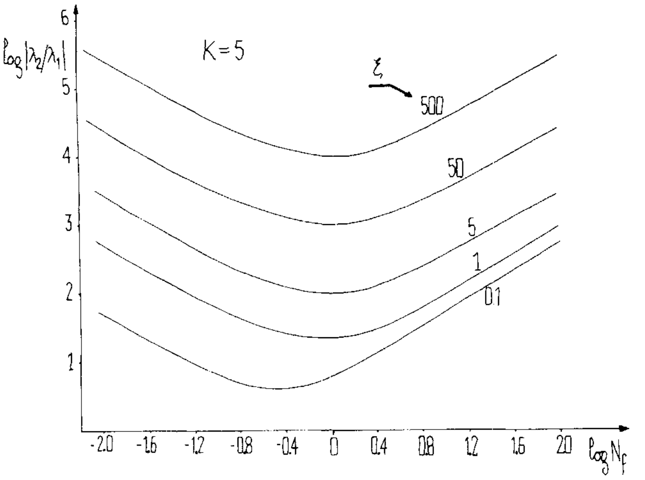

Fig. 6. Stiffness ratio | λ_2/λ_1 | vs. film mass transfer conductance N_f. Nonequilibrium model.

$$\left[\begin{array}{ll} -(1+\xi)(1+N_f) & (1+\xi)N_f\dfrac{K}{[y_1+K(1-y_1)]^2} \\[2ex] N_f\dfrac{(1+\xi)}{\xi} & -N_f\dfrac{1+\xi}{\xi}\,\dfrac{K}{[y_1+K(1-y_1)]^2} \end{array}\right]$$

Then, the eigenvalues of J, obtained from det $[\mathbf{J}-\lambda\mathbf{I}] = 0$ (I is the unit or identity matrix), are given by Equation (9):

$$[y_1+K(1-y_1)]^2\lambda^2 + \left\{ N_f\frac{1+\xi}{\xi}K + \{(1+\xi)(1+N_f)\}\,[y_1+K(1-y_1)]^2 \right\}\lambda + \frac{(1+\xi)^2}{\xi}N_f K = 0 \tag{9}$$

The eigenvalues λ_1 and λ_2 can be calculated for different sets of K, ξ, and N_f; the ratio $|\lambda_2/\lambda_1|$ is a measure of the degree of stiffness where λ_2 is the root of higher absolute value and λ_1 the root of lower absolute value.

As the departure of $|\lambda_2/\lambda_1|$ from unity increases, the integration step for the solution by a classic numerical method decreases.

The plot of $|\lambda_2/\lambda_1|$ as a function of N_f with K and ξ as parameters is shown in Figure 6 (for $y = 0$). These curves at fixed K show that the stiffness ratio increases with ξ and has a minimum as a function of N_f.

The numerical solution of this model will be efficient only with the introduction of appropriate methods for the integration of stiff systems. The Gear method (Gear, 1971*a*) is frequently used. However, the code suggested by Gear (1971*b*) is complex, and its use with minicomputers of little memory core is difficult, especially if languages like BASIC are used.

Michelsen (1976*a*) shows that semiimplicit third-order Runge-Kutta methods are efficient for integration of autonomous stiff systems when combined with a simple algorithm of adjusted integration step. The code proposed by Michelsen (1976*b*) is easily translated to BASIC and adapted for minicomputers.

The integration of the system of Equations (8*a*) and (8*b*) using fourth-order Runge-Kutta method (RK) with variable step is compared with the Michelsen method (M) in the domain $0 < x_1 < 1$, as shown in Table 1.

Caution must be taken when comparing time consumption for different cases. Time consumption should increase when $|\lambda_2/\lambda_1|$ increases, but we should take into account that the stiffness ratio changes with y; it results that discrepancies in Table 1 are only apparent.

DISCUSSION OF COMPUTER RESULTS

Computer calculations were made for many combinations of the three-model parameters: N_f, ξ, and K. In order to analyze the influence of a parameter, we plot the effluent concentrations as a function of time for a fixed pair of values of the other two parameters.

Influence of *K*

Figures 7*a* and 7*b* present the responses of the perfectly mixed sorber for different values of K (at fixed pairs of ξ and N_f). Higher K means higher affinity of the solid to the solute; then the fluid concentration at the interface is lower. As a consequence, the driving force is higher and so is the rate of mass transfer to the solid.

For unfavorable isotherms ($K < 1$), the other parameters have no strong influences in the form of the response curves.

Influence of N_f

Figures 8*a* and 8*b* show the effluent concentration at two fixed pairs of K and ξ for various N_f. For low N_f, that is, high film mass transfer resistance, the outlet concentration increases fast to a plateau concentration mainly dependent on the N_f value.

When film diffusion is the controlling step, this concentration increases slowly during most of the time of the sorption operation to a point where the film gradient is so small that equilibrium is established.

Figure 9 compares $y = g_1(x^*)$ in the equilibrium model with $y = g_2(x)$ in the nonequilibrium model. We can observe that the driving force $x - x^*_{eq}$, or the rate of mass transfer (for a fixed y value) decreases during most of the time of the operation. Again, the influence of N_f is observed; the sharp increase in y corresponds to the plateau in effluent concentration. For high N_f, that is, low mass transfer resistance, the equilibrium is easily reached.

Table 1. Comparison of Computing Times for Runge-Kutta (RK) and Michelsen (M) Methods Using a Minicomputer WANG 2200S

K	N_f	ξ	Time(s) RK	M	RK/M	$\lvert\log_{10} \lambda_2/\lambda_1\ (y = 0)\rvert$
5	0.1	0.1	100	30	3.33	0.799
		5	100	44	2.27	2.481
		500	6 400	109	58.72	4.481
	5	0.1	240	82	2.93	1.372
		5	450	85	5.29	2.279
		500	24 500	55	445.45	4.255
	50	0.1	1 640	120	13.67	2.354
		5	3 360	69	48.70	3.146
		500	7.37×10^5	73	1 009.6	5.114

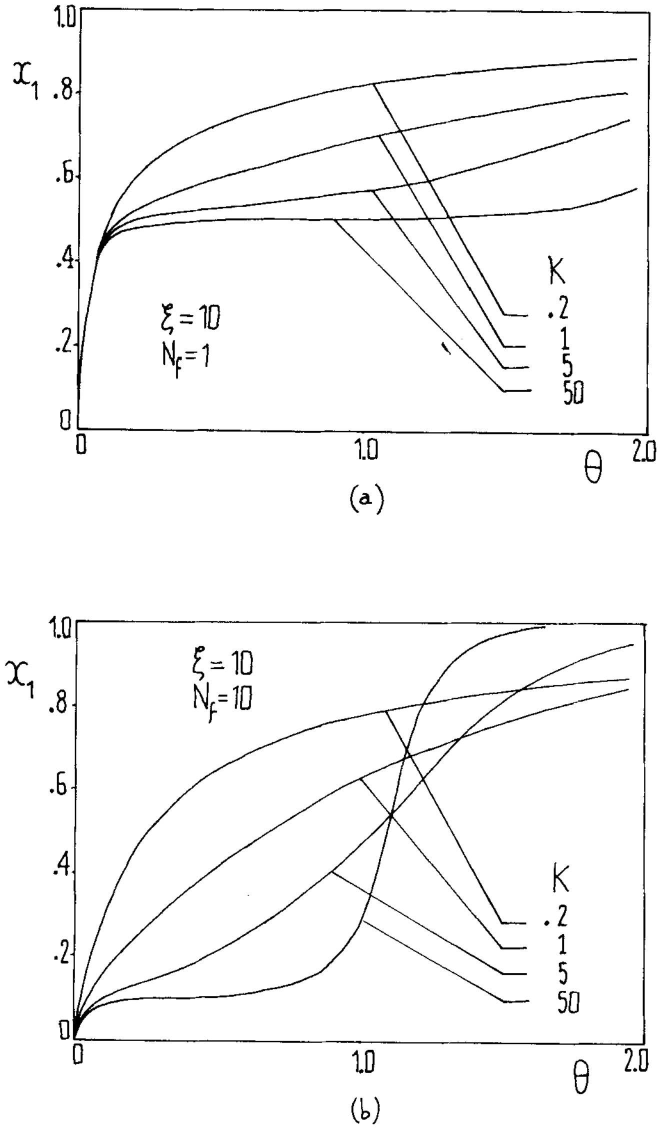

Fig. 7. Influence of the equilibrium constant K on the breakthrough curve x_1 (θ). Nonequilibrium model. *a*. High external mass transfer resistance. *b*. Low external mass transfer resistance.

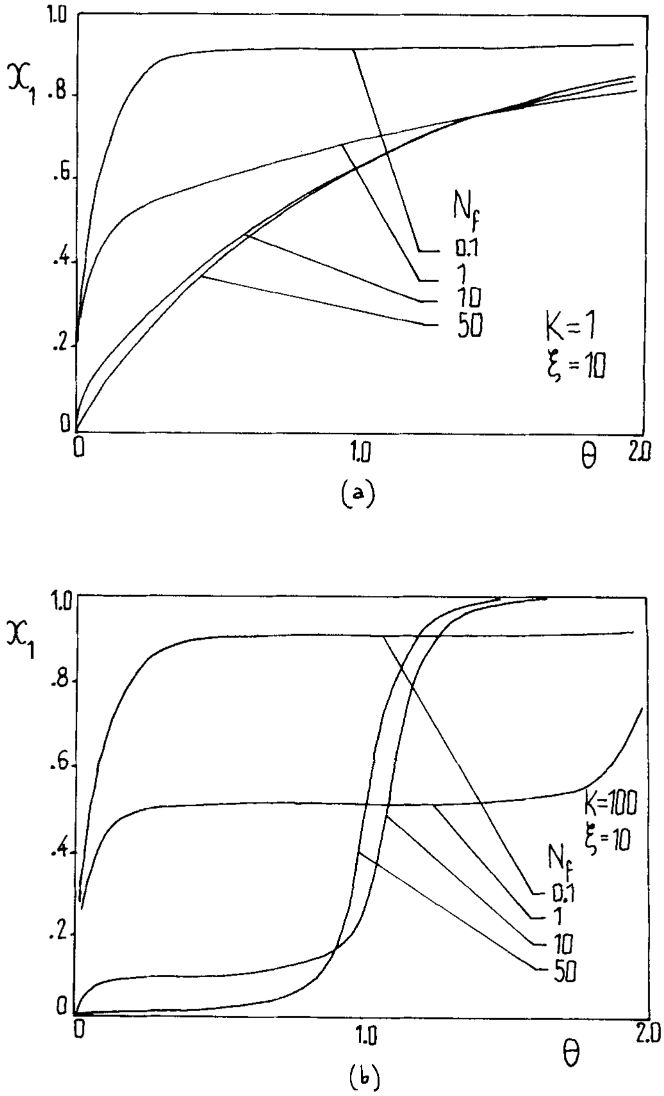

Fig. 8. Influence of the external mass transfer resistance on the breakthrough curve. Nonequilibrium model. *a*. Linear isotherm. *b*. Highly favorable isotherm.

Influence of ξ

When equilibrium prevails, that is, for high N_f, the conclusions are drawn from the equilibrium model. Then the higher is ξ, the higher is the uptake of solute by the solid phase at the initial stage of the operation. However, when N_f is low, the conclusions are reversed. This is shown in Figures 10*a* and 10*b*; we observe for $\xi = 100$, $K = 50$, and $N_f = 1$ a plateau in the effluent concentration, meaning an operation strongly controlled by external diffusion. This agrees with the well-established principle that low concentrations (or high ξ) favor film diffusion.

Breakthrough Time

For design purposes, we are interested in the calculation of the solid volume necessary to treat a certain flow rate of fluid at concentration c_0. If the design parameter is θ_{Bp}, we can compare the values of the breakthrough time given by the equilibrium model and by the film diffusion model. We plotted in Figure 11 θ_{Bp} as a function of K, having ξ and N_f as parameters.

For very low N_f, the mass transfer resistance is so high that in such cases the effluent concentration increases sharply to the plateau concentration; as a consequence, N_f does not affect θ_{Bp} very much in this range, in spite of the value of K.

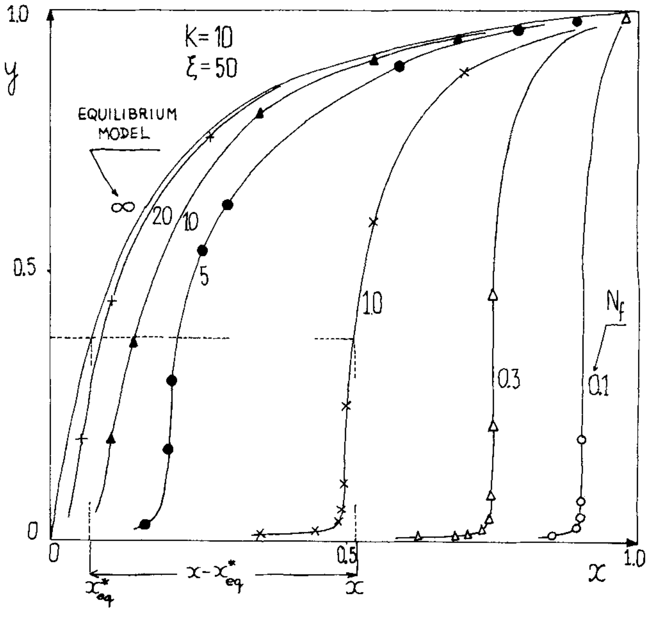

Fig. 9. Comparison between $y = g_1(x^*)$ and $y = g_2(x)$.

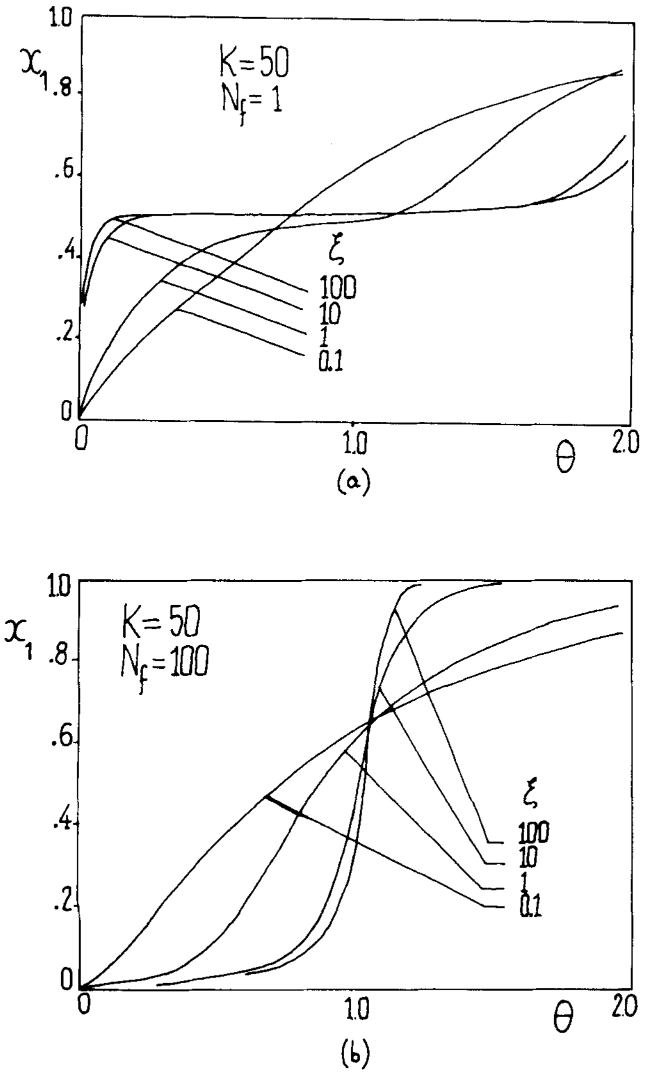

Fig. 10. Effect of the capactiy parameter ξ on the breakthrough curve. Nonequilibrium model. *a*. High film mass transfer resistance. *b*. Low film mass transfer resistance.

CONCLUSIONS

From the previous observations, we are able to predict when the assumption of equilibrium model is valid. To do this, we observe again Figure 9. We can say that the assumption is reasonable if the difference $x - x^*_{eq} < e$, where e is the deviation admitted (say 0.01) during all the operation. Then the methodology to obtain this criterion is as follows. For given conditions (N_f, ξ, and K), we obtain a figure like Figure 9 representing $y = g_1(x^*)$ and $y = g_2(x)$. At fixed y, we find the maximum $x - x^*_{eq}$, that is, $(x - x^*)_{\max}$, which must be lower than e. By a method of nonlinear regression, we obtain

$$(x - x^*)_{\max} = \frac{\xi K}{(a_1 K + b_1)\,\xi N_f + (a_2 K + b_2)\,N_f + a_3\,\xi\,K + a_4\,K^{b_4}} \tag{10}$$

where

$a_1 = 0.986 \quad b_1 = 0.113 \quad a_2 = 0.142 \quad b_2 = 0.903$

$a_3 = 1 \quad a_4 = 0.149 \quad b_4 = 0.398$

Figures 12*a* and 12*b* represent the values $(x - x^*)_{\max}$ obtained from computer results as a function of N_f with ξ as parameter for different K.

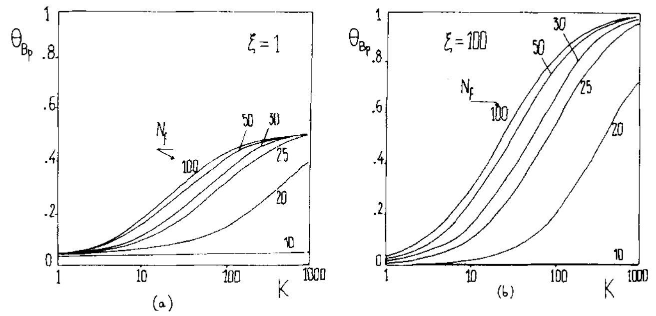

Fig. 11. Breakthrough time θ_{Bp} vs. equilibrium constant K at fixed ξ. Influence of N_f.

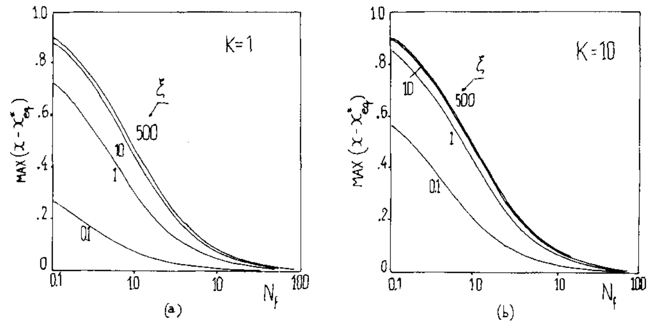

Fig. 12. Maximum deviation between bulk fluid concentration and interface fluid concentration during a sorption operation vs. N_f. *a*. Linear isotherm. *b*. Favorable isotherm.

We observe that at fixed N_f and ξ, the difference $(x - x^*)_{\max}$ is greater for higher K. In fact, if the favorable character of the isotherm increases, the fluid concentration at the interface decreases and then a greater $x - x^*$ appears.

Equation (10) has asymptotic expressions. For instance, for high K and ξ, we get

$$(x - x^*)_{\max} = \frac{1}{a_3 + a_1 N_f} < e$$

This agrees with the above mentioned fact that the plateau concentration is mainly determined by the mass transfer resistance (related to N_f). Then, for high K and ξ, if $e = 0.01$ is imposed, we must choose $N_f > 100$ in order to apply the equilibrium model and neglect effects of mass transfer resistance.

The design of a perfectly mixed sorber based on the plot of θ_{Bp} as a function of ξ, N_f, and K follows the procedure described before by adding to step 1 the estimation of N_f. This can be done using correlations for estimation of film mass transfer coefficients

$$Sh = \frac{K_f\, d_T}{D} = a\, Re^b\, Sc^{1/3} \tag{11}$$

where a and b depend on the geometry of the system (stirrer, reactor).

Further work extends this methodology to a percolation column viewed as a series of perfectly mixed reactors; then the inclusion of internal diffusion is made and sigmoid isotherms considered. Afterwards, the final balance of these effects will be studied in cyclic regime of operation.

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NOTATION

a = constant defined in Equation (11)
a_p = specific area of particles, cm^{-1}
a_1, a_2, a_3, a_4 = constants defined in Equation (10)
b = constant defined in Equation (11)
b_1, b_2, b_3, b_4 = constants defined in Equation (10)
c_0 = inlet fluid phase concentration
c_1 = outlet fluid phase concentration
c_1^* = equilibrium fluid concentration at the interface fluid/solid
d_a = stirrer diameter
d_T = sorber diameter
D = fluid diffusivity
f_1, f_2 = functions defined in Equations (8a) and (8b)
H = Heaviside function
K_f = film mass transfer coefficient, cm s^{-1}
K = separation factor
N_f = number of mass transfer units
N = speed of the stirrer
q_1 = solid phase concentration
Q = capacity of the solid
Re = Reynolds number, defined as $\rho N d_a^2/\mu$
Sc = Schmidt number
Sh = Sherwood number
t = time
t_{st} = stoichiometric time
U = flow rate
v_R = volume of solid in the sorber
v_s = volume of fluid in the sorber
V = volume of the sorber
x_1 = dimensionless fluid phase concentration
y_1 = dimensionless solid phase concentration

Greek Letters

ϵ = void fraction of perfectly mixed sorber
θ = dimensionless time variable
θ_{Bp} = dimensionless breakthrough time
λ_1, λ_2 = eigenvalues of the Jacobian
ρ = fluid density
ξ = capacity parameter
τ = space time
μ = fluid viscosity

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A Thermodynamic Approach to Heat Integration in Distillation Systems

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Starting from a conventional distillation system without heat integration, a series of bottlenecks from the viewpoint of energy conservation is sequentially found by a thermodynamic analysis using a heat availability diagram, and modified systems are evolutionally synthesized as the result of debottlenecking. The present approach has made possible a unified interpretation of various energy integrated distillation systems with multieffect columns, intercondensers/interreboilers, heat pumps, etc.

SCOPE

Distillation is a well-established method of separating multicomponent mixtures and is widely used in the petroleum refining, petrochemical, and other process industries. Distillation systems, however, are highly energy intensive and always consume a large amount of energy to achieve the objective. In view of energy conservation, it is impor-

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