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Increasing Feed Throughput in Preparative Two-Dimensional Separations

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Abstract

Feed throughput in preparative, steady-state two-dimensional chromatographic separations can be improved by injecting feed along a line that is slanted into the two-dimensional apparatus while solvent is continuously fed to the bottom of the apparatus. The local equilibrium model of adsorption is applied to the rotating annulus geometry to show that throughput can be increased without decreasing resolution. The model is then related to the solute trajectories, and the results for two-dimensional paper and gel permeation chromatography are derived. Two-dimensional countercurrent distribution is also considered and an exact solution is developed. The slanted feed line technique decreases thermodynamically irreversible mixing and thus is more efficient.

INTRODUCTION

Two-dimensional systems have been used for a variety of chromatographic separations such as paper chromatography, gas–liquid chromatography, electrophoresis, gel permeation, and countercurrent distribution. The two-dimensional technique can provide steady-state multicomponent separations and it has considerable promise for preparative applications. Since the two-dimensional systems have been extensively reviewed by Sussman and Rathore (*1*) and Sussman (*2*), a literature review will not be given here.

The two-dimensional techniques do have the disadvantage that even for continuous operation, relatively small amounts of material are separated per kilogram of adsorbent and the adsorbent utilization is poor. Throughput can be increased by feeding material to be separated along a line instead of at a point. This usual preparative method is still inefficient since there is mixing of solute near the feed location and extensive mixing of solute and solvent. Since mixing is thermodynamically irreversible, it is desirable to reduce or eliminate it to have an efficient process.

In this paper a new feed technique for continuous two-dimensional chromatographic separations is proposed. This new technique allows one to increase the throughput of feed with the same or improved resolution.

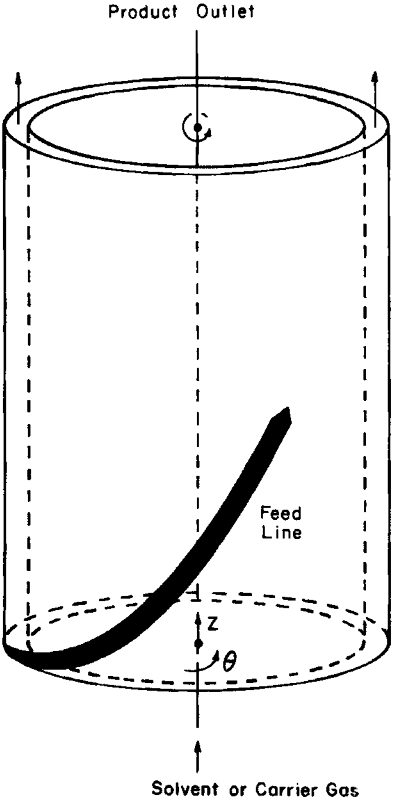

FIG. 1. Rotating annulus device for two-dimensional chromatography with slanted feed line.

The technique is based on the concept of preventing mixing of solutes which have been separated. To do this, the feed is not introduced on a line along one edge of the apparatus, but instead is introduced on a line that is slanted into the two-dimensional bed. This is shown in Fig. 1 for the rotating annulus device which has been used in gas, paper, and gel permeation chromatography (*1*, *2*). The slope of the feed line is chosen so that it lies between the slopes of the solutes being separated. Thus, for a separation of two solutes, the faster moving Solute A will be above and to the left of the feed line and the slower moving Solute B will be below and to the right. This arrangement reduces mixing of the solutes after they have been separated and, as will be shown below, increases the feed throughput.

This technique is applicable to many chromatographic techniques in a variety of two-dimensional geometries. The method will be analyzed for gas and liquid chromatography in the common rotating annulus device by the local equilibrium model. Then the application of the technique to two-dimensional paper chromatography and gel permeation chromatography will be considered by following the trajectories of the average solute molecule. Finally, zone broadening will be considered using a countercurrent distribution (CCD) model applicable to a two-dimensional CCD apparatus.

LOCAL EQUILIBRIUM MODEL

The local equilibrium model of adsorption or chromatography [see Sherwood et al. (*3*) or Vermeulen et al. (*4*)] has been applied to rotating annulus systems with continuous regeneration by Wankat et al. (*5*). This model will be applied to a gas or liquid two-dimensional chromatography in a rotating annulus system as shown in Fig. 1. Then the results, which do not include zone broadening effects, will be related to the simple picture of the separation developed by considering the velocity of the average solute molecule. For a steady-state isothermal system the following assumptions are made: (1) equal and constant fluid and solid angular velocities in the θ direction, (2) plug flow of fluid in the axial direction, (3) constant densities, (4) negligible heat of adsorption, (5) negligible dispersion effects, (6) solutes do not interact, and (7) local equilibrium between the fluid and solid phases. With these assumptions the mass balance for one of the solutes becomes

$$\varepsilon V \frac{\partial C}{\partial z} + \varepsilon W \frac{\partial C}{\partial \theta} + (1 - \varepsilon)\rho_s W \frac{\partial q}{\partial \theta} = 0 \qquad (1)$$

where V is the interstitial velocity of the fluid, ε is the fractional void space in the column, W is the angular velocity of rotation, ρ_s is the solid density, C is the solute concentration in the fluid, and q is the solute concentration on the solid.

The mass balance for each solute can be solved independently, and the results can be superimposed since we have assumed that the solutes are independent. For an isotherm of the general form

$$q = q(T, C) \tag{2}$$

Eq. (1) can be simplified to

$$\frac{\partial C}{\partial \theta} + S_c \frac{\partial C}{\partial z} = \frac{-(1-\varepsilon)\rho_s W \dfrac{\partial q}{\partial T}\dfrac{\partial T}{\partial \theta}}{\varepsilon W + (1-\varepsilon)\rho_s W \partial q/\partial C} \tag{3}$$

where

$$S_c = \frac{\varepsilon V}{\varepsilon W + (1-\varepsilon)\rho_s W \partial q/\partial C} \tag{4}$$

is the slope at which a concentration wave moves up the annulus. For isothermal systems the right-hand side of Eq. (3) is zero and the resulting equation is easily solved by the method of characteristics. Appropriate boundary conditions are

$$C = C_F, \qquad 0 \leq \theta \leq \theta_F, \qquad z = S_F \theta \tag{5}$$

$$C = 0, \qquad \theta > 0, \qquad z = 0 \tag{6}$$

for the slanted feed line and

$$C = C_F, \qquad 0 \leq \theta \leq \theta_F, \qquad z = 0 \tag{7}$$

$$C = 0, \qquad \theta_F < \theta < 360^\circ, \qquad z = 0 \tag{8}$$

for the usual preparative case. The solution is that concentration is constant along characteristics given by

$$dz/d\theta = S_C \tag{9}$$

The simplest isotherm form is the linear form

$$q = K(T)C \tag{10}$$

for which

$$S_C = \frac{\varepsilon V}{\varepsilon W + (1-\varepsilon)\rho_s W K} \tag{11}$$

For the linear isotherm, S_C is constant and all characteristics are parallel to each other. Thus the concentration will be either zero or C_A (C_B). These results are shown in Fig. 2 for the case of a slanted feed line and in Fig. 3 for the usual preparative case. The local equilibrium theory predicts the solute trajectories, but does not predict the zone broadening. In Fig. 2 the feed line slope has been chosen so that the two solutes will not intermix. Mixing will be minimized if

$$S_A > S_F > S_B \tag{12}$$

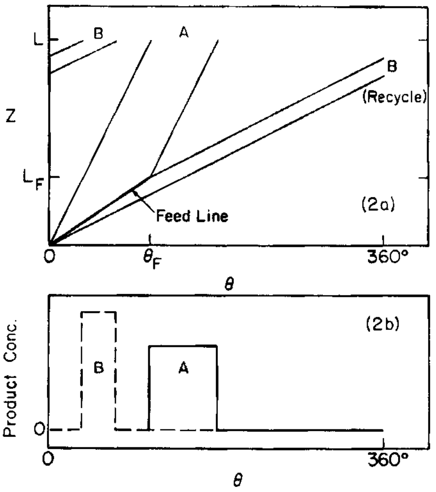

FIG. 2. (a) Characteristics for local equilibrium model solution with a slanted feed line. (b) Predicted product concentrations.

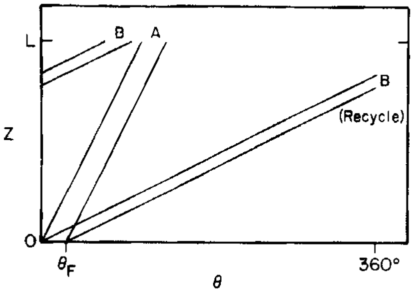

FIG. 3. Characteristics for local equilibrium model solution for the usual preparative system.

The solution by method of characteristics shows that the concentration will be constant along characteristics but this concentration is still undetermined. The slanted feed line system will change the solute concentration depending on the slope of the solute wave and the slope of the feed line. The appropriate concentration can be determined by a macroscopic balance over a section of the apparatus from $z = 0$ to L_F. Solute is input from $\theta = 0$ to $\theta = \theta_F = L_F/S_F$ at a rate of F moles/min. For solute B which has a lower slope than the feed line, $S_B < S_F$, the solute exits from the control volume at $z = L_F$ from $\theta = \theta_F$ to $\theta = L_F/S_B$. This can be seen in Fig. 2. The macroscopic mass balance gives

$$C_B = \frac{F_B}{V\varepsilon A_c\left(\frac{S_F}{S_B} - 1\right)}, \quad \text{for} \quad S_B < S_F \tag{13}$$

For solute A, $S_A > S_F$ and solute exits from the control volume at $z = L_F$ from $\theta = L_F/S_A$ to $\theta = \theta_F$. The macroscopic mass balance gives

$$C_A = \frac{F_A}{V\varepsilon A_C\left(1 - \frac{S_F}{S_A}\right)}, \quad S_A > S_F \tag{14}$$

In the usual preparative case, $S_F = 0$ and Eq. (14) reduces to $C_A = F_A/V\varepsilon A_C$ which is the expected feed concentration. Equation (14) predicts C_A will always be concentrated and Eq. (13) predicts C_B will be concentrated if $S_F/S_B < 2$.

Equations (13) and (14) predict infinite concentrations when S_A or S_B equals S_F. An infinite concentration is physically impossible and implies that the assumption of a linear isotherm cannot be valid. With a nonlinear isotherm the solute wave slope will increase as the concentration increases and the solute wave will move above the feed line. The nonlinear analysis is straightforward but does complicate the diagram and calculations.

A comparison of the results shown in Figs. 2 and 3 for the slanted feed line and the usual preparative system, respectively, will illustrate the increased separation that could be expected for the slanted feed line system. Figures 2 and 3 are drawn for rotating annulus of the same dimensions and for the same solutes. In both cases the entire separation must fit within 360°. With these restrictions, feed can be introduced over a much wider percentage of the apparatus perimeter with the slanted feed line while at the same time obtaining better resolution between the trailing edge of solute B and the leading edge of solute A. As shown in Fig. 2, the resolution between the trailing edge of *A* and the leading edge of *B* will be poorer for the slanted feed line. This occurs since less length of column is allowed to achieve this separation between *A* and *B*. However, these results do not include the effect of zone spreading. Since zone spreading is proportional to the square root of the migration distance, the trailing edge of band *A* and the leading edge of band *B* in Fig. 2 will be less spread than in Fig. 3. As shown in Eqs. (13) and (14), the concentrations of solutes will be considerably greater in the slanted feed case.

In the slanted feed system, solute *A* does not mix with solute *B* once it has been separated. In the usual preparative case, Fig. 3 shows that solute *B* in the leading part of the feed pulse is mixed with solute *A* from the center and trailing edge of the pulse. With a slanted feed the leading edge of the band for solutes which travel at a slope which is less than S_F consists of material which was input last.

In Fig. 2(b) the predicted product concentrations are shown. The local equilibrium model does not predict zone spreading. If nonlinear isotherms are used in the analysis, the model will predict sharp leading edges, but the rear edges will trail off. With nonlinear isotherms the slopes of the solutes are no longer constant and both shock and diffuse waves result (*3*, *4*, *6*). The results for nonlinear isotherms will be similar to those obtained in columns with the analogous moving feed injection system (*6*).

The results shown in Figs. 2 and 3 have not been optimized for either maximum throughput or maximum resolution. If the slanted feed line method is compared to the usual preparative system for the case where feed is introduced for the same fraction of the annulus circumference, redrawing Fig. 2 will quickly show that the slanted feed line case will give better resolution of the peaks. Also, for this separation, resolution can be improved if the annulus dimensions are changed. If we desire to optimize the feed throughput, this can easily be done in the slanted feed line case by increasing the length of the feed line. The separation between the trailing edge of A and the leading edge of B will be reduced; however, this separation is more than adequate in Fig. 2(b). Any attempt to introduce more feed in Fig. 3 will destroy the separation unless the packing depth is changed. Increasing the percentage of time that feed is introduced to the column affects different portions of the separation in the two techniques.

Figures 2 and 3 are drawn for separation of two solutes, but more components can easily be separated. For the slanted feed line system the separation can be optimized by placing the feed line either between the two most important components, between the two most difficult to separate

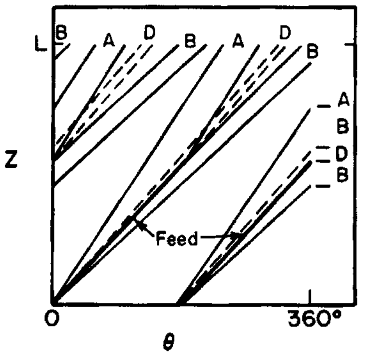

FIG. 4. Local equilibrium model solution for multicomponent separation with feed injection to entire circumference of rotating annulus.

components, or at an angle which will increase the concentration of a trace component. For example, if a trace component, *D*, were present in the slanted feed line system shown in Fig. 2, a three-component separation would result if $S_D \sim S_F$. Some mixing of solutes would occur near the feed line, but the amount would be a minimum compared to the mixing that must occur in the usual preparative system. The slanted feed line system can separate more of a multicomponent feed at the same or better resolution than the usual preparative technique.

In some circumstances where zone broadening is kept to a minimum, it is possible to separate a multicomponent feed with feed around the entire circumference of the two-dimensional apparatus. The local equilibrium model solution is illustrated in Fig. 4 for a three-component system where the components are assumed to have independent linear isotherms. In this case the slanted feed system obviously increases the feed throughput. Some mixing of solutes is inevitable and the solutes are still mixed with solvent, but mixing and the resulting irreversibilities are minimized. In order to achieve a multicomponent separation or to have a separation with feed around the entire annulus, it is not necessary that the inequality in Eq. (12) be satisfied; however, satisfaction of this inequality will produce a more efficient system.

SOLUTE TRAJECTORY ANALYSIS

The rotating annulus system for gas or liquid chromatography can also be analyzed by looking at the trajectory of an average solute molecule based on solute retention times. This analysis will be illustrated and compared to the local equilibrium analysis.

Assuming that the solutes have linear isotherms, each component moves through the column at a solute velocity which can be determined from the retention time.

$$v_A = L/t_A \tag{15}$$

where t_A is the retention time and v_A the solute vertical velocity. In addition to its vertical velocity, the solid and fluid are rotated at an angular velocity W. The net solute velocity can be obtained by vector addition. The slope at which the solute moves up the annulus is

$$S'_A = \frac{v_A}{W} = \frac{L}{Wt_A} \tag{16}$$

where S'_A is also the solute slope on a graph of axial distance, z, versus θ. To achieve separation without mixing at the feed point, the feed line should have slopes between those of the solutes:

$$S'_A > S'_F > S'_B \tag{17}$$

These results are the same as obtained previously with the local equilibrium model, and the solute trajectories will look like the characteristics in Figs. 2 to 4. Relating Eqs. (16) to (11) for a linear isotherm

$$v_A = \frac{\varepsilon V}{\varepsilon + (1 - \varepsilon)\rho_s K} \tag{18}$$

Thus, as expected, v_A is the fraction of time in the mobile phase times the carrier velocity, and the two methods of attacking the problem agree. The one major advantage of the local equilibrium model is that it can be applied to situations where nonlinear isotherms are important and the solute velocities are concentration dependent.

PAPER CHROMATOGRAPHY

Continuous two-dimensional applications of paper chromatography have been developed using a rotating drum apparatus similar to the rotating annulus shown in Fig. 1 (*1*, *2*). Once again, to use a slanted feed line we pick its slope so that the feed line lies between the trajectories of the two key solutes. The paths of the two key solutes will then be on opposite sides of the feed line and the desired separation will be obtained with a minimum of mixing.

The slopes of the solutes can be estimated from their R_F values. For a constant rate of advance of the solvent front, the R_F value is

$$R_F = \frac{\text{velocity of solute}}{\text{solvent velocity}} \tag{19}$$

The paper and solvent are also rotated at an angular velocity W. The net solute velocity is found by vector addition, and the solute slope up the drum is

$$S_A'' = R_{FA}V/W \tag{20}$$

To achieve a separation without mixing, we desire

$$S_A'' > S_F > S_B'' \tag{21}$$

The solute trajectories will look like the characteristics in Figs. 2, 3, and 4 with slopes of S_A'' and S_B''. The observations made previously about increased throughput and resolution are valid for paper chromatography also. The multicomponent separation with continuous feed shown in Fig. 4 is also possible in paper chromatography.

A flexible thin-layer plate could also be formed into a cylinder for two-dimensional thin-layer chromatography. The analysis would follow that presented for paper chromatography.

GEL PERMEATION CHROMATOGRAPHY

Continuous two-dimensional gel permeation chromatography in a rotating annulus system similar to Fig. 1 was developed by Fox and his co-workers (*7–9*). Once again, throughput can theoretically be increased by using a slanted feed line.

The slope of a solute molecule moving up the annulus will be

$$S_A''' = v_A/W \tag{22}$$

where v_A is the vertical solute velocity, W the angular velocity, and S_A''' the slope on a graph of z vs θ. If the solute elution volume is known, v_A can be found as

$$v_A = \frac{\bar{V}_0}{\bar{V}_A} v_0 = \frac{\bar{V}_t}{\bar{V}_A} v_s \tag{23}$$

where $\bar{V}_A$ = elution volume of A, $\bar{V}_0$ = elution volume of an excluded species, $\bar{V}_t$ = total bed volume, v_0 = velocity of an excluded species, and v_s = superficial solvent velocity. Alternatively, v_A, and hence S_A''', can be estimated from the solute molecular weight and the K_{av} calibration curve for the gel being used. K_{av} is usually defined as

$$K_{av_A} = \frac{\bar{V}_A - \bar{V}_0}{\bar{V}_t - \bar{V}_0} \tag{24}$$

Since the elution volumes are inversely related to the velocities, Eq. (24) can be written in terms of velocities. Solution for v_A gives

$$v_A = \left[\frac{1}{v_0} + K_{av}\left(\frac{1}{v_s} - \frac{1}{v_0}\right)\right]^{-1} \tag{25}$$

To achieve the desired separation we again desire S_F to lie between the two solute slopes. Trajectories will again look like the characteristics shown in Figs. 2, 3, and 4. The separation will have the same properties as were discussed previously.

COUNTERCURRENT DISTRIBUTION

Continuous two-dimensional countercurrent distribution was developed by Wankat and his co-workers (*5*, *10*, *11*). In this system the two phases were transferred at right angles to each other. To avoid the necessity of purifying large amounts of solvent, the solvent can be recycled so that only diluent streams are removed as products. The slanted feed line is again designed so that it lies between the trajectories of the two solutes. These trajectories can be estimated from the distribution coefficients.

Define the distribution coefficient as

$$K'_A = \frac{C_A \text{ (diluent phase)}}{C_A \text{ (solvent phase)}} \tag{26}$$

then for constant K'_A the fraction of solute in the diluent phase, f_A, in a given stage is

$$f_A = \frac{K'_A V_{dil}/V_{sol}}{1 + K'_A V_{dil}/V_{sol}} \tag{27}$$

where V_{dil} and V_{sol} are the constant volumes of diluent and solvent phase per stage. Since the fraction of solute in the solvent phase is $1 - f_A$, the solute slope is

$$S_A{}^{IV} = f_A/(1 - f_A) \tag{28}$$

To achieve separation without mixing, the slope of the feed line should lie between the slopes of the solutes. Since this is a discrete staged system, it may not be possible to achieve exactly the desired slope.

For two-dimensional CCD an exact solution can be obtained. Wankat (*11*) found the following solution for steady-state operation with feed to the lower left hand corner, stage (0, 0),

$$\frac{M_{A_{i,j}}}{M_{A_F}} = \frac{(i + j)!}{i!j!} f_A{}^i(1 - f_A)^j \tag{29}$$

$M_{A_{i,j}}$ is the moles of solute A in stage (i, j), and M_{A_F} is the moles of solute A fed during each transfer step.

For the usual preparative case feed is introduced to stages $j = 0, 1, 2, \ldots, N_F$ of row $i = 0$. The solution for the usual preparative case can be obtained as the sum of the solution for each feed stage.

$$M_{A_{i,j}} = \sum_{k=0}^{N_F} M_{A_F} f_A{}^i(1 - f_A)^{j-k} \frac{(i + j - k)!}{(i)!(j - k)!} \tag{30}$$

where $j \geq N_F$. The moles of product withdrawn from column j of row N are $f_A M_{A_{N,j}}$.

With a slanted feed line the solution can also be obtained as the sum of solutions with different feed stages. A completely general solution is difficult to write since an arbitrary slope will not fit onto the integer values required for a staged system. Once the stages to receive feed have been chosen, the solution can be written. For example, if we desire a slope of 1.0 so that the feed stages are (0, 0), (1, 1), (2, 2), (3, 3), (4, 4), etc., then the solution is

$$M_{A_{i,j}} = \sum_{k=0}^{N_F} M_{A_F} f_A{}^{i-k}(1 - f_A)^{j-k} \frac{(i - k + j - k)!}{(i - k)!\,(j - k)!} \tag{31}$$

for $i, j \geq N_F$.

The solutions given in Eqs. (30) and (31) both assume linear isotherms and noninteracting solutes. The CCD model will predict zone broadening effects. The slanted feed line will concentrate solute bands and provide larger throughput with the same or improved resolution. Multicomponent separations can be obtained by the methods discussed previously.

For nonideal systems where the K' values and volumes are not constant, the mass balances can be solved as recursion equations (*10*). The solutions presented here or obtained for the nonideal case can also be applied to a continuous flow mixer-settler type system at steady-state if the appropriate changes in variables are made (*10*, *11*).

DISCUSSION

This paper has presented a theoretical analysis of the advantage of using a slanted feed line in steady-state two-dimensional separations. The actual application of the technique should be relatively easy in systems where the separation surface is relatively open, such as paper or thin-layer chromatography or electrophoresis. Meltzer et al. (*12*) developed an automatic two-dimensional, three-phase CCD apparatus which would be fairly easy to modify for steady-state operation with two phases. Modification of rotating annulus equipment to achieve a slanted feed line might be quite difficult. However, the method can be applied to other two-dimensional geometries, and in some of these, such as the rotating disk system (*1*, *2*), the technique would be considerably easier to apply. In all these systems the slanted feed system can increase feed throughput with the same or better resolution.

One of the major purposes of this research has been to reduce mixing of solutes when the feed is introduced. To have a thermodynamically efficient process irreversible, steps such as mixing must be reduced or eliminated. For ideal solutions the entropy increase due to mixing is given as

$$\Delta S = \sum X_i \ln X_i$$

where X_i is the mole fraction. Entropy production is decreased in the slanted feed system since there is less mixing of solutes with each other and with the solvent. This elimination of irreversible mixing is evident in the increased feed that can be processed.

Steady-state two-dimensional processes are related to time-dependent one-dimensional systems where the time variable has been transformed into the second spatial dimension. During the course of this research it became evident that the usual one-dimensional chromatography systems could be modified by using a feed which moves inside the column as the feed is introduced. In theory, this method increases column throughput as is discussed elsewhere (*6*). The analyses for the time-dependent one-dimensional system and the steady-state two-dimensional system are very similar. The nonlinear isotherm solutions obtained for the one-dimensional system (*6*) can be applied to the two-dimensional system by the appropriate changes in variables.

SYMBOLS

A_C	cross sectional area of column, cm^2

C	fluid concentration, moles/ml
f	fraction solute in diluent phase, Eq. (27)
F	solute feed rate, moles/min
i	row number of stage in CCD
j	column number of stage in CCD
K'	distribution coefficient for CCD, Eq. (26)
K	solid-fluid equilibrium distribution parameter for linear isotherm, Eq. (10)
K_{av}	gel permeation chromatography distribution, Eq. (24)
L	length of bed, cm
$M_{i,j}$	moles solute in stage (i, j)
N	row number of last stages in CCD. Total number of rows is $N + 1$
N_F	column number of last feed stage in CCD. Total number of feed stages is $N_F + 1$
q	solid-phase concentration, moles/g of dry solid
R_F	R_F value. See Eq. (19)
S	slope of wave, cm/degree
T	temperature, °C
t	retention time, min
u	wave velocity, cm/min
V	interstitial fluid velocity, cm/min
$\bar{V}$	elution volume, ml
v	solute velocity, cm/min
V_{dil}, V_{sol}	in CCD volumes of diluent and solvent phase per stage, ml
W	angular velocity of rotation, degrees/min
z	axial distance, cm

Greek Letters

ε	void fraction
ρ_s	density of solid, g/cm^3
θ	angle, degrees

Subscripts

A, B, D	solute species
c	concentration-related value
F	feed

N, N_F	same definitions as in main nomenclature section
o	excluded species
s	superficial solvent elution volume
t	total bed volume

Superscripts

′	slope values obtained from solute trajectory analysis
″	slope values obtained for paper chromatography
‴	slope values obtained for gel permeation chromatography
IV	slope values for CCD
–	volumes

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