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Comparison of Equilibrium and Nonequilibrium Models in the Simulation of Multicomponent Sorption Processes

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Abstract

A mathematical model has been developed to describe the process of equilibrium adsorption from a finite bath. A nonlinear Fritz-Schluender isotherm model was used to describe the equilibrium between solid and liquid phases. Finite-difference numerical solutions for single, binary, and ternary systems were obtained and shown to match previously published experimental data satisfactorily. These solutions were also compared with nonequilibrium models for the three cases. It was shown that the nonequilibrium model is superior to the equilibrium one since 1) it is applicable to both equilibrium and nonequilibrium conditions, 2) its computer program is general and can be used for any number of sorbates, 3) it can be used for any type of linear or nonlinear equilibrium isotherms without the need to any modifications in the program, and 4) its numerical solutions are of high accuracy compared to experimental data.

INTRODUCTION

The separation of sorbates (pollutants) from a fluid stream by adsorption onto an adsorbent surface is an important process and is especially important in the advanced treatment of municipal and industrial wastewaters. It has been considered as an attractive treatment concept in the Best Available Treatment Economically Achievable (BATEA) process models to be used to produce the 1983 quality level suggested for United States treatment plant effluents (*1*): Design and analysis of such systems require consideration of multisolute nonlinear adsorption phenomena in conjunction with intraparticle and interparticle diffusional effects.

While the results of the equilibrium theory are useful from a qualitative or semiquantitative point of view, they do not provide sufficient accuracy for more demanding design work. A more quantitative predictive model of multicomponent sorption can be obtained only if the assumption of local equilibrium is removed. Unfortunately, most of the workers who presented analytical and numerical solutions to multicomponent sorption problems assumed that equilibrium exists between solid and liquid phases throughout the whole period of the sorptional process. Although this assumption is made to simplify the numerical solution by removing the nonequilibrium terms from the governing model equations, it causes a departure from practical conditions of both transient and steady-state sorptional processes.

The objective of this paper is to compare the equilibrium and nonequilibrium multisolute adsorption processes physically and mathematically. In a previous work (*2*) a single-solute system was studied. In this work, case studies of binary (two solute) and ternary (trisolute) systems are considered. Numerical solutions for both equilibrium and nonequilibrium conditions are presented and compared with previously published experimental data.

MATHEMATICAL ANALYSIS

Physical Model

The adsorption operation can be described by the following physical processes:

1. Solute transport from bulk liquid to pore liquid at the sorbent surface
2. Solute molecular diffusion into sorbent pores and onto its surface
3. Sorption of solute onto sorbent surface
4. Chemical reaction of the sorbed species

In this paper the following assumptions are made:

1. Sorbent particles are of spherical shape
2. Constant-temperature sorption process
3. Constant-pressure sorption process
4. The sorption process is not followed by chemical reactions
5. Mutual external and internal diffusional effects are neglected

6. Nonlinear equilibrium isotherms exist
7. Equilibrium conditions are assumed for the equilibrium model, while nonequilibrium conditions are assumed for the nonequilibrium model
8. The reactor contents are continuously and perfectly mixed
9. Pore and surface diffusivities are not dependent upon the solute concentration

Mathematical Models

A. Nonequilibrium Model Equations

1. Solid-Phase Governing Equations. Mass balance on the pore concentration of solute i gives Eq. (1), while mass balance for the surface concentration of the same solute gives Eq. (2):

$$\varepsilon_p D_{pi} \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial C_{pi}}{\partial r}\right) - K_{1,i}(C_{si}^* - C_{si}) = \varepsilon_p \frac{\partial C_{pi}}{\partial t} \tag{1}$$

$$D_{si} \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial C_{si}}{\partial r}\right) + K_{1,i}(C_{si}^* - C_{si}) = \frac{\partial C_{si}}{\partial t} \tag{2}$$

for $i = 1, 2, 3, \ldots, n$, where n is the number of solutes. (The symbols are defined in the symbols section.) The initial and boundary conditions needed for Eqs. (1) and (2) are:

$$\text{at } t = 0,\ C_{pi} = C_{si} = 0 \text{ for all } 0 \leqslant r \leqslant R$$

$$\text{at } r = 0,\ \partial C_{si}/\partial r = 0 \text{ and } \partial C_{pi}/\partial r = 0 \text{ for any } t > 0$$

$$\text{at } r = R,\ \varepsilon_p D_{pi} \frac{\partial C_{pi}}{\partial r} = K_{fi}(C_{di} - C_{pi})$$

and

$$\partial C_{si}/\partial r = 0 \text{ for any } t > 0$$

where C_{di} is the concentration of solute in the bulk fluid.

2. Liquid-Phase Governing Equations. Mass balance on the solute concentration in the liquid phase gives

$$\frac{dC_{di}}{dt} = \frac{3K_{pi}}{R}\left(\frac{1-\varepsilon_B}{\varepsilon_B}\right)(C_{pi} - C_{di})_{r=R} \tag{3}$$

The initial condition needed for Eq. (3) is

$$C_{di}(t) = C_{di0} \qquad \text{at } t = 0$$

Equilibrium between fluid and solid phases are given by the Fritz-Schleunder nonlinear general isotherm (*3*):

$$C_{si}^{*} = \frac{a_{i0}C_{pi}^{b_{i0}}}{c_i + \sum_{i=1}^{n} a_{ij}c_{pj}^{b_{ij}}} = f_i(C_{p1}, C_{p2}, \ldots, C_{pn}) \tag{4}$$

where C_{si}^{*} = the amount of solute i sorbed per unit volume of particle at equilibrium with C_{pi} in n-solute mixture.

The Langmuir isotherm is a special simplified case of Eq. (4) when $b_{i0} = b_{ij} = c_i = 1$. For a one-solute system, Eq. (4) reduces to the Freundlich isotherm.

For the system of butanol-2 (Solute 1) and *t*-amyl alcohol (Solute 2), Eq. (4) becomes (*3*):

$$C_{s1}^{*} = \frac{1.06C_{p1}^{1.27}}{C_{p1}^{0.82} + 0.626C_{p2}^{0.764}} = f_1(C_{p1}, C_{p2}) \tag{5}$$

$$C_{s2}^{*} = \frac{1.07C_{p2}^{1.254}}{C_{p2}^{0.906} + 0.045C_{p1}^{0.634}} = f_2(C_{p1}, C_{p2}) \tag{6}$$

For the trisolute system butanol-2, *t*-amyl alcohol, and phenol (Solute 3), Eq. (4) becomes (*3*):

$$C_{s1}^{*} = \frac{1.05C_{p1}^{1.314}}{C_{p1}^{0.73} + 1.44C_{p2}^{0.793} + C_{p3}^{0.467}} = f_3(C_{p1}, C_{p2}, C_{p3}) \tag{7}$$

$$C_{s2}^{*} = \frac{1.05C_{p1}^{1.134}}{C_{p2}^{0.831} + 0.52C_{p1}^{0.884} + 0.30C_{p3}^{0.536}} = f_4(C_{p1}, C_{p2}, C_{p3}) \tag{8}$$

$$C_{s3}^{*} = \frac{0.79C_{p3}^{0.224}}{C_{p3}^{0.002} + 1.07C_{p1}^{0.286} + 0.79C_{p2}^{0.235}} = f_5(C_{p1}, C_{p2}, C_{p3}) \tag{9}$$

B. Equilibrium Model Equations

When local equilibrium is assumed to exist between liquid and solid phases, C_{si}^{*} becomes equal to C_{si} and hence Eqs. (1) and (2) can be combined to give

$$\varepsilon_p \frac{\partial C_{pi}}{\partial t} + \frac{\partial C_{si}}{\partial t} = \varepsilon_p D_{pi} \frac{1}{r^2} \frac{\partial}{\partial r}\left[r^2 \frac{\partial C_{pi}}{\partial r}\right] + D_{si} \frac{1}{r^2} \frac{\partial}{\partial r}\left[r^2 \frac{\partial C_{si}}{\partial r}\right] \tag{10}$$

For this case $C_{si}^{*} = C_{si} = f_i(C_{p1}, C_{p2}, \ldots, C_{pn})$, and thus by introduction of the equilibrium relationships from Eq. (4), Eq. (10) can be transformed to

$$\varepsilon_p \frac{\partial C_{pi}}{\partial t} + \sum_{j=1}^{n} \left(\frac{\partial f_i}{\partial C_{pj}}\right)\left(\frac{\partial C_{pi}}{\partial t}\right) = \varepsilon_p D_{pi} \frac{1}{r^2} \frac{\partial}{\partial r}\left[r^2 \frac{\partial C_{pi}}{\partial r}\right]$$

$$+ D_{si} \frac{1}{r^2}\left[\sum_{j=1}^{n} \left(\frac{\partial f_i}{\partial C_{pj}}\right)\left(\frac{\partial C_{pj}}{\partial r}\right)\right] \tag{11}$$

Notice that Eq. (11), which represents the solid-phase model, has for any Solute *i* one dependent variable which is C_{pi}. Details for single-solute, bisolute, and trisolute equilibrium models are presented in the Appendix.

Numerical Solutions for Models

A. Solution of Nonequilibrium Model

A stable backward-finite difference technique (*4*) was used by Mansour (*5*, *6*) to solve Eqs. (1) and (2) simultaneously. A special and efficient computer subroutine was designed by Mansour (*5*) to solve the bitridiagonal matrices resulting from Eqs. (1) and (2). Full details of the iterative numerical solution and finite-difference equations are described elsewhere (*5*, *6*).

The finite-difference equation resulting from Eq. (3) is substituted into the difference equation of the boundary condition

$$\varepsilon_p D_{pi} \frac{\partial C_{pi}}{\partial r} = K_{fi}(C_{di} - C_{pi})_{r=R}$$

at the outer radius of the sorbent particle, i.e., at $r = R$, each time step such that the liquid concentration C_{di} is expressed as a function of C_{pi} at $r = R$ and its value in the previous time step. After each time step the value of the solute concentration C_{di} is updated and the procedure is repeated.

B. Numerical Solution of Equilibrium Model

1. Solution of Single-Solute Model. The finite-difference equation arising from Eq. (A1) forms a tridiagonal system which can be iteratively solved by using the Thomas algorithm (*4*).

2. Solution of Bisolute Model. The finite-difference equations arising from Eqs. (A2) and (A3) form a bitridiagonal system which can be iteratively solved by using the bitridiagonal algorthm (*4*, *5*). A special subroutine has been designed for this purpose.

3. Solution of Trisolute Model. The finite-difference equations arising from Eqs. (A4), (A5), and (A6) form a tritridiagonal system which can be iteratively solved by using the tritridiagonal algorithm (*4*). A new special subroutine has been written (*7*) to solve such systems.

RESULTS AND DISCUSSION

The purpose of this study is to quantify the differences between equilibrium and nonequilibrium models in predicting the kinetics of multicomponent processes. Three systems were studied in this work; these systems are 1) single-solute system, 2) bisolute system, and 3) trisolute system.

Results for the Single-Solute System

The solutions of equilibrium and nonequilibrium models have been discussed in a previous study published by Mansour (*2*), and since most of the practical sorptional processes involve more than one solute, the concentration in this study has been focused onto multicomponent systems.

Results for the Bisolute System

The values of parameters for this system were used experimentally by Balzli (*8*) where butanol is taken as Solute 1 and *t*-amyl alcohol as Solute 2. These values are given in Table 1.

Figure 1 shows an excellent agreement between the theoretical predictions of both equilibrium and nonequilibrium models obtained in this study and experimental data obtained by Balzli (*8*). Notice that the deviations of equilibrium model in the initial times of sorption (the transient portion of the process) from the experimental values are of larger magnitude than the ones of the nonequilibrium model. However, the deviations of the nonequilibrium model in this interval of the sorptional process are due to the uncertainties in the values of diffusivities D_{pi}'s and D_{si}'s which were obtained by Liapis and Rippin (*9*) and used for a slightly different model.

The computer time consumed in solving the equilibrium model was 190 s, while it was only 75 s for solving the nonequilibrium model.

Results for the Trisolute Model

The values of parameters used in this model (Table 2) are given in Fig. 2, and also show an excellent agreement between theoritical and experimental results. The differences between the equilibrium and nonequilibrium models observed in the bisolute system can also be noticed in the trisolute system.

The computer time used for the equilibrium model solution was about 260 s, while it was only 100 s for the nonequilibrium model solution.

TABLE 1
Values of Parameters Used in the Bisolute System

Solute 1:
$C_{01} = 0.0005$
$K_{f1} = 4.472 \times 10^{-3}$
$K_{1,1} = 1.92$
$D_{p1} = 7.4 \times 10^{-6}$
$D_{s1} = 1.25 \times 10^{-7}$

Solute 2:
$C_{02} = 0.0005$
$K_{f2} = 4.132 \times 10^{-3}$
$K_{1,2} = 1.76$
$D_{p2} = 13 \times 10^{-6}$
$D_{s2} = 2.2 \times 10^{-7}$

Parameters of the reactor:
$R = 0.05$
$\varepsilon_p = 0.94$
$\varepsilon_B = 0.9859$

Parameters of the isotherm:
$a_{10} = 1.06, a_{11} = 1.00, a_{12} = 0.626, c_1 = 0$
$b_{10} = 1.27, b_{11} = 0.82, b_{12} = 0.764$
$b_{20} = 1.254, b_{21} = 0.906, b_{22} = 0.634$

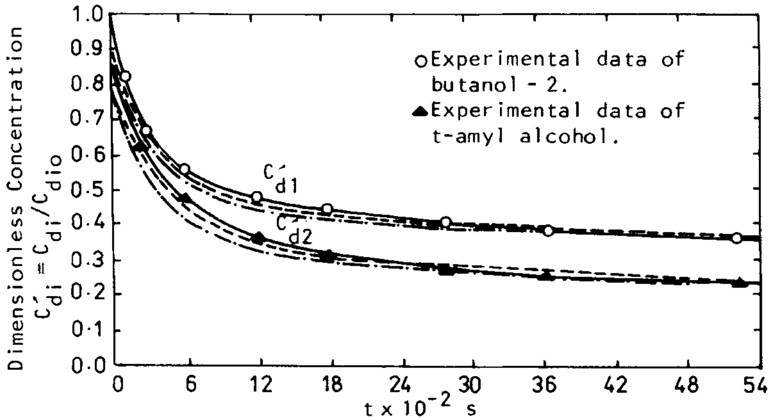

FIG. 1. Bisolute sorption of butanol-2 and *t*-amyl alcohol in a stirred tank reactor. (- -) Mathematical data of nonequilibrium model. (-·-) Mathematical data of equilibrium model.

TABLE 2
Values of Parameters Used in the Trisolute System

Solute 1:
$C_{01} = 0.0005$
$K_{f1} = 4.472 \times 10^{-3}$
$K_{1,1} = 1.92$
$D_{p1} = 7.4 \times 10^{-6}$
$D_{s1} = 1.25 \times 10^{-7}$

Solute 2:
$C_{02} = 0.0005$
$K_{f2} = 4.132 \times 10^{-3}$
$K_{1,2} = 1.76$
$D_{p2} = 13.03 \times 10^{-6}$
$D_{s2} = 2.20 \times 10^{-7}$

Solute 3:
$C_{03} = 0.0005$
$K_{f3} = 4.380 \times 10^{-3}$
$K_{1,3} = 1.18$
$D_{p3} = 19.2 \times 10^{-6}$
$D_{s3} = 3.2 \times 10^{-7}$

Parameters of the isotherm:
$a_{10} = 1.05, a_{11} = 1.00, a_{12} = 1.44, a_{13} = 0.53, c_1 = 0$
$b_{10} = 1.134, b_{11} = 0.73, b_{12} = 0.793, b_{13} = 0.467$
$a_{20} = 1.09, a_{21} = 0.52, a_{22} = 1.00, a_{23} = 0.30, c_2 = 0$
$b_{20} = 1.182, b_{21} = 0.884, b_{22} = 0.831, b_{23} = 0.536$
$a_{30} = 0.79, a_{31} = 1.07, a_{32} = 0.79, a_{33} = 1.00, c_3 = 0$
$b_{30} = 0.224, b_{31} = 0.286, b_{32} = 0.235, b_{33} = 0.002$

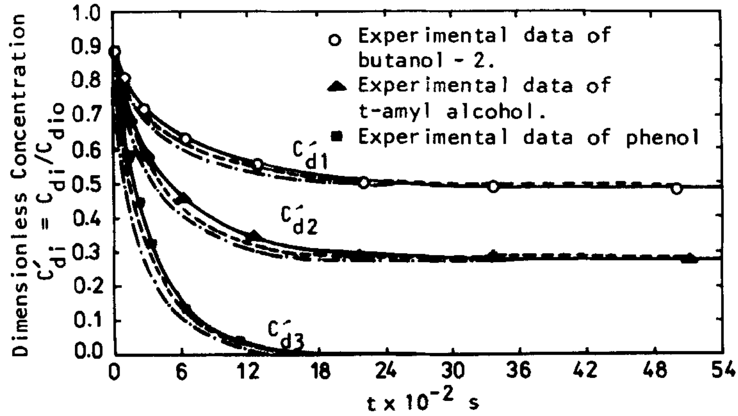

FIG. 2. Trisolute sorption of butanol-2 and *t*-amyl alcohol in a stirred tank reactor. (- -) Mathematical data of nonequilibrium mode. (-··-) Mathematical data of equilibrium model.

CONCLUSIONS

Two computer solutions using two different models have been presented and compared. In conclusion, the advantages and the disadvantages of both equilibrium and nonequilibrium models in the simulation of multicomponent sorption processes can be summarized in Table 3.

From Table 3 it can be concluded that the advantages of the nonequilibrium model are superior to those of the equilibrium model and hence it is highly recommended for multicomponent systems.

APPENDIX

Single-Solute Equilibrium Model

By introducing the equilibrium isotherm $C_s^* = C_s = a_0 C_p^b$ into Eq. (10) for a single-solute system, it becomes

$$(\varepsilon_p + a_0 b C_p^{b-1}) \frac{\partial C_p}{\partial t} = [\varepsilon_p D_p + D_s a_0 b(b-1) C_p^{b-1}]\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C_p}{\partial r}\right)\right] + D_s a_0 b(b-1) C_p^{b-2}\left(\frac{\partial C_p}{\partial r}\right)^2 \qquad \text{(A1)}$$

TABLE 3
Comparison between Equilibrium and Nonequilibrium Models

Model specification	Equilibrium model	Nonequilibrium model
1. Mathematical formulation of multicomponent model	Complex especially for large number of solutes; e.g., it requires the evaluation of 10 and 27 partial derivates for bisolute and trisolute systems, respectively	Only one equation is used for any number of solutes
2. Capability of using nonlinear isotherms	It is too difficult to use nonlinear isotherms, especially for large number of solutes, i.e., three solutes and above	It is highly capable to be used with any isotherm for any degree of nonlinearity
3. Capability of model to solve systems of large number of solutes	It needs different solution and computer program for each system	One general program is used for any number of solutes
4. Computer time	Relatively long	Considerably shorter than that consumed by the equilibrium model
5. Capability for using in different physical conditions	It can be used for equilibrium conditions only	It can be used for both equilibrium and nonequilibrium conditions

Bisolute Equilibrium Model

Introducing the equilibrium relationships for Solute 1 and Solute 2

$$C_{s1}^{*} = C_{s1} = \frac{a_{10}C_{p1}^{b_{10}}}{a_{11}C_{p1}^{b_{11}} + a_{12}C_{p2}^{b_{12}}} = f_1(C_{p1}, C_{p2})$$

$$C_{s2}^{*} = C_{s2} = \frac{a_{20}C_{p2}^{b_{20}}}{a_{21}C_{p1}^{b_{21}} + a_{22}C_{p2}^{b_{22}}} = f_2(C_{p1}, C_{p2})$$

into Eq. (10) for the two solutes, it becomes:

For solute 1:

$$\left[\frac{(\varepsilon_p + a_{10}b_{10}C_{p1}^{b_{10}-1})(\mathrm{DEN1}) - (a_{10}C_{p1}^{b_{10}})(a_{11}b_{11}C_{p1}^{b_{11}-1})}{(\mathrm{DEN1})^2}\right]\frac{\partial C_{p1}}{\partial t}$$

$$- \left[\frac{a_{10} C_{p1}^{b_{10}} (a_{12} b_{12} C_{p2}^{b_{12}-1})}{(\mathrm{DEN1})^2} \right] \frac{\partial C_{p2}}{\partial t}$$

$$= \frac{2}{r} | \varepsilon_p D_{p1} + D_{s1} (a_{10} b_{10} C_{p1}^{b_{10}-1})(\mathrm{DEN1}) - (a_{10} C_{10}^{b_{10}})(a_{11} b_{11}^{b_{11}-1}) | \frac{\partial C_{p1}}{\partial r}$$

$$- \frac{2}{r} \left[\frac{D_{s1} (a_{10} C_{p1}^{b_{10}})(a_{12} b_{12} C_{p2}^{b_{12}-1})}{(\mathrm{DEN1})^2)} \right] \frac{\partial C_{p2}}{\partial r} + \varepsilon_p D_{p1} \frac{\partial^2 C_{p1}}{\partial r^2}$$

$$+ D_{s1} \left[\frac{(a_{10} b_{10} C_{p1}^{b_{10}-1})(\mathrm{DEN1}) - (a_{10} C_{p1}^{b_{10}})(a_{11} b_{11} C_{p1}^{b_{11}-1})}{(\mathrm{DEN1})^2} \right] \frac{\partial^2 C_{p1}}{\partial r^2}$$

$$+ D_{s1} \left[\frac{(\mathrm{DEN1})(a_{10} b_{10} (b_{10} - 1)(C_{p1}^{b_{10}-2} - (a_{11} b_{11} (b_{11} - 1) C_{p1}^{b_{11}-2})(a_{10} C_{p1}^{b_{10}})}{(\mathrm{DEN1})^2} \right] \left(\frac{\partial C_{p1}}{\partial r} \right)^2$$

$$- D_{s1} \left[\frac{(2a_{11} b_{11} C_{p1}^{b_{11}-1})(\mathrm{DEN1})(a_{10} b_{10} C_{p1}^{b_{10}-1}) - (a_{10} C_{p1}^{b_{10}})(a_{11} b_{11} C_{p1}^{b_{11}-1})}{(\mathrm{DEN1})^3} \right] \left(\frac{\partial C_{p1}}{\partial r} \right)^2$$

$$- D_{s1} \left[\frac{(a_{10} C_{p1}^{b_{10}})(a_{12} b_{12} C_{p2}^{b_{12}-1})}{(\mathrm{DEN1})^2} \right] \frac{\partial^2 C_{p2}}{\partial r^2}$$

$$- D_{s1} \left[\frac{(\mathrm{DEN1})(a_{10} C_{p1}^{b_{10}})(a_{12} b_{12})(b_{12} - 1) - (a_{10} C_{p1}^{b_{10}})(a_{12} b_{12} C_{p2}^{b_{12}-1})(2a_{12} b_{12} C_{p2}^{b_{12}-1})}{(\mathrm{DEN1})^3} \right]$$

$$\cdot \left(\frac{\partial C_{p2}}{\partial r} \right)^2 \qquad \text{(A2)}$$

where

$$\mathrm{DEN1} = a_{11} C_{p1}^{b_{11}} + a_{12} C_{p2}^{b_{12}}$$

For Solute 2 a similar equation (Eq. A3) is obtained. For a bisolute system, Eqs. (A2) and (A3) should be solved simultaneously for C_{p1} and C_{p2}.

Trisolute Equilibrium Model

The equilibrium isotherms for the three solutes are:

For Solute 1:

$$C_{s1}^{*} = C_{s1} = \frac{a_{10}C_{p1}^{b_{10}}}{a_{11}C_{p1}^{b_{11}} + a_{12}C_{p2}^{b_{12}} + a_{13}C_{p3}^{b_{13}}} = f_3(C_{p1}, C_{p2}, C_{p3})$$

For Solute 2:

$$C_{s2}^{*} = C_{s2} = \frac{a_{20}C_{p2}^{b_{20}}}{a_{21}C_{p1}^{b_{21}} + a_{22}C_{p2}^{b_{22}} + a_{23}C_{p3}^{b_{23}}} = f_4(C_{p1}, C_{p2}, C_{p3})$$

For Solute 3:

$$C_{s3}^{*} = C_{s3} = \frac{a_{30}C_{p3}^{b_{30}}}{a_{31}C_{p1}^{b_{31}} + a_{32}C_{p2}^{b_{32}} + a_{33}C_{p3}^{b_{33}}} = f_5(C_{p1}, C_{p2}, C_{p3})$$

By introducing the first isotherm into Eq. (10) for Solute 1, it is transformed to:

$$\varepsilon_p \frac{\partial C_{p1}}{\partial t} + \frac{\partial C_{s1}}{\partial t} = \varepsilon_p D_{p1} \frac{1}{r^2} \frac{\partial}{\partial r}\left[r^2 \frac{\partial C_{p1}}{\partial r}\right] + D_{s1} \frac{1}{r^2} \frac{\partial}{\partial r}\left[r^2 \frac{\partial C_{s1}}{\partial r}\right] \quad \text{(A4)}$$

where

$$\frac{\partial C_{s1}}{\partial t} = \frac{\partial C_{s1}}{\partial C_{p1}}\left(\frac{\partial C_{p1}}{\partial t}\right) + \frac{\partial C_{s1}}{\partial C_{p2}}\left(\frac{\partial C_{p2}}{\partial t}\right) + \frac{\partial C_{s1}}{\partial C_{p3}}\left(\frac{\partial C_{p3}}{\partial t}\right)$$

$$= \left[\left(\frac{a_{10}b_{10} \cdot C_{p1}^{(b_{10}-1)} \cdot (\mathrm{DHP1})}{(\mathrm{DHP1})^2}\right) - \left(\frac{a_{10} \cdot a_{11} \cdot b_{11} \cdot C_{p1}^{(b_{10}+b_{11}-1)}}{(\mathrm{DHP1})^2}\right)\right] \cdot \frac{\partial C_{p1}}{\partial t}$$

$$- \left[\left(\frac{a_{10} \cdot a_{12} \cdot b_{12} \cdot C_{p1}^{b_{10}} \cdot C_{p2}^{(b_{12}-1)}}{(\mathrm{DHP1})^2}\right)\right] \cdot \frac{\partial C_{p2}}{\partial t}$$

$$- \left[\left(\frac{a_{10} \cdot a_{13} \cdot b_{13} \cdot C_{p1}^{b_{10}} \cdot C_{p3}^{(b_{13}-1)}}{(\mathrm{DHP1})^2}\right)\right] \frac{\partial C_{p3}}{\partial t}$$

$$\frac{\partial C_{s1}}{\partial r} = \frac{\partial C_{s1}}{\partial C_{p1}}\left(\frac{\partial C_{p1}}{\partial r}\right) + \frac{\partial C_{s1}}{\partial C_{p2}}\left(\frac{\partial C_{p2}}{\partial r}\right) + \frac{\partial C_{s1}}{\partial C_{p3}}\left(\frac{\partial C_{p3}}{\partial r}\right)$$

$$= \left[\left(\frac{a_{10} \cdot b_{10} \cdot C_{p1}^{(b_{10}-1)} \cdot (\mathrm{DHP1})}{(\mathrm{DHP1})^2}\right) - \left(\frac{a_{10} \cdot a_{11} \cdot b_{11} \cdot C_{p1}^{(b_{10}+b_{11}-1)}}{(\mathrm{DHP1})^2}\right)\right] \cdot \frac{\partial C_{p1}}{\partial r}$$

$$- \left[\left(\frac{a_{12} \cdot b_{12} \cdot C_{p2}^{(b_{12}-1)} \cdot a_{10} \cdot C_{p1}^{b_{10}}}{(\mathrm{DHP1})^2}\right)\right] \cdot \frac{\partial C_{p2}}{\partial r}$$

$$- \left[\left(\frac{a_{10} \cdot a_{13} \cdot b_{13} \cdot C_{p1}^{b_{10}} \cdot C_{p3}^{(b_{13}-1)}}{(\mathrm{DHP1})^2}\right)\right] \cdot \frac{\partial C_{p3}}{\partial r}$$

$$\frac{\partial^2 C_{s1}}{\partial r^2} = \left(\frac{\partial C_{s1}}{\partial C_{p1}}\right)\left(\frac{\partial^2 C_{s1}}{\partial r^2}\right) + \left(\frac{\partial^2 C_{p1}}{\partial C_{p1}^2}\right)\left(\frac{\partial C_{p1}}{\partial r}\right)^2 + \left(\frac{\partial C_{s1}}{\partial C_{p2}}\right)\left(\frac{\partial^2 C_{p2}}{\partial r^2}\right)$$

$$+ \left(\frac{\partial^2 C_{s1}}{\partial C_{p2}^2}\right)\left(\frac{\partial C_{p2}}{\partial r}\right)^2 + \left(\frac{\partial C_{s1}}{\partial C_{p3}}\right)\left(\frac{\partial^2 C_{p3}}{\partial r^2}\right) + \left(\frac{\partial^2 C_{s1}}{\partial C_{p3}^2}\right)\left(\frac{\partial C_{p3}}{\partial r}\right)^2$$

$$= \left[\left(\frac{a_{10} \cdot b_{10} \cdot C_{p1}^{(b_{10}-1)} \cdot (\mathrm{DHP1})}{(\mathrm{DHP1})^2}\right) - \left(\frac{a_{10} \cdot a_{11} \cdot b_{11} \cdot C_{p1}^{(b_{10}+b_{11}-1)}}{(\mathrm{DHP1})^2}\right)\right] \frac{\partial^2 D_{p1}}{\partial r^2}$$

$$+ \left[\left(\frac{a_{10} \cdot b_{10} \cdot (b_{10} - 1) \cdot C_{p1}^{(b_{10}-2)} \cdot (\mathrm{DHP1})}{(\mathrm{DHP1})^2}\right)\right.$$

$$\left. - \left(\frac{a_{10} \cdot a_{11} \cdot b_{11}(b_{11} - 1) \cdot C_{p1}^{(b_{10}+b_{11}-2)}}{(\mathrm{DHP1})^2}\right)\right]$$

$$- \left[\left(\frac{2a_{10} \cdot b_{10} \cdot a_{11} \cdot b_{11} \cdot C_{p1}^{(b_{10}+b_{11}-2)}}{(\mathrm{DHP1})^2}\right)\right.$$

$$\left. + \left(\frac{2a_{10} \cdot a_{11}^2 \cdot b_{11}^2 \cdot C_{p1}^{(b_{10}+2b_{11}-2)}(\mathrm{DHP1})}{(\mathrm{DHP1})^4}\right)\right] \cdot \left(\frac{\partial C_{p1}}{\partial r}\right)^2$$

$$+ \left[\left(\frac{-a_{10} \cdot a_{12} \cdot b_{12} \cdot C_{p1}^{(b_{10})} \cdot C_{p2}^{(b_{12}-1)}}{(\mathrm{DHP1})^2}\right)\right] \cdot \frac{\partial^2 C_{p2}}{\partial r^2}$$

$$- \left[\left(\frac{a_{10} \cdot a_{12} \cdot b_{12} \cdot (b_{12} - 1) \cdot C_{p1}^{b_{10}} \cdot C_{p2}^{(b_{12}-2)}}{(\mathrm{DHP1})^2}\right)\right.$$

$$\left. + \left(\frac{2a_{10} \cdot a_{12}^2 \cdot b_{12}^2 \cdot C_{p1}^{(b_{10})} \cdot C_{p2}^{2(b_{12}-1)}}{(\mathrm{DHP1})^3}\right)\right] \cdot \left(\frac{\partial C_{p2}}{\partial r}\right)^2$$

$$- \left[\left(\frac{a_{10} \cdot a_{13} \cdot b_{13} \cdot C_{p1}^{b_{10}} \cdot C_{p3}^{(b_{13}-1)}}{(\mathrm{DHP1})^2}\right)\right] \cdot \left(\frac{\partial^2 C_{p3}}{\partial r^2}\right)$$

$$+ \left[\left(\frac{-a_{10} \cdot a_{13} \cdot b_{13}(b_{13} - 1) \cdot C_{p1}^{b_{10}} \cdot C_{p3}^{(b_{13}-2)}}{(\mathrm{DHP1})^2} \right) \right.$$

$$\left. + \left(\frac{2a_{10} \cdot a_{13}^2 \cdot b_{13}^2 \cdot C_{p1}^{(b_{10})} \cdot C_{p3}^{2(b_{13}-1)}}{(\mathrm{DHP1})^2} \right) \right] \cdot \left(\frac{\partial C_{p3}}{\partial r} \right)^2$$

where

$$\mathrm{DHP1} = a_{11}C_{p1}^{b_{11}} + a_{12}C_{p2}^{b_{12}} + a_{13}C_{p3}^{b_{13}}$$

For Solutes 2 and 3, similar equations (Eqs. A5 and A6) are obtained. Equations (A4), (A5), and (A6) form a tritridiagonal system when they are transformed into difference equations, and they should be solved simultaneously for C_{p1}, C_{p2}, and C_{p3}.

SYMBOLS

a_{i0}, a_{ij}	coefficients in Eq. (4)
b_{i0}, b_{ij}	exponents in Eq. (4)
C_{di}	concentration of solute i in fluid phase of the bath (g/cm^3)
C_{0i}	initial value of C_{di}
C_{pi}	concentration of solute i in pore-fluid phase (g/cm^3)
C_{si}	concentration of solute i in the solid phase (per unit volume of particles) (g/cm^3)
D_{pi}	effective diffusivity of solute i in pore fluid (cm^2/s)
D_{si}	effective diffusivity of solute i in particle-solid phase (cm^2/s)
K_{fi}	mass-transfer coefficient of solute i between liquid and particle (cm/s)
$K_{1,i}$	adsorption rate constant of solute i (h^{-1})
n	number of adsorbed solutes
r	radial distance in particle (cm)
R	radius of particle (cm)
t	time (s)

Greek Letters

ε_B	bath void fraction
ε_P	particle void fraction

Superscripts

*	equilibrium value

Subscripts

i	index for solute
p	pore
s	solid

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