

Applications of mathematical modelling to the simulation of binary perfusion chromatography

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(First received January 20th, 1993; revised manuscript received April 5th, 1993)

ABSTRACT

A mathematical model of binary (competitive adsorption involving two components) perfusion chromatography is used to simulate and study the behavior of a binary adsorption system. The dynamic behavior of column systems (frontal analysis) is examined for different particles sizes, column fluid superficial velocities, V_f , and intraparticle fluid velocities, v_p . Column systems with perfusive ($v_p > 0$) and purely diffusive ($v_p = 0$) adsorbent particles are studied. The results obtained from the binary system studied in this work suggest that the times at which breakthrough begins for components 1 and 2, and the dynamic (unsteady state) relative separation between components 1 and 2 obtained from the column with perfusive particles, are higher than those obtained from the column having purely diffusive particles, especially as the particle size, z_0 , and the column fluid superficial velocity, V_f , increase. The improved separation efficiency obtained from the chromatographic columns with perfusive adsorbent particles studied in this work, is mainly due to the intraparticle fluid flow which enhances intraparticle mass transport.

INTRODUCTION

Perfusion chromatography represents the separation process that involves the flow of a mobile phase (*i.e.* liquid phase) through porous chromatographic particles [1–5]. In perfusive adsorbent particles the intraparticle convective fluid velocity, v_p , is non-zero [3], while in purely diffusive adsorbent particles the value of v_p is considered to be equal to zero. Liapis and McCoy [3] constructed a theory of perfusion chromatography, and their mathematical models could describe the dynamic behavior of single and multicomponent adsorption in columns having perfusive ($v_p > 0$) adsorbent particles, as well

as in columns having purely diffusive ($v_p = 0$) adsorbent particles. The model expressions [3] for the adsorbent particles include the intraparticle mass transfer mechanisms of convection and diffusion, as well as the mass transfer step involving the interaction between the adsorbate molecules and the active sites on the surface of the porous adsorbent particles. The perfusion chromatography model was solved and used to study the dynamic behavior of single-component adsorption systems [3] for different column lengths, particle sizes, column fluid superficial velocities, intraparticle fluid velocities, as well as for different values of the effective pore diffusivity and of the total number of active sites per volume of adsorbent. The dynamics of the interaction mechanisms of the adsorption step of the single component adsorption systems studied by

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Liapis and McCoy [3] were (a) relatively not fast, (b) relatively fast and (c) infinitely fast. The values of certain variables which could be used to evaluate column performance, as well as the breakthrough curves obtained from columns having perfusive adsorbent particles, were compared [3] with those obtained from columns having purely diffusive adsorbent particles. The results from the single-component adsorption systems [3] suggest that for single-component adsorption systems having relatively fast or infinitely fast interaction kinetics (that is, the dynamics of the interaction step between the adsorbate molecules and the active sites are relatively fast or infinitely fast), the use of perfusive particles could have the potential to provide improved column performance. The results obtained from single component adsorption systems suggest [3,6] that the dynamic behavior of columns with perfusive adsorbent particles could be more effective than the dynamic behavior of columns with purely diffusive particles when both the intraparticle Peclet number [6–8] and the Porath parameter [6–8] are large. The intraparticle Peclet number [6] is a general measure of the importance of intraparticle convection—as a means of mass transfer—compared to pore diffusion. The Porath parameter may be considered [6–8] to provide a measure of the speed of the adsorbate-active site (adsorbate–ligand) association step relative to the pore diffusion of the adsorbate in the pores of the adsorbent particle. It should be emphasized that the intraparticle Peclet number alone is inadequate to fully describe intraparticle mass transfer when adsorption occurs [3,6]. In adsorption systems, a second quantity, the Porath parameter [6–8] comes also into play.

In this work, one of the theoretical mathematical models constructed by Liapis and McCoy [3] for multicomponent adsorption in columns is solved and used to study the dynamic behavior of binary (competitive adsorption involving two components) perfusion chromatography.

MATHEMATICAL MODEL

Adsorption is considered to take place from a flowing liquid stream in a fixed bed of perfusive

adsorbent particles under isothermal conditions. Two of the components in the feed solution to the bed are considered to be the adsorbates which compete for the available active sites for adsorption. One of the adsorbates is taken to be component 1 ($i = 1$ in ref. 3) and the second adsorbate is taken to be component 2 ($i = 2$ in ref. 3). The differential mass balance for each adsorbate i ($i = 1, 2$) in the flowing fluid stream is given by eqn. 1 in ref. 3 and equations 2, 4 and 5 in ref. 3 are considered to provide the initial and boundary conditions for these differential mass balance equations. Eqn. 8 in ref. 3 is taken to represent the differential mass balance for each adsorbate i ($i = 1, 2$) in a perfusive adsorbent particle, and its initial and boundary conditions are given by eqns. 12–14 in ref. 3. The term $\partial \bar{C}_{psi}/\partial t$ ($i = 1, 2$) of eqn. 1 in ref. [3] is obtained from eqn. 19 in ref. 3, while the intraparticle velocity, v_p , could be estimated from eqn. 20 in ref. 3.

Eqn. 8 in ref. 3 can be solved if mathematical expressions for the terms $\partial C_{s1}/\partial t$ and $\partial C_{s2}/\partial t$ are available. These terms represent the accumulation of components 1 and 2 in the adsorbed phase, which is on the internal surface of the perfusive adsorbent particle. For isothermal adsorption systems, the term $\partial C_{si}/\partial t$ ($i = 1, 2$) could be of the form given by eqn. 9 in ref. 3, which is as follows:

$$\frac{\partial C_{si}}{\partial t} = f_i(C_p, C_s, k), \quad i = 1, 2 \quad (1)$$

In eqn. 1, f_i represents the functional form of the dynamic adsorption mechanism for adsorbate i ; C_p represents the concentration vector of the adsorbates in the pore fluid, $C_p = (C_{p1}, C_{p2})$; C_s denotes the concentration vector of the adsorbates in the adsorbed phase, $C_s = (C_{s1}, C_{s2})$, and k represents the vector of the rate constants that characterize the interaction kinetics between the adsorbates and the active sites. For certain multicomponent adsorption systems, adsorption models of the form given in eqn. 1 have been constructed and presented in the literature [3,6–11]. In this work, the expressions for $\partial C_{s1}/\partial t$ and $\partial C_{s2}/\partial t$ are taken to be as follows:

$$\frac{\partial C_{s1}}{\partial t} = k_{11} C_{p1} \left(C_{T1} - \sum_{j=1}^2 C_{sj} \right) - k_{21} C_{s1} \quad (2)$$

$$\frac{\partial C_{s2}}{\partial t} = k_{12} C_{p2} \left(C_{T2} - \sum_{j=1}^2 C_{sj} \right) - k_{22} C_{s2} \quad (3)$$

Eqs. 2 and 3 represent one model of a dynamic adsorption mechanism of the form given in equation 1, for the competitive adsorption of components 1 and 2 [8-11]. The initial conditions of eqns. 2 and 3 are given by eqn. 15 in ref. 3. In this study, the mathematical model of binary perfusion chromatography is then represented by eqn. 1 (eqns. 2 and 3 provide one possible dynamic adsorption mechanism of the form given in eqn. 1) of this work and by equations 1, 2, 4, 5, 8 and 12-15 of ref. 3.

The dynamic behavior of a binary adsorption system involving perfusive adsorbent particles packed in a column, could be obtained by solving eqns. 2 and 3 of this work simultaneously with equations 1, 2, 4, 5, 8 and 12-15 of ref. 3. The solution of the equations of this mathematical model of binary perfusion chromatography, was obtained [6] by employing the method of orthogonal collocation [12,13] on the space variable of the perfusive particle and the method of orthogonal collocation on finite elements [6] on the space variable along the axis of the column. The resulting ordinary non-linear differential equations were integrated [6] by using Gear's method [13] which is employed in the LSODES component of the ODEPACK [14] software package. It should be mentioned at this point that if the intraparticle velocity, v_p , is set equal to zero in eqn. 8 of ref. 3, then the solution of the above mentioned equations would provide the dynamic behavior of a binary adsorption system in a column having purely diffusive adsorbent particles.

RESULTS AND DISCUSSION

The mathematical model of binary perfusion chromatography presented in this work, was used to study the dynamic behavior of a binary adsorption system whose parameter values are presented in Table I. The values of the parameters in Table I are in the range of the values of such parameters measured and/or estimated from experiments involving affinity adsorption of

TABLE I

PARAMETER VALUES OF THE BINARY PERFUSION CHROMATOGRAPHY SYSTEM

$C_{d1,in} = 0.1 \text{ kg/m}^3$; $C_{d2,in} = 0.1 \text{ kg/m}^3$; $C_{T1} = 2.2 \text{ kg/m}^3$;
$C_{T2} = 2.2 \text{ kg/m}^3$; $D_{p1} = 6.9 \cdot 10^{-12} \text{ m}^2/\text{s}$;
$D_{p2} = 17.885 \cdot 10^{-12} \text{ m}^2/\text{s}$;
$k_{11} = 2.35 \cdot 10^{-1} \text{ m}^3/(\text{kg}) (\text{s})$; $k_{21} = 5.17 \cdot 10^{-5} \text{ s}^{-1}$;
$K_{a1} = k_{11}/k_{21} = 4545.45 \text{ m}^3/\text{kg}$; $k_{12} = 4.108 \cdot 10^{-1} \text{ m}^3/(\text{kg}) (\text{s})$;
$k_{22} = 2.222 \cdot 10^{-2} \text{ s}^{-1}$; $K_{a2} = k_{12}/k_{22} = 18.488 \text{ m}^3/\text{kg}$;
$K_1 = K_{a1}/K_{a2} = 245.859$; $\varepsilon = 0.35$; $\varepsilon_p = 0.50$

biologically active macromolecules [7,8,15-20]. Two different values for the particle size, z_0 , have been considered: (i) $z_0 = 8.06 \cdot 10^{-6} \text{ m}$, and (ii) $z_0 = 16.12 \cdot 10^{-6} \text{ m}$. The values of other parameters of the binary perfusion model are reported in the captions of the figures. In the simulations of this study, the dynamic behavior of the binary perfusion chromatography system was examined for the following intraparticle velocities (for a given column fluid superficial velocity, V_f): $v_p = 0$, $v_p = 0.02V_f$, $v_p = 0.03V_f$ and $v_p = 0.05V_f$. The range of the values of V_f examined in this work is similar to the range of the experimental values of V_f considered by Afeyan *et al.* [1]. Furthermore, the resulting range of the non-zero values of the intraparticle velocity, v_p , examined in this study, is in the range suggested by the data of Afeyan *et al.* [1] and by calculations performed [6] with eqn. 20 in ref. 3. It is worth noting again that the adsorbent particles are considered to be purely diffusive when $v_p = 0$. For the binary system studied in this work, adsorbate 1 represents the most preferentially adsorbed component while adsorbate 2 is the least strongly adsorbed component. Furthermore, in the figures of this paper the results for component 1 are represented by solid curves while those of component 2 are denoted by dashed curves.

In Figs. 1-3, the breakthrough curves of components 1 and 2 are shown for different values of V_f , v_p and z_0 . The results in Fig. 1 indicate that there are no large differences between the breakthrough curves of purely diffusive ($v_p = 0$) and perfusive ($v_p > 0$) particles when $V_f = 0.138 \cdot 10^{-3} \text{ m/s}$, especially with par-

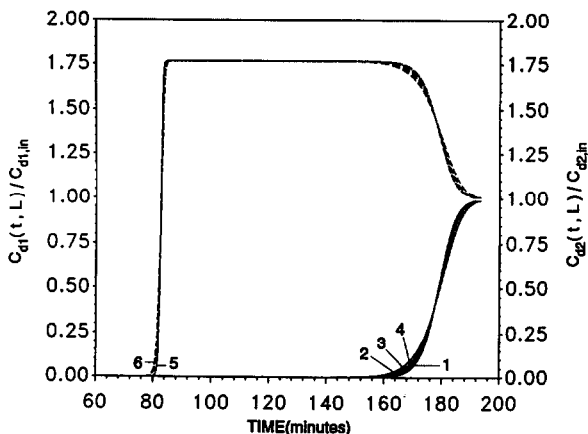


Fig. 1. Breakthrough curves for components 1 and 2 of the binary system (the solid curves are for component 1 and the dashed curves are for component 2). $V_f = 0.138 \cdot 10^{-3}$ m/s; $L = 0.1$ m; 1 = $z_0 = 8.06 \cdot 10^{-6}$ m, $v_p = (0.00, 0.02, 0.03, 0.05)V_f$; 2 = $z_0 = 16.12 \cdot 10^{-6}$ m, $v_p = 0$; 3 = $z_0 = 16.12 \cdot 10^{-6}$ m, $v_p = 0.02V_f$; 4 = $z_0 = 16.12 \cdot 10^{-6}$ m, $v_p = (0.03, 0.05)V_f$; 5 = $z_0 = 8.06 \cdot 10^{-6}$ m, $v_p = (0.00, 0.02, 0.03, 0.05)V_f$; 6 = $z_0 = 16.12 \cdot 10^{-6}$ m, $v_p = (0.00, 0.02, 0.03, 0.05)V_f$.

ticles of size $z_0 = 8.06 \cdot 10^{-6}$ m. It can be observed in Fig. 1 that when $z_0 = 16.12 \cdot 10^{-6}$ m, the breakthrough of component 1 for the systems having perfusive particles, begins to occur slightly later than that obtained from the system

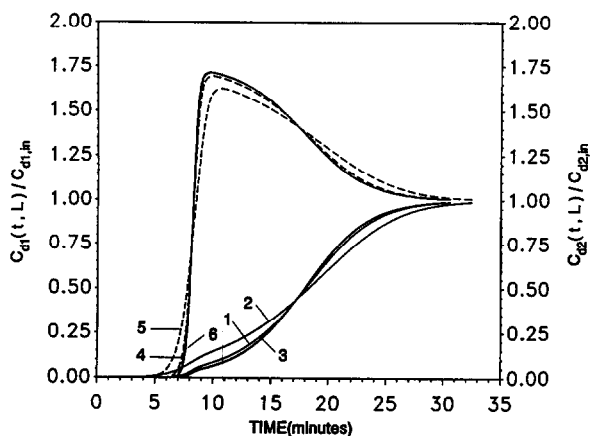


Fig. 2. Breakthrough curves for components 1 and 2 of the binary system (the solid curves are for component 1 and the dashed curves are for component 2). $V_f = 2.778 \cdot 10^{-3}$ m/s; $L = 0.2$ m; 1 = $z_0 = 8.06 \cdot 10^{-6}$ m, $v_p = 0$; 2 = $z_0 = 16.12 \cdot 10^{-6}$ m, $v_p = 0$; 3 = $z_0 = 8.06 \cdot 10^{-6}$ and $16.12 \cdot 10^{-6}$ m, $v_p = (0.02, 0.03, 0.05)V_f$; 4 = $z_0 = 8.06 \cdot 10^{-6}$ m, $v_p = 0$; 5 = $z_0 = 16.12 \cdot 10^{-6}$ m, $v_p = 0$; 6 = $z_0 = 8.06 \cdot 10^{-6}$ m and $16.12 \cdot 10^{-6}$ m, $v_p = (0.02, 0.03, 0.05)V_f$.

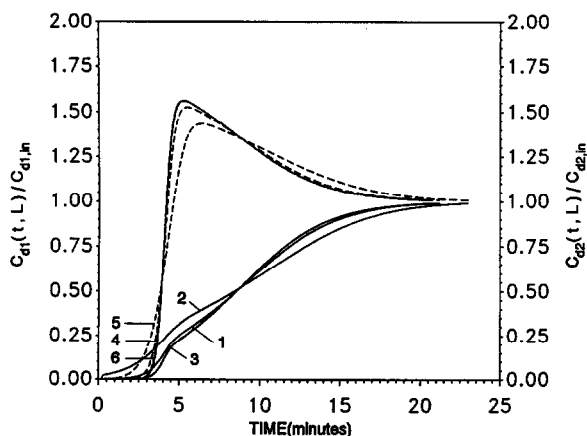


Fig. 3. Breakthrough curves for components 1 and 2 of the binary system (the solid curves are for component 1 and the dashed curves are for component 2). $V_f = 5.556 \cdot 10^{-3}$ m/s; $L = 0.2$ m; 1 = $z_0 = 8.06 \cdot 10^{-6}$ m, $v_p = 0$; 2 = $z_0 = 16.12 \cdot 10^{-6}$ m, $v_p = 0$; 3 = $z_0 = 8.06 \cdot 10^{-6}$ and $16.12 \cdot 10^{-6}$ m, $v_p = (0.02, 0.03, 0.05)V_f$; 4 = $z_0 = 8.06 \cdot 10^{-6}$ m, $v_p = 0$; 5 = $z_0 = 16.12 \cdot 10^{-6}$ m, $v_p = 0$; 6 = $z_0 = 8.06 \cdot 10^{-6}$ m and $16.12 \cdot 10^{-6}$ m, $v_p = (0.02, 0.03, 0.05)V_f$.

involving purely diffusive particles. Also, the results in Fig. 1 indicate that as the particle size is increased the time at which breakthrough begins is decreased, and this decrease is smaller for the systems using perfusive particles.

When the superficial velocity, V_f , in the column is increased to $2.778 \cdot 10^{-3}$ m/s and $5.556 \cdot 10^{-3}$ m/s, then the results in Figs. 2 and 3 indicate that when perfusive adsorbent particles are used, the times at which breakthrough begins for components 1 and 2 are larger than the corresponding times obtained when purely diffusive particles are employed. The results in Figs. 2 and 3 show that the differences in the initial breakthrough times obtained from perfusive and purely diffusive particles increase as the particle size increases, and the breakthrough curves obtained from the column having perfusive particles are steeper and their shape is not significantly affected when the particle size, z_0 , and the column fluid superficial velocity, V_f , are increased. On the contrary, in Figs. 2 and 3 it can be observed that the shape of the breakthrough curves obtained from the column having purely diffusive particles, is influenced significantly when the particle size and the column fluid superficial velocity are increased. Furthermore,

the steepness of the breakthrough curves obtained from columns having perfusive particles, as well as the times at which breakthrough begins for components 1 and 2, increase [6] with increasing intraparticle velocity, v_p , and the effect of the magnitude of the intraparticle velocity becomes more important as the particle size increases. It should be noted at this point that the differences in the breakthrough curves obtained from $v_p = 0.02V_f$, $v_p = 0.03V_f$, and $v_p = 0.05V_f$, for the system studied in this work, are not large; in fact, for the systems with $V_f = 2.778 \cdot 10^{-3}$ m/s and $V_f = 5.556 \cdot 10^{-3}$ m/s (Figs. 2 and 3), the differences in the breakthrough curves cannot be shown graphically because of the graphical scale that was used in the presentation of the results.

The results in Figs. 2 and 3 also show that the magnitude of the maximum outlet concentration of component 2 (component 2 is the least preferentially adsorbed component) obtained from the systems with perfusive particles, is higher than that obtained from the systems using purely diffusive particles. Also, it can be observed that the magnitude of the maximum outlet concentration of component 2 decreases as the superficial fluid velocity, V_f , increases. Furthermore, the differences in the magnitudes of the maximum outlet concentrations of component 2 obtained from the systems with perfusive and purely diffusive particles, increase as the superficial fluid velocity, V_f , increases. It is also observed that the magnitude of the maximum outlet concentration of component 2 obtained from systems with purely diffusive particles, decreases as the particle size, z_0 , increases (see Figs. 2 and 3). The results obtained from the systems with perfusive particles indicate that the effect of particle size on the magnitude of the maximum outlet concentration of component 2 is not significant; of course, it is worth mentioning that the magnitude of the maximum outlet concentration of component 2 is slightly higher when the smaller size of perfusive particles is used, but the difference is so small that it is considered to be insignificant. Component 2 attains its maximum outlet concentration faster in the systems with the perfusive adsorbent particles, and furthermore, the time period required for the

outlet concentration of component 2 to return to its feed concentration is shorter than that required in the systems with purely diffusive particles (see Figs. 2 and 3).

The results in Figs. 1-3 discussed above and additional results reported in ref. 6, suggest that the dynamic (unsteady state) relative separation between components 1 and 2 obtained from the systems with perfusive particles, is higher than that obtained from the systems with purely diffusive particles. This occurs because the intraparticle fluid flow enhances intraparticle mass transfer and causes the overall intraparticle mass transfer resistance of the perfusive particles, for a given particle size, to become smaller [3,6] than the overall intraparticle mass transfer resistance of the purely diffusive particles, when practical values for the column fluid superficial velocity, V_f , are employed. Furthermore, the results reported in ref. 6 indicate that complete separation of the two adsorption fronts (one adsorption front is for component 1 and the second adsorption front is for component 2) always occurred in the columns with the perfusive adsorbent particles; also, McCoy [6] found that the location in the column with purely diffusive particles at which complete separation of the two adsorption fronts occurs, is longer than the corresponding location in the column with perfusive particles. The findings reported in ref. 6 and the results in Figs. 1-3, suggest that in systems having perfusive particles the most preferentially adsorbed component 1 could utilize the capacity of the active sites on the adsorbent particles more effectively than in systems with purely diffusive particles. This could lead to a higher dynamic relative separation between components 1 and 2 in columns having perfusive particles than the dynamic relative separation that could be obtained in columns with purely diffusive particles.

In Fig. 4, the dimensionless concentration profiles of components 1 and 2 in the pore fluid of a single particle are shown, while in Fig. 5 the dimensionless concentration profiles of components 1 and 2 in the adsorbed phase of the same particle are presented. The results in Figs. 4 and 5 have been obtained when $V_f = 2.778 \cdot 10^{-3}$ m/s, $L = 0.5$ m, $z_0 = 16.12 \cdot 10^{-6}$ m, and represent the

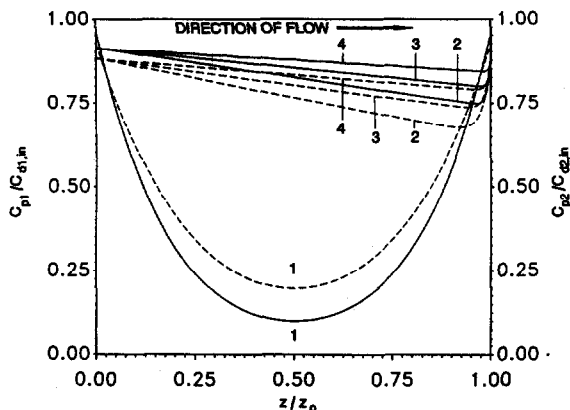


Fig. 4. Dimensionless concentration profiles of components 1 and 2 of the binary system in the pore fluid of the porous adsorbent particle at time $t = 0.15$ min and at location $x = 1.2723 \cdot 10^{-3}$ m in the column (the solid curves are for component 1 and the dashed curves are for component 2). $V_t = 2.778 \cdot 10^{-3}$ m/s; $L = 0.5$ m; $z_0 = 16.12 \cdot 10^{-6}$ m; $1 = v_p = 0$; $2 = v_p = 0.02V_t$; $3 = v_p = 0.03V_t$; $4 = v_p = 0.05V_t$.

dynamic behavior of the concentration profiles at time $t = 0.15$ min at the column location of $x = 1.2723 \cdot 10^{-3}$ m. It can be clearly observed that for the purely diffusive ($v_p = 0$) particle the concentrations of components 1 and 2 in the pore fluid and in the adsorbed phase are substantially lower than the corresponding concentrations in the perfusive ($v_p > 0$) particle for a significant portion of the particle. This difference

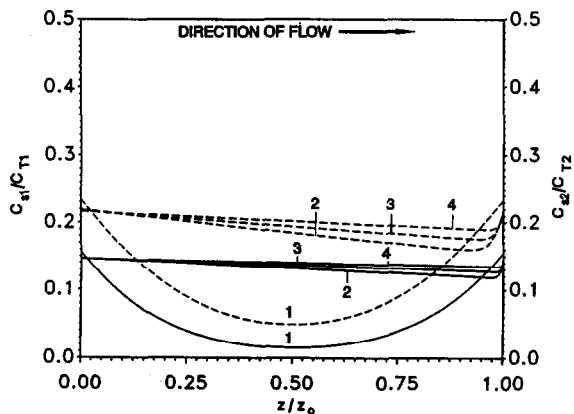


Fig. 5. Dimensionless concentration profiles of components 1 and 2 of the binary system in the adsorbed phase of the porous adsorbent particle at time $t = 0.15$ min and at location $x = 1.2723 \cdot 10^{-3}$ m in the column (the solid curves are for component 1 and the dashed curves are for component 2). $V_t = 2.778 \cdot 10^{-3}$ m/s; $L = 0.5$ m; $z_0 = 16.12 \cdot 10^{-6}$ m; $1 = v_p = 0$; $2 = v_p = 0.02V_t$; $3 = v_p = 0.03V_t$; $4 = v_p = 0.05V_t$.

is due to the fact that the intraparticle fluid flow in the perfusive particle provides within the particle additional amounts of components 1 and 2, and thus, the total contents of components 1 and 2 provided by intraparticle fluid flow and pore diffusion in a perfusive particle could be higher than those provided only by pore diffusion in a purely diffusive particle. Furthermore, the concentration profiles of the purely diffusive particle are symmetric, as expected, and the point of symmetry is located at the center of the particle where $z/z_0 = 0.5$. For the perfusive particle, the results in Figs. 4 and 5 show that as the intraparticle velocity, v_p , increases, the concentration minima for components 1 and 2 in the pore fluid and in the adsorbed phase move downstream while the overall contents of components 1 and 2 increase within the particle.

In Fig. 5, the values of C_{s2}/C_{T2} for a given v_p are higher than the values of C_{s1}/C_{T1} . The reason for this is that for short operational times the magnitudes of the forward rate constants k_{11} and k_{12} (see Table I) play a very significant role in determining the relative amounts of components 1 and 2 in the adsorbed phase. For the system in Figs. 4 and 5 the forward rate constant of component 2 is higher than the forward rate constant of component 1 ($k_{12} > k_{11}$), but the reverse rate constant of component 1, k_{21} , is significantly smaller than the reverse rate constant of component 2, k_{22} ($k_{22} > k_{21}$). Therefore, since $K_{a1} > K_{a2}$ (see Table I), component 1 is the most preferentially adsorbed component and displaces previously adsorbed component 2 as the operational time increases and the adsorption front of component 1 proceeds downstream (as shown in Figs. 1-3 that they were discussed above). Thus, at larger operational times the values of C_{s1}/C_{T1} for a given v_p become higher than the values of C_{s2}/C_{T2} in the adsorbent particle.

CONCLUSIONS AND REMARKS

A mathematical model of binary perfusion chromatography was presented, solved, and used to study the dynamic behavior of a binary adsorption system. The equations of the model for the adsorbent particles include the intrapar-

ticle mass transfer mechanisms of convection (intraparticle fluid flow) and pore diffusion, as well as the mass transfer steps involving the dynamic interactions of components 1 and 2 (the dynamics of the adsorption steps are finite) with the active sites on the surface of the porous adsorbent particles. The values of the parameters that characterize the mass transfer and interaction mechanisms of the binary system studied in the simulations of this work, are in the range of the values of such parameters measured and/or estimated from experiments involving affinity adsorption of biologically active macromolecules [7,8,15-20]. The dynamic behavior of column systems (frontal analysis) was examined for different particle sizes (z_0), column fluid superficial velocities (V_f) and intraparticle fluid velocities (v_p). The studies in this work examined column systems having perfusive ($v_p > 0$) and purely diffusive ($v_p = 0$) adsorbent particles.

It was found that for the binary system studied in this work, the breakthrough curves obtained from the column having perfusive particles are not significantly different from the breakthrough curves obtained from the column with purely diffusive particles when the column fluid superficial velocity is low (Fig. 1). When the column fluid superficial velocity is high (Figs. 2 and 3), then the breakthrough curves obtained from the column involving perfusive particles are different from those obtained from the column with purely diffusive particles, and their differences become larger as the particle size and the column fluid superficial velocity increase. The steepness of the breakthrough curves of components 1 and 2 obtained from the column with perfusive particles, as well as the times at which breakthrough begins for components 1 and 2, were found to increase with increasing intraparticle fluid velocity, v_p ; in general, the breakthrough curves from the column with perfusive particles were less disperse than those obtained from the column with purely diffusive particles. As the particle size was increased, the increase in the value of the intraparticle fluid velocity had a more significant effect on the shape of the breakthrough curves and on the time at which breakthrough begins. It was also found that the magnitude of the maximum outlet concentration

of the least preferentially adsorbed component 2 obtained from the systems with perfusive particles, is higher than that obtained from the corresponding systems having purely diffusive particles, and the difference increases as the column fluid superficial velocity increases. Component 2 attains its maximum outlet concentration faster in the systems having perfusive particles, and furthermore, it appears that the time period required for the outlet concentration of component 2 to return to its feed concentration in the systems with perfusive particles, is shorter than that required in the systems having purely diffusive particles.

The results obtained from the binary adsorption system studied in this work suggest that the times at which breakthrough begins for components 1 and 2, and the dynamic (unsteady state) relative separation between components 1 and 2 obtained from the column with perfusive particles, are higher than those obtained from the column having purely diffusive particles, especially as the particle size and the column fluid superficial velocity increase. These results occur because the overall intraparticle mass transfer resistance of the perfusive particles, for a given particle size, is smaller [3,6] than the overall intraparticle mass transfer resistance of the purely diffusive particles, when practical values for the column fluid superficial velocity, V_f , are employed. In systems having perfusive particles, the most preferentially adsorbed component 1 could utilize the capacity of the active sites on the adsorbent particles more effectively than in systems with purely diffusive particles, and this could lead to a higher dynamic relative separation between components 1 and 2. The results of this study also suggest that when the column fluid superficial velocity is increased, the effect on the dynamic relative separation between components 1 and 2, is substantially smaller in columns with perfusive particles than in columns having purely diffusive particles. These findings suggest that for a given overall operational time, a larger number of binary adsorption cycles having high dynamic relative separations between components 1 and 2, could be realized, when columns with perfusive particles and high values of V_f are employed.

In conclusion, the improved separation efficiency obtained from the chromatographic columns with perfusive adsorbent particles studied in this work, is mainly due to the intraparticle fluid flow which enhances intraparticle mass transport. The intraparticle fluid flow causes the overall intraparticle mass transfer resistance of the perfusive particles to become smaller than the overall intraparticle mass transfer resistance of the purely diffusive particles.

SYMBOLS

C_{di}	concentration of component i ($i = 1, 2$) in the flowing fluid stream of the column, kg/m^3
$C_{di,in}$	concentration of component i ($i = 1, 2$) at $x = 0$, kg/m^3
C_p	vector of concentration variables defined after eqn. 1
C_{pi}	concentration of component i ($i = 1, 2$) in pore fluid, kg/m^3
C_s	vector of concentration variables defined after eqn. 1
C_{si}	concentration of component i ($i = 1, 2$) in adsorbed phase, kg/m^3 particle
C_{T1}	saturation value (limiting value) of C_{s1} , kg/m^3 particle
C_{T2}	saturation value (limiting value) of C_{s2} , kg/m^3 particle
D_{pi}	effective pore diffusion coefficient of component i ($i = 1, 2$), m^2/s
$f(C_p, C_s, k)$	functional form defined after eqn. 1
K_{a1}	$K_{a1} = k_{11}/k_{21}$ (see Table I), m^3/kg
K_{a2}	$K_{a2} = k_{12}/k_{22}$ (see Table I), m^3/kg
K_I	parameter defined in Table I
k	vector of adsorption rate constants defined after eqn. 1
k_{11}	adsorption rate constant for component 1 in eqn. 2, $\text{m}^3/(\text{kg})(\text{s})$
k_{12}	adsorption rate constant for component 2 in eqn. 3, $\text{m}^3/(\text{kg})(\text{s})$
k_{21}	adsorption rate constant for component 1 in eqn. 2, s^{-1}
k_{22}	adsorption rate constant for component 2 in eqn. 3, s^{-1}
L	column length, m
t	time, s

V_t	column fluid superficial velocity, m/s
v_p	intraparticle fluid velocity (intraparticle convective velocity), m/s
x	axial distance along column, m
z	space coordinate of adsorbent, m
z_0	size of adsorbent particle, m

Greek letters

ε	void fraction in column
ε_p	void fraction in porous adsorbent particle

ACKNOWLEDGEMENTS

The authors gratefully acknowledge that this work was supported by the Monsanto Company and the NATO Scientific Affairs Division under Grant No. 880770.

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