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Continuous Separations of Amino Acids by Using an Annular Chromatograph with Rotating Inlet and Outlet

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Abstract

A continuous rotating annular chromatograph was developed for preparative multicomponents separations. An annular bed was fixed while a nozzle of feed and collectors of products were rotated at the same speed. To evaluate the performance of this device, three kinds of amino acids were separated by an ion-exchange resin. Rotation speeds, feed rates, and feed concentrations were varied. Experimental concentration profiles were compared with results calculated by using a model with interactions of amino acids. This system was found to be promising for continuous preparative chromatographic separations.

INTRODUCTION

A continuous chromatographic system has been proposed for preparative separations. Continuous introduction of feed and continuous withdrawal of products can be realized by using moving chromatographic beds and simulated moving beds. The systems may be classified as counterflow (*1*). However, most counterflow systems are restricted to two-components separation.

In crossflow systems the chromatographic bed moves perpendicularly in the direction of fluid motion within the bed. Crossflow systems have no restriction on the number of components that can be separated. The annular chromatograph is one of the two-dimensional separation processes (*2*). An annular chromatograph rotating with respect to a feed stream and product collection points was first proposed by Martin (*3*). Fox et al. (*4*) applied the system to the separation of biological mixtures. Begovich et al. (*5*) used a rotating annular bed with a stationary feed stream and product collection ports. Their device was operated with an overpressure of gas and gradient elution as well as isocratic elution. A series of experiments has been performed for the separation of metal ions.

The continuous rotating annular chromatograph (CRAC) developed in this work consists of a stationary annular bed, rotating feed nozzle, and product collectors. It operates in a fashion opposite to the device of Begovich et al. (*5*). A device of this type has the following advantages. Since a heavy bed does not have to be rotated, rotating power can be saved, and scaling up of the device is easy. The bed can be easily kept at constant temperature with a thermostat jacket, which is especially important for biological separations.

The principle of the CRAC is shown schematically in Fig. 1. Feed is introduced at one rotating point and eluent fluid is supplied everywhere else. The products are collected by collectors which rotate at the same angular rate as the feed point. As elution proceeds, solutes progress down the annulus, giving the appearance of helices as the feed point rotates. The more strongly retained solutes exit from the annulus bottom at a greater distance from the feed point. Thus, steady-state multicomponents separation is accomplished with simultaneous movement in the two spatial directions.

This system has earlier proposed by Dunnill and Lilly (*6*) and Andrew (*7*). However, flow rates were very low because there was no way to pressurize their apparatus. In a previous paper (*8*) we constructed a new

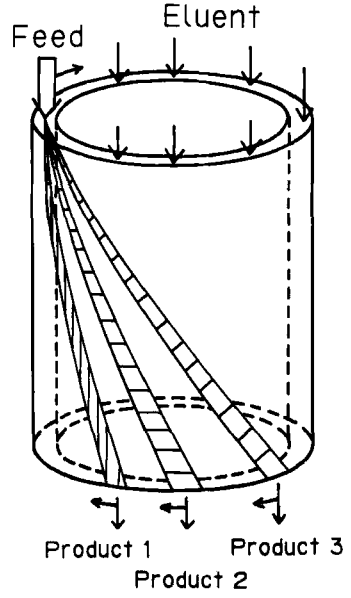

FIG. 1. Principle of continuous rotating annular chromatography.

CRAC in which flow rates could increase. Two components of sodium chloride and methanol could be separated by ion exclusion (*9*).

In this paper, multicomponents are separated to confirm the merits of this CRAC compared with counterflow systems such as moving chromatographic beds. Three amino acids (aspartic acid, glutamic acid, and glycine) were chosen as the multicomponents. Adsorption isotherms and kinetic parameters were determined in a companion paper (*10*).

THEORY

Analytical Solutions without Solute–Solute Interactions

The mathematical description for the CRAC is similar to that for conventional column chromatography. The mass balance of solute i on a differential element in the CRAC yields the following equation when radial gradients in velocity and concentration are assumed to be negligible. It is also assumed that each solute is not interrupted by the other solutes.

$$\omega \frac{\partial C_i}{\partial \Theta} + \frac{u \partial C_i}{\epsilon_B \partial z} + \frac{3\overline{D}_i(1 - \epsilon_B)}{R_P \epsilon_B} \frac{\partial \overline{C}_i}{\partial r}\bigg|_{r=R_P} = D_L \frac{\partial^2 C_i}{\partial z^2} + D_\theta \frac{1}{R_a^2} \frac{\partial^2 C_i}{\partial \Theta^2} \quad (1)$$

Mass balance in the particle gives

$$\overline{D}_i \left(\frac{\partial^2 \overline{C}_i}{\partial r^2} + \frac{2}{r} \frac{\partial \overline{C}_i}{\partial r} \right) = \omega \frac{\partial \overline{C}_i}{\partial \theta} \quad (2)$$

The boundary conditions are

$$\overline{D}_i \frac{\partial \overline{C}_i}{\partial r}\bigg|_{r=R_P} = k_f(C_i - C_i^*) \qquad \text{at } r = R_P \quad (3)$$

$$\partial \overline{C}_i / \partial r = 0 \qquad \text{at } r = 0, \theta > 0 \quad (4)$$

$$C_i = \overline{C}_i = 0 \qquad \text{at } z \geq 0, \theta = 0 \quad (5)$$

$$C_i = C_{i0} \qquad \text{at } z = 0, 0 < \theta < \theta_F \quad (6)$$

$$C_i = 0 \qquad \text{at } z = 0, \theta_F < \theta < 2\pi \quad (7)$$

where θ_F is given by $2\pi Q_F/(Q_E + Q_F)$.

If the angular dispersion in the second term of the right-hand side in Eq. (1) can be neglected, these equations are transformed into equations for a conventional one-dimensional column system by the replacement of θ/ω by t. In the case of a linear equilibrium isotherm, the analytical solution derived by Rasmuson et al. (*11*) can be used, as shown by the following equation:

$$\overline{C}_i = K_i C_i^* \tag{8}$$

Numerical Solutions with Solute–Solute Interactions

Wilson (*12*) proposed a new model with significant interactions of solutes in which association complexes might be formed.

It is assumed that the concentration of a complex of solute i and solute j in the particle, $\overline{C}_{ij}$, can be related to the concentrations of solutes i and j, $\overline{C}_i$, and $\overline{C}_j$.

$$\overline{C}_{ij} = K_{ij}\overline{C}_i\overline{C}_j \qquad (i \neq j) \tag{9}$$

and $\overline{C}_{ii}$ is equal to $\overline{C}_i$.

The term of $\omega(\partial\overline{C}_{ij}/\partial\theta)$ should be added to the right-hand side of Eq. (2).

These equations were solved numerically by the orthogonal collocation method (*13*).

EXPERIMENTALS

Apparatus

The continuous chromatographic apparatus is shown in Fig. 2. The annulus was formed from three acrylic cylinders (150 mm o.d. × 142 mm i.d., 170 mm o.d. × 160 mm i.d., and 200 mm o.d. × 188 mm i.d.). The outer two cylinders were attached to flanges. The inner cylinder and the outer ones were clamped concentrically to a polyvinyl chloride baseplate. The annulus was 5.0 mm wide and 490 mm long, with an outside diameter of 160 mm. There were 90 exit holes, drilled equidistant on a circumference in the center of the columnar space between two cylinders. The exit holes were plugged with porous plastics to prevent the ion-exchange resins from falling through the holes.

Capillary tubes of stainless steel were inserted into the bottoms of the exit holes to collect the effluent liquid. The rotating feed nozzle was a 1.5 mm o.d. stainless steel pipe. It was placed in the center of the annulus, typically about 30 mm beneath the surface of the bed to prevent the overflow of feed.

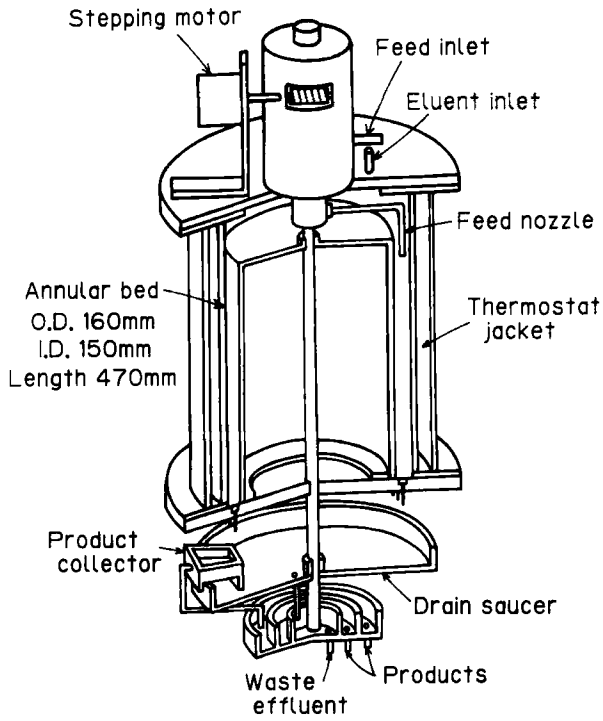

FIG. 2. Continuous rotating annular chromatograph apparatus.

The effluent from the bottom of the column dripped into a rotating drain saucer under the column. Two systems used for product collection were in the continuous and batchwise modes.

(1) The continuous mode can be used for commercial purposes. The product collectors are placed on the drain saucer as shown in Fig. 2. The collected products and waste effluent flow into a stationary saucer which is concentrically divided into three parts. The products flow to product reservoirs, and the waste effluents flow to a drain or recirculating eluent reservoir.

(2) The batchwise mode is for product sampling. In order to obtain the concentration profile at the bottom of the bed, this device consists of 60 evenly spaced sampling tubes of 1.5×10^{-6} m^3 used in place of the product reservoirs in Fig. 2. After steady-state was reached the concentrations of the solutions in the sampling tubes were measured.

Operation

The cation-exchange resin Dowex 50W-X8, in the sodium form, was packed to a depth of 470 mm. The resin was sieved in the eluate and a portion of average diameter, 0.14 mm, was adopted. The void fraction in the bed, ϵ_B, was 0.394. The 0.1 M sodium citrate buffer solution was used for the eluate. The pH value of the buffer solution was 3.4. Feed solutions consisted of aspartic acid, glutamic acid, and glycine. The feed concentration, C_{i0}, was adjusted to be identical for each amino acid. The exit concentrations of the amino acids were measured with a UV-meter by using the ninhydrine method.

Experimental conditions are described in Table 1. Run No. 1 was the standard condition in this work. The eluent rate in Run No. 2 was increased by 7.5 times while the ratios of rotation speed to eluent rate, ω/Q_E, and of feed rate to eluent rate, Q_F/Q_E, were kept constant. The feed rate in Run No. 3 and the feed concentration in Run No. 4 were decreased by 0.27 and 0.5 times, respectively, from the standard condition in Run No. 1 while the other parameters were kept constant.

RESULTS

Chromatogram in Conventional Column

First, a conventional column was used for comparison with CRAC. The inside diameter of the column was 6.0×10^{-3} m and the bed length was 0.43 m, as used in our companion paper (*10*).

Figure 3 shows one example of chromatograms for the three amino acid components. For preparative separations, the volume of the pulse injection, V_F, was 17 times larger than that of Fig. 6 in the companion paper (*10*). Dotted lines indicate analytical solutions of Rasmuson (*11*). The values of the kinetic parameters determined by the moment method in

TABLE 1
Experimental Condition for Separations of Amino Acids in CRAC

Run No.	Eluent rate, $Q_E \times 10^7$ (m^3/s)	Feed rate, $Q_F \times 10^8$ (m^3/s)	Feed concentration, C_{i0} (mol/m^3)	Rotation speed, ω (deg/s)
1	1.0	1.0	20	0.024
2	7.5	7.5	20	0.18
3	1.0	0.27	20	0.024
4	1.0	1.0	10	0.024

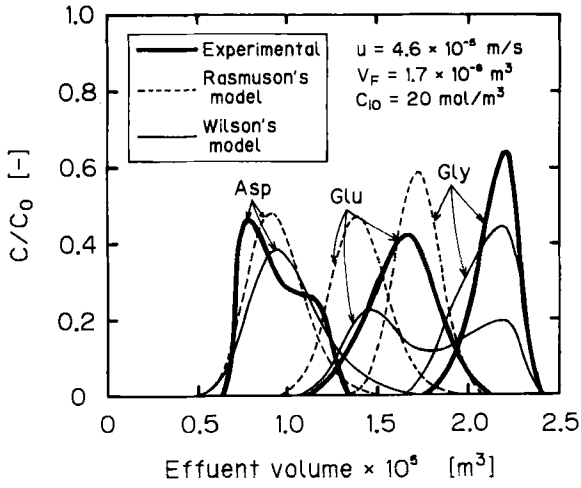

FIG. 3. Chromatogram in the conventional column.

Table 1 of the companion paper (*10*) were used for the simulations in this work. Experimental data did not agree well with calculated curves, contrary to the good agreement shown in Fig. 6 of the companion paper. This might be due to the higher concentrations of the amino acids and interactions among the amino acids. The solid lines indicate numerical solutions with the interactions described later.

Chromatogram in CRAC

Figure 4 shows the superposition of three chromatograms of a single amino acid component for the standard conditions in Run No. 1 of Table 1. There are no interactions between amino acids in nature; the shapes are almost symmetric. Each experimental concentration profile could be well simulated by the analytical solution of Rasmuson (*11*), as shown by the dashed lines. Figures 5–8 show the chromatograms for mixtures of three amino acids components corresponding to the run numbers in Table 1, respectively. In these figures the shapes for all the amino acids are unsymmetric, and elutions of glutamic acid and glycine are retarded. The glycine peak appears after one rotation from the nozzle position, and the angular displacement in the abscissa should be added to 360°.

It is seen from a comparison of Figs. 4 and 5 at the same experimental condition that there are large interactions among the amino acids. Good resolutions were obtained in Fig. 5 because of the retardations of glutamic acid and glycine. As is evident in Figs. 5 and 6, the peak concentration decreased with an increase in the eluent rate. Also, the peak concentration

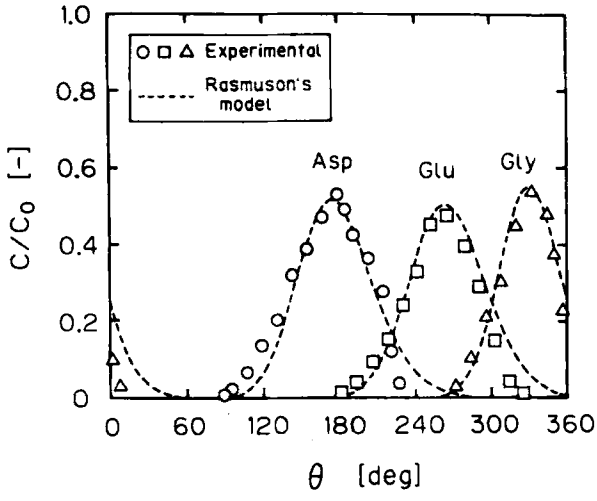

FIG. 4. Elution of a single component in CRAC for Run No. 1.

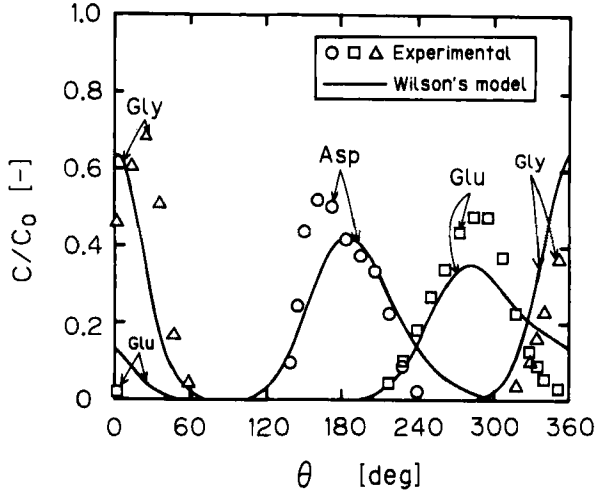

FIG. 5. Concentration profiles in CRAC for Run No. 1.

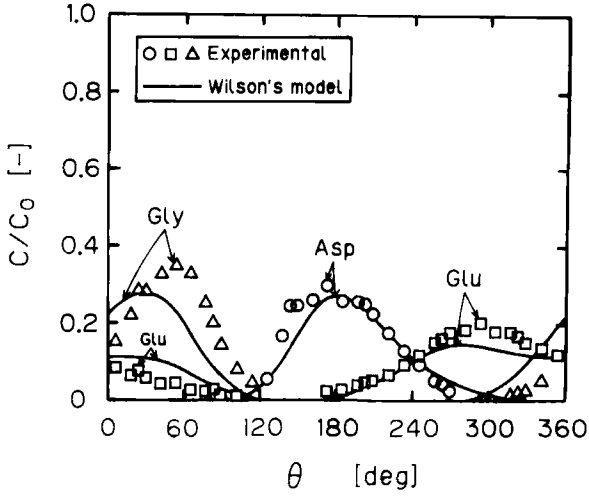

FIG. 6. Concentration profiles in CRAC for Run No. 2.

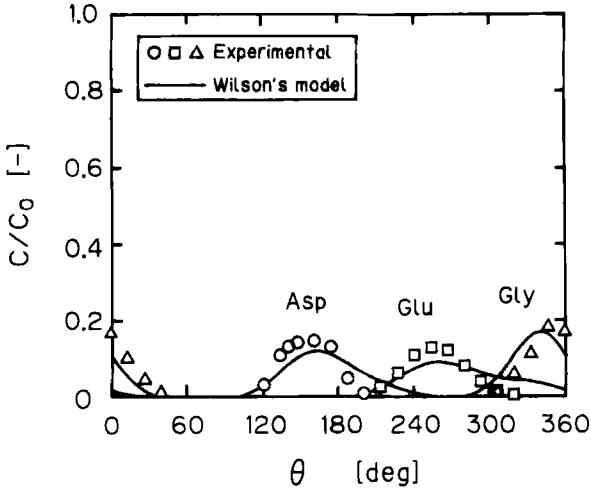

FIG. 7. Concentration profiles in CRAC for Run No. 3.

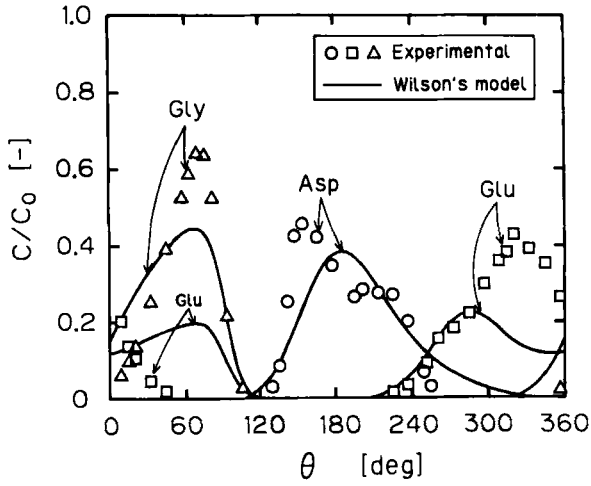

FIG. 8. Concentration profiles in CRAC for Run No. 4.

decreased with a decrease in the feed rate in Figs. 5 and 7. It is seen from Figs. 5 and 8 that the effect of feed concentration may not be significant.

DISCUSSION

Comparison between the Elution of CRAC and Column

Figure 9 shows a comparison between the elutions of CRAC and of a conventional column. The abscissa is the dimensionless elution position $\theta u/\omega L\epsilon_B$ or $tu/L\epsilon_B$. The profiles for the CRAC agree with those in a conventional column. Both of them may contain interactions among the three amino acids components. This agreement means that angular dispersion in a CRAC may be negligible, as pointed out by Begovich et al. (*5*). Therefore, the performance of a CRAC can be predicted by preliminary experiments in a conventional column.

Effect of Interactions

Figure 10 shows the effect of the interaction parameter, K_{ij}, defined by Eq. (9), on numerical elution curves, together with experimental data for Run No. 1 of Table 1. For simplicity, the values of K_{ij} are assumed to be independent of the species of amino acids (i and j). For the case of $K_{ij} = 0$, there are no interactions, and the profiles calculated by the orthogonal collocation method (*13*) are the same as the anlytical solutions of Rasmuson (*11*). As the interaction parameter increased, the time to amino acids

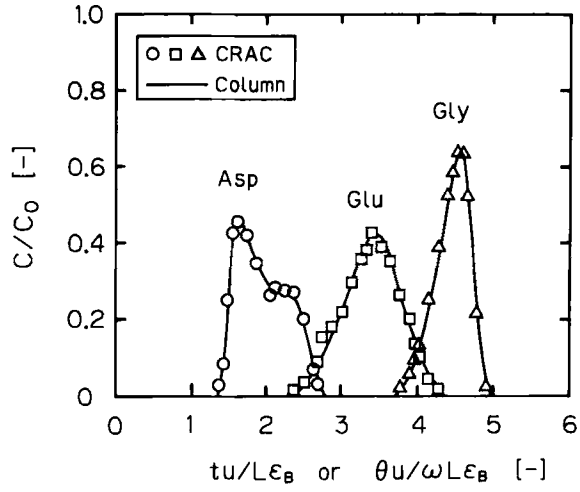

FIG. 9. Comparison of chromatograms between CRAC and the conventional column for Run No. 1.

eluation increased. Two peaks of glutamic acid appeared for $K_{ij} \geq 0.8 \times 10^{-3}$ m^3/mol.

Solutions of $K_{ij} = 1.6 \times 10^{-3}$ m^3/mol gave comparatively good agreement with experimental data, but the peak of glycine could be improved by changing K_{ij} (i = glutamic acid and j = glycine) to 2.0×10^{-3} m^3/mol.

The solid lines in Figs. 3–8 and 10 show numerical solutions for the

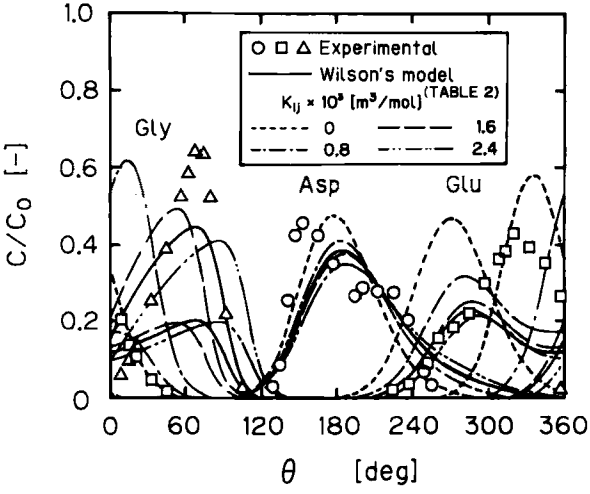

FIG. 10. Effect of the interactions on concentration profiles in CRAC for Run No. 1.

TABLE 2
Parameters for Interactions

Species	K_{ij} (m^3/mol)
Aspartic acid and glutamic acid	1.6×10^{-3}
Aspartic acid and glycine	1.6×10^{-3}
Glutamic acid and glycine	2.0×10^{-3}

values of K_{ij} indicated in Table 2. Although the agreements are not satisfactory, their tendencies can be explained by Wilson's model (*12*).

On the other hand, in our companion paper (*10*) the adsorption isotherms in binary mixtures are the same as those in a single solute and there were no interactions among amino acids at equilibrium. This means that the interactions may take place only in an unsteady state. The mechanism of interactions among amino acids is still to be determined.

CONCLUSION

Three amino acids (aspartic acid, glutamic acid, and glycine) could be continuously separated in a continuous rotating annular chromatograph (CRAC). The chromatograms of the CRAC are in excellent agreements with those from conventional column by the replacement of angular displacement with time.

In the mixture solution, there were interactions among the amino acids. The elution position could be roughly predicted by using Wilson's method (*12*). The CRAC was shown to be effective for preparative continuous separations.

SYMBOLS

C_i concentration of amino acid in the liquid phase (mol/m^3)
$\overline{C}_i$ concentration of amino acid in the resin phase based on the volume of swollen resin (mol/m^3)
$\overline{C}_{ij}$ complex concentration of i and j in the resin phase (mol/m^3)
C_{i0} feed concentration (mol/m^3)
C_i^* equilibrium concentration (mol/m^3)
$\overline{D}_i$ intraparticle diffusivity (m^2/s)
D_L axial dispersion coefficient (m^2/s)
D_θ circumferential dispersion coefficient (m^2/s)
K_i adsorption equilibrium constant (—)
K_{ij} complex equilibrium constant (m^3/mol)
k_f liquid film mass transfer coefficient (m/s)
Q_E eluent rate (m^3/s)

Q_F feed rate (m^3/s)
R_a radius of the annular bed (m)
R_P radius of adsorbent particle (m)
r radial coordinate (m)
t time (s)
u superficial velocity (m/s)
V_F volume of pulse injection (m^3)
z axial coordinate (m)

Subscripts

i component i
ij complex of i and j
j component j

Greek

ϵ_B interparticle void fraction in the bed (—)
θ angular coordinate (rad or deg)
θ_F angular distance of feed injection (rad or deg)
ω rotation speed (rad/s or deg/s)

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