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Dong Kwon Keum[a]; Won Kook Lee[a]
[a] DEPARTMENT OF CHEMICAL, ENGINEERING KOREA ADVANCED INSTITUTE OF SCIENCE AND TECHNOLOGY DONGDEAMUM, SEOUL, KOREA

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Simulation of Moving Feed Port Chromatography by Rate Model with Mass Transfer Effect

DONG KWON KEUM and WON KOOK LEE*

DEPARTMENT OF CHEMICAL ENGINEERING
KOREA ADVANCED INSTITUTE OF SCIENCE AND TECHNOLOGY
DONGDEAMUM, SEOUL, KOREA

Abstract

Moving feed port chromatography (MFPC) was simulated by a rate model with mass transfer effect, and two criteria are presented for selection of the feed port velocity to obtain the best separation. When the moving feed port velocity simultaneously satisfied these two criteria, the resulting concentration profiles for MFPC had narrower bandwidth, higher concentration, and improved resolution than those of conventional chromatography. In addition, there existed an optimum number of feed ports (or column length for feed injection) to obtain the best resolution at a fixed total feed time.

INTRODUCTION

In continuous chromatographic techniques, various equipment with different operations and constructions such as moving beds, rotating beds, and simulated moving bed have been developed for the separation of multicomponent mixtures and for increasing the separation capacity.

Among such processes the simulated moving bed developed by UOP (*1*) has been the most practical in commercial applications, but, although it is efficient, it is very complex in operation and equipment construction. An alternative method for improving the efficiency of conventional chromatography was developed by Wankat (*2*) in 1977. It is known as "moving feed port chromatography (MFPC)." It is intermediate be-

*To whom correspondence should be addressed.

tween conventional preparative chromatography and simulated moving systems.

Since the MFPC was developed, it has been applied to gel permeation chromatography (*3*), liquid-solid chromatography (*4*), and, more recently, to gas-liquid chromatography (*5*). A mathematical model including mass transfer effects has not yet been developed despite the fact that those effects are always encountered in chromatographic columns packed with porous materials. Thus, a realistic model which includes external mass transfer or internal mass transfer or both is needed. Moreover, the operating conditions for the best separation is not well understood. The main purpose of this article is to simulate MFPC by applying more realistic model equations and by introducing a new operating criteria to obtain the best separation.

MATHEMATICAL MODEL

The physical phenomena occurring in MPFC are practically the same as those in common chromatographic columns because MPFC is constructed as a segmented column (see Fig. 1). Hence, the models describing MFPC are basically of two types. One is the plate model (*5, 6*) and the other is the rate model (*2–4*). Here, the rate model including mass transfer effects is applied. The differential mass balance of the solute in the column is described as follows.

Fluid phase:

$$\varepsilon \frac{\partial C}{\partial t} + \varepsilon v \frac{\partial C}{\partial x} + (1 - \varepsilon)\rho_p \frac{\partial q}{\partial t} = 0 \tag{1}$$

Solid phase:

$$\frac{\partial q}{\partial t} = \frac{3}{R} k_{so}(KC - q) \tag{2}$$

where k_{so} is the overall mass transfer coefficient, K is the linear equilibrium constant, and R is the particle radius. Axial dispersion is neglected. The initial concentration is

$$C = q = 0 \tag{3}$$

and the boundary conditions are

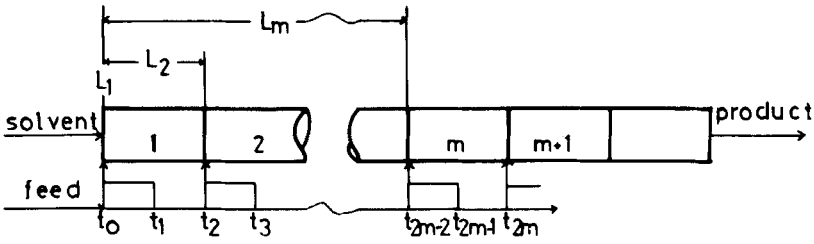

FIG. 1. Schematic diagram of MFPC.

$$C = C_0, t_{2m-2} < t \leqslant t_{2m-1} \text{ at } x = L_m, m = 1, 2, \ldots, NP \qquad (4)$$

where L_m is the length of the column up to mth injection port, t_{2m-2} and t_{2m-1} are the starting and ending times of injection at the mth feed port, and NP is the number of ports used.

With the assumption that the concentration profiles in the column for the feed input at each injection port do not interact, the solution for MPFC can be obtained. Let the individual solution for a pulse input at the mth port be

$$C_m = C_m(L_t - L_m, t - t_{2m-2}), t > 0, m = 1, 2, \ldots, NP \qquad (5)$$

Then each outlet concentration calculated from the individual feed pulse can be summed to give the solution of the elution profile resulting from using MPFC when the change in velocity is ignored. That is:

$$C_T = \sum_{m=1}^{NP} C_m = \sum_{m=1}^{NP} C_m(L_t - L_m, t - t_{2m-2}) \qquad (6)$$

The first absolute moment of one pulse can be obtained from the solution in the Laplace domain (*7*, *8*), and for the present model this is expressed by

$$\mu_1 = \frac{t_{in}}{2} + \frac{L}{v}\left(1 + \frac{1-\varepsilon}{\varepsilon}\rho_p K\right) \qquad (7)$$

where t_{in} is the injection time of the pulse. Since the first absolute moment characterizes the position of the center of gravity of the peak, this relation can be used to obtain the solute velocity for each component.

CRITERIA FOR MOVING FEED PORT VELOCITY (V_{feed})

(1) Criteria to Obtain Minimum Intermixing Zone (Criterion I)

The criteria to obtain the minimum intermixing zone can be determined with reference to Fig. 2, although it is for the local equilibrium model without the mass transfer effect. In this figure the characteristic lines represent the position of each component with time in the column, and u_A and u_B are equivalent to the slopes of the characteristic lines for each component. If V_{feed} is less than u_B, then the feed injection line will exist under the characteristic lines for Solute B. Hence, there will be a region where the solutes are not separated and are intermixed. If V_{feed} is greater than u_A, then the feed injection line will exist above the characteristic lines for Solute A. In this case the characteristic lines for Solute B leaving the feed injection line will intersect with those of A, and the intermixing zone will also exist below the feed injection line. Thus the moving feed velocity needed to obtain the minimum intermixing zone

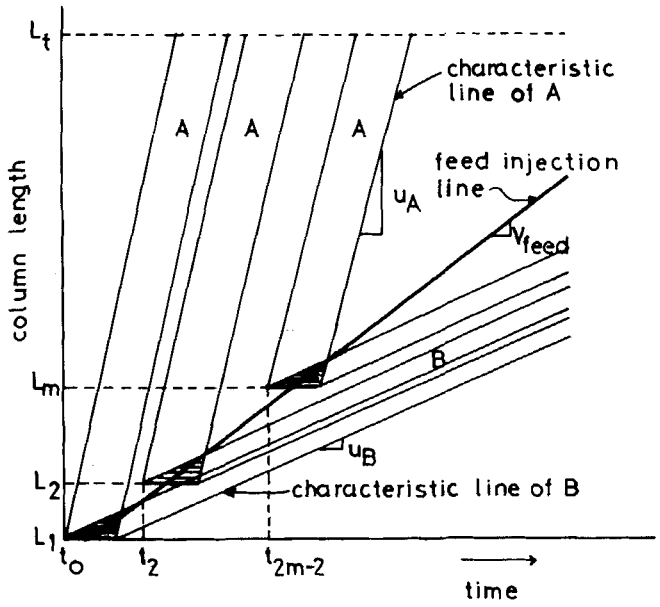

FIG. 2. Displacement of the solute in the column with time for MFPC.

should be between the two solute velocities, u_A and u_B, and hence Criterion I is (*3–5*)

$$u_B < V_{feed} < u_A \qquad \text{(Criterion I)} \tag{8}$$

Since the component velocity (u_c) is commonly regarded as

$$u_c = \frac{\text{column length}}{\text{retention time of center of peak}}$$

it can be determined by using Eq. (7) that

$$u_c = \frac{L}{\mu_1 - t_{in}/2} = \frac{\varepsilon v}{\varepsilon + (1-\varepsilon)\rho_p K} = \frac{F_R/A}{\varepsilon + (1-\varepsilon)\rho_p K} \tag{9}$$

Accordingly, Eq. (8) can be expressed in a more practical form as

$$\frac{\varepsilon v}{\varepsilon + (1-\varepsilon)\rho_p K_B} < V_{feed} < \frac{\varepsilon v}{\varepsilon + (1-\varepsilon)\rho_p K_A} \tag{10}$$

Once V_{feed} is selected, the starting and ending time of injection at the mth feed port are also determined from the relations

$$t_{2m-2} = \frac{L_m}{V_{feed}}, \quad t_{2m-1} = \frac{L_m}{V_{feed}} + \Delta t \tag{11}$$

with the assumption that the injection time of the feed input at each port is the same ($\Delta t = t_1 - t_0 = t_3 - t_2 = t_{2m-1} - t_{2m-2} = t_f/NP$). When the feed is continuously injected without a time delay between the mth and $(m-1)$th feed ports, as was done by McGary and Wankat (*4*), t_{2m-2} becomes identical with t_{2m-3}. To do this and satisfy Criterion I, Δt should be between $(L_m - L_{m-1})/u_A$ and $(L_m - L_{m-1})/u_B$ since V_{feed} is $(L_m - L_{m-1})/\Delta t$ at that time. This also implies that the total feed time (t_f) should be between $NP(L_m - L_{m-1})/u_A$ and $NP(L_m - L_{m-1})/u_B$.

(2) Criteria to Obtain High Concentration (Criterion II)

Even though V_{feed} is within the range satisfying Criterion I, the resulting peak for MFPC can be diluted if the pulses injected at different times and places do not overlap (for example, as Component A in Fig. 2). Thus, another criterion is required to obtain higher concentrations.

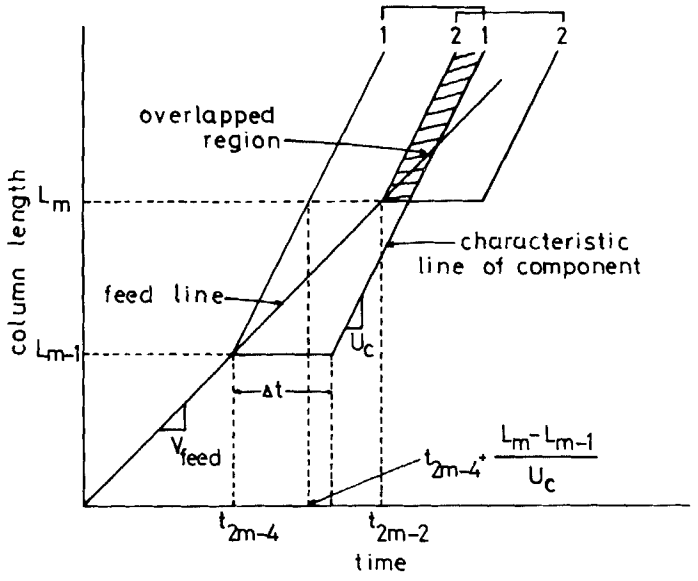

FIG. 3. Region for start time of injection at the mth port to overlap with feed input at the $(m-1)$th port.

By reference to Fig. 3, for the starting time (t_{2m-2}) of pulse input at the mth feed port (2-2 in that figure) to overlap with the feed pulse input at the $(m-1)$th port (1-1 in that figure) should satisfy the following inequality:

$$t_{2m-4}+\frac{L_m-L_{m-1}}{u_c}-\Delta t<t_{2m-2}<t_{2m-4}+\frac{L_m-L_{m-1}}{u_c}+\Delta t,$$

$$m=2,3,\ldots,NP \qquad (12)$$

When Eq. (11) is substituted into the above criteria, the final compact form is expressed as

$$u_c^l<V_{\text{feed}}<u_c^h \qquad \text{(Criterion II)} \qquad (13)$$

where

$$u_c^l=\frac{u_c}{1+\frac{u_c\Delta t}{\Delta L}},\ u_c^h=\frac{u_c}{1-\frac{u_c\Delta t}{\Delta L}},\ \Delta L=L_m-L_{m-1}$$

Here, the distance between two adjacent feed ports, ΔL, can be treated as a constant when each port is positioned at the same interval. u_c^h does not have a physical meaning when $u_c \Delta t/\Delta L > 1$. A binary mixture can have a common V_{feed} for Criteria I and II if

$$u_A^l < u_B^h \tag{14}$$

for a two-component system in which $u_A > u_B$. There then exists a V_{feed} to obtain elution profiles for a MFPC having a higher concentration (or narrower bandwidth) than those for conventional chromatography.

RESULTS AND DISCUSSION

The simulating conditions are summarized in Table 1. The chromatographic system used for simulation had a total column length (L_t) of 0.6 m packed Lichroprep SI 100 (Merck Co.) as the adsorbent. The column

TABLE 1
Simulating Conditions[a]

		$\Delta t\ (= t_{2m-1} - t_{2m-2})$ (min)			
		PF			
Run	*NP*	L_1	L_2	L_3	L_4
RC-12-1-12	1	12	—	—	—
RM-12-2-6	2	6	6	—	—
RM-12-3-4	3	4	4	4	—
RM-12-4-3	4	3	3	3	3

[a]Solvent (0.3% isopropanol in hexane) flow rate: 3 cm^3/min. Absorbent: Lichroprep SI 100 ($R = 3.25 \times 10^{-5}$ m). Total column length (L_t): 0.6 m. $L_1 = 0.0$ m; $L_2 = 0.1$ m; $L_3 = 0.2$ m; $L_4 = 0.3$ m. Chemical system selected: 1-naphthol, *m*-cresol, quninoline. Input concentration: 9 mol/m^3 for all components. Total injection time (t_f): 12 min. Time (Δt) and position (L_m) of feed injection are presented in the body of the table. PF = position of feed injection. *NP* = number of feed port used. Key to Run: M = moving feed port; C = conventional chromatography; first two digits indicate the total injection time (min); third digit indicates the number of feed ports used; the final digits indicate the injection time at each port (min).

was divided into four sections, with the first three of them positioned 0.1 m apart. The chemical systems selected were *m*-cresol, 1-naphthol, and quinoline, all chemicals contained in coal tar (*9*).

The physical parameters used for calculation were obtained by the moment technique (*7*) with concentration profiles obtained from experiments with a single column. The values for each component are listed in Table 2.

The output concentration profile for the individual pulse inputs at each feed port was calculated by the orthogonal collocation method (*10*) for ease and speed of computation, and the elution profile for MFPC was obtained by summing a series of individual solutions.

In order to discuss the simulation results, it is important to determine the velocity of each component. The calculated solute velocities are given in Table 2, and Criteria I and II determined from these are summarized in Table 3.

A comparison between the elution profiles of conventional and moving feed port chromatographies is shown in Fig. 4. The elution profiles for the latter evidently had much higher concentrations than those of the former when Criterion II was fulfilled, regardless of how unsatisfactory Criterion I was [see the elution profile of 1-naphthol (2A) or the elution profile of quinoline (4B) in that figure]. On the contrary, when Criterion II was not fulfilled, the results were reversed (see 4A and 2B in that figure).

To further clarify the importance of Criterion II, Fig. 5 is presented. The MFPC runs in this figure had V_{feed} satisfying Criterion I, but the resulting profiles are somewhat different. When V_{feed} is 7.143×10^{-3} m/min, the elution profile of the 1-naphthol (3A) had a much lower peak height and a wider bandwidth than that (1A) of conventional chromatography because this value of V_{feed} did not satisfy Criterion II for 1-naphthol (refer to Table 3). When V_{feed} is 8.333×10^{-3} m/min, which satisfies Criterion II, the resulting profile for 1-naphthol (2A) had a higher concentration and a narrower bandwidth. While these values of V_{feed} for MFPC satisfied Criterion II for quinoline, the resulting profiles

TABLE 2
Equilibrium Constant, Overall Mass Transfer Coefficient, and Component Velocity for Each Component

Solute	K (m^3/kg)	$k_{so} \times 10^5$ (m/min)	$u_c \times 10^3$ (m/min)
m-Cresol	0.01836	8.6900	8.237
1-Naphthol	0.01340	9.4299	11.109
Quinoline	0.02298	7.7473	6.638

TABLE 3
Criteria I and II under Present Simulating Conditions

Criterion I:

6.638×10^{-3} (m/min) $< V_{feed} < 8.237 \times 10^{-3}$ (m/min) for quinoline/*m*-cresol
6.638×10^{-3} (m/min) $< V_{feed} < 11.11 \times 10^{-3}$ (m/min) for quinoline/1-naphthol
8.237×10^{-3} (m/min) $< V_{feed} < 11.11 \times 10^{-3}$ (m/min) for *m*-cresol/1-naphthol

Criterion II of Each Component for RM-12-2-6 ($NP = 2$, $\Delta t = 6$):

Solute	u_c^l (m/min)	$<$	V_{feed}	$<$	u_c^h (m/min)
m-Cresol	5.5126×10^{-3}				16.2857×10^{-3}
Quinoline	4.7473×10^{-3}				11.0317×10^{-3}
1-Naphthol	6.6659×10^{-3}				33.3143×10^{-3}

Criterion II of Each Component for RM-12-3-4 ($NP = 3$, $\Delta t = 4$):

Solute	u_c^l (m/min)	$<$	V_{feed}	$<$	u_c^h (m/min)
m-Cresol	6.1957×10^{-3}				12.2845×10^{-3}
Quinoline	5.2453×10^{-3}				9.0377×10^{-3}
1-Naphthol	7.6913×10^{-3}				19.9932×10^{-3}

Criterion II of Each Component for RM-12-4-3 ($NP = 4$, $\Delta t = 3$):

Solute	u_c^l (m/min)	$<$	V_{feed}	$<$	u_c^h (m/min)
m-Cresol	6.6049×10^{-3}				10.9405×10^{-3}
Quinoline	5.5356×10^{-3}				8.2886×10^{-3}
1-Naphthol	8.3321×10^{-3}				16.6619×10^{-3}

of quinoline (2B, 3B) for MFPC had a higher concentration than those for conventional chromatography. This indicates that Criterion II as well as Criterion I should be considered.

It can be seen that the elution profiles for MFPC had a narrower bandwidth, a higher concentration, and a shorter retention time than those for conventional chromatography when Criteria I and II were fulfilled simultaneously. These results are more evident when compared with the elution profiles obtained with an improper V_{feed} (see Fig. 6). These improvements in MFPC are due to such operational characteristics as a small intermixing zone for the components, a shorter distance for the solutes to travel in the column, and the superposition of pulses injected into the column at each feed port, which leads to a higher outlet concentration.

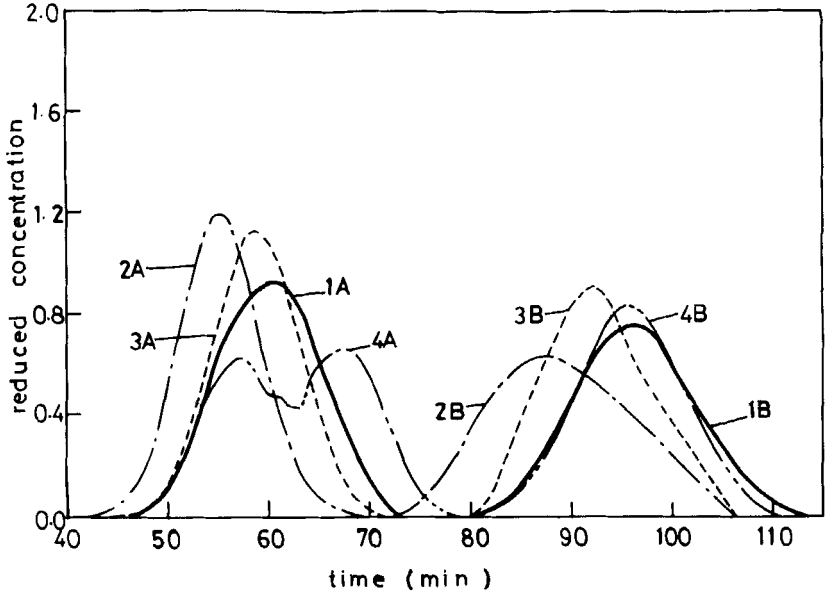

FIG. 4. Comparison between the elution profiles of conventional and moving feed port chromatography. A: 1-Naphthol. B: Quinoline. 1: RC-12-1-12 (conventional method). 2: RM-12-2-6 (V_{feed} = 16.667 × 10^{-3} m/min). 3: RM-12-2-6 (V_{feed} = 7.692 × 10^{-3} m/min). 4: RM-12-2-6 (V_{feed} = 5.000 × 10^{-3} m/min).

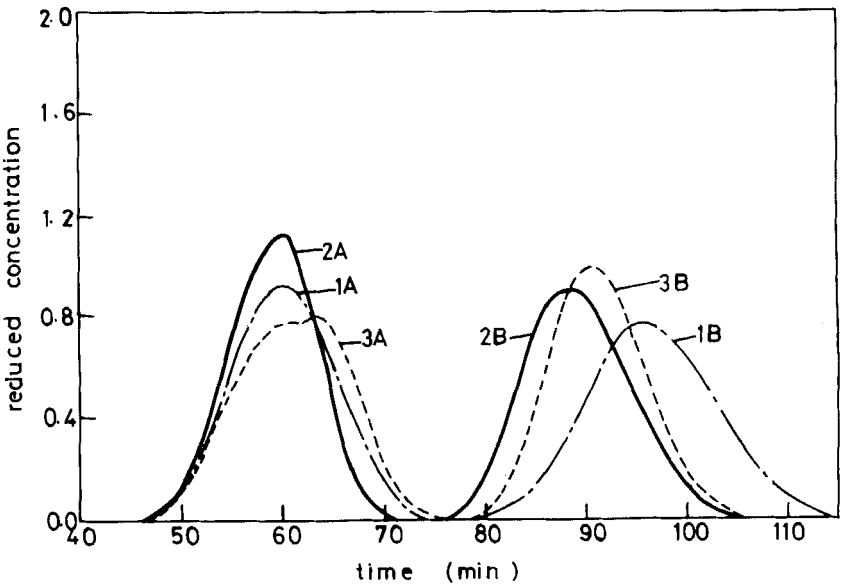

FIG. 5. Comparison between the elution profiles of conventional and moving feed port chromatography. A: 1-Naphthol. B: Quinoline. 1: RC-12-1-12 (conventional method). 2: RM-12-3-4 (V_{feed} = 8.333 × 10^{-3} m/min). 3: RM-12-3-4 (V_{feed} = 7.143 × 10^{-3} m/min).

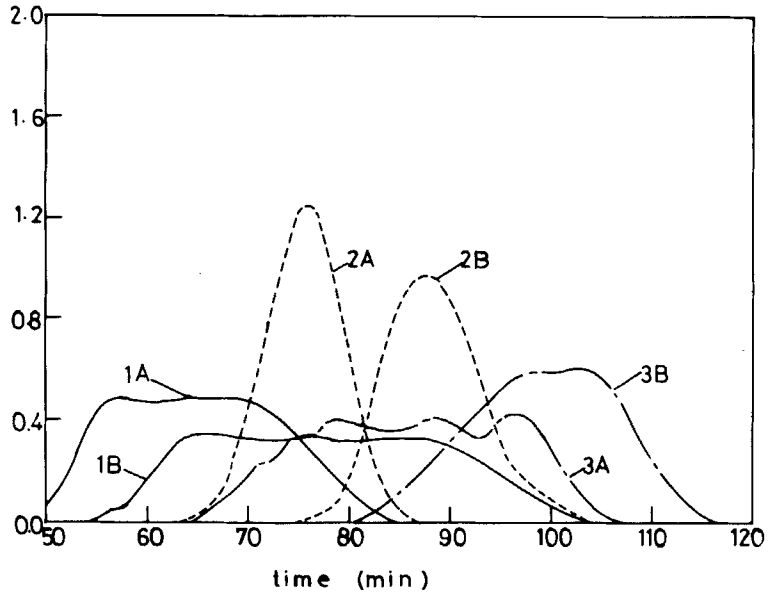

FIG. 6. Comparison between the elution profiles for MFPC obtained from the proper and improper V_{feed}. A: *m*-Cresol. B: Quinoline. 1: RM-12-4-3 (V_{feed} = 16.667 × 10^{-3} m/min). 2: RM-12-4-3 (V_{feed} = 7.692 × 10^{-3} m/min). 3: RM-12-4-3 (V_{feed} = 5.000 × 10^{-3} m/min).

The effect of V_{feed} on the maximum reduced concentration and peak bandwidths for Run RM-12-3-4 are illustrated in Figs. 7 and 8, respectively. As expected, the maximum peak height (or minimum bandwidth) was obtained when V_{feed} was the same as the component velocity. As explained by Wankat (*4*), the solute input into the column builds on the solute already present, and this results in very little additional zone spreading. Furthermore, it is shown in Fig. 7 that for the system *m*-cresol/quinoline, which has a small affinity difference, it is easier to select values of V_{feed} needed to obtain a higher concentration than for the system 1-naphthol/quinoline, which has a larger affinity difference. This suggests that MFPC is especially suitable for the separation of mixtures which are difficult to separate by conventional chromatography. Also, it can be seen for Run RC-12-1-12 in Fig. 8 that the bandwidths of the peaks were increased in the order 1-naphthol, *m*-cresol, and quinoline. This results was caused entirely by the difference of the overall mass transfer coefficient (see Table 2) since band spreading was decreased with k_{so}.

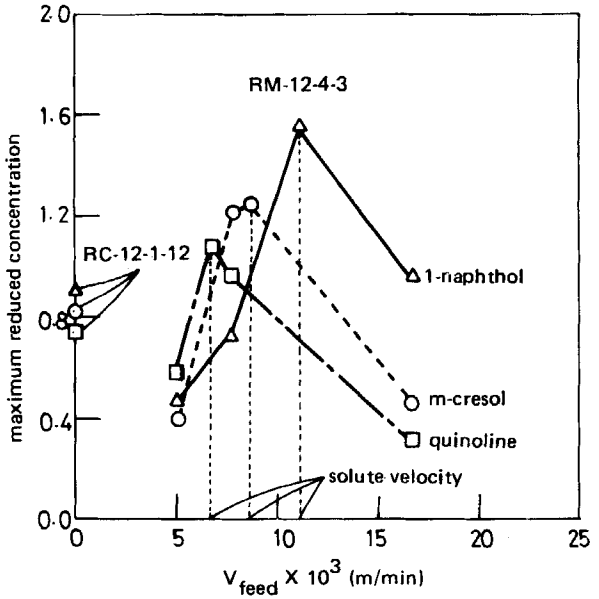

FIG. 7. Effect of V_{feed} on the maximum reduced concentration of a peak for Run RM-12-4-3.

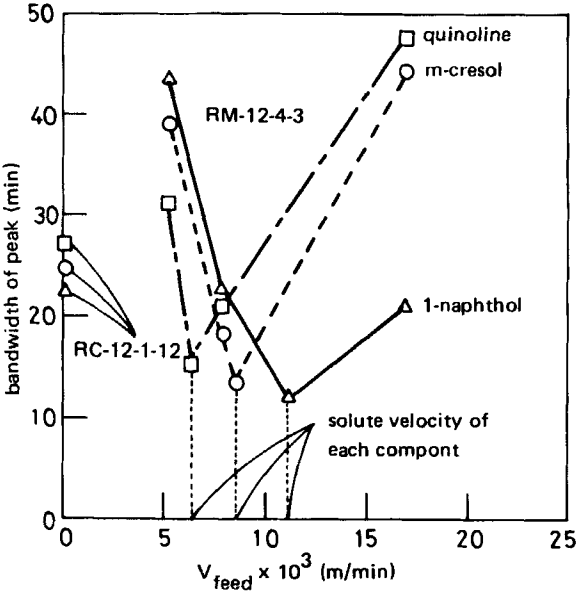

FIG. 8. Effect of V_{feed} on the bandwidth of a peak for Run RM-12-4-3.

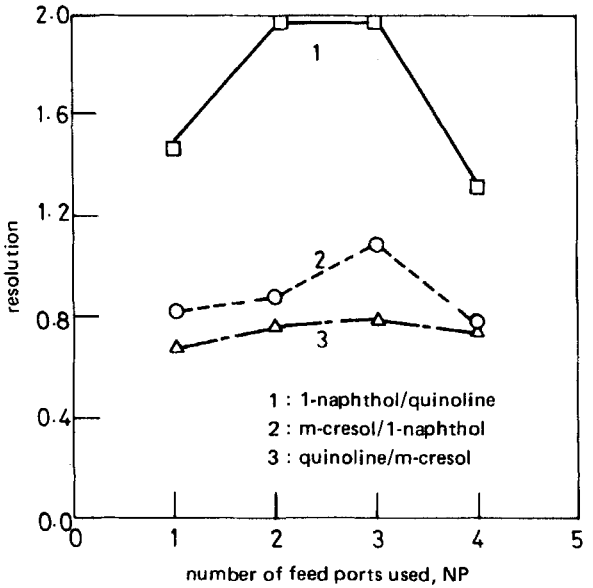

FIG. 9. Effect of the number of feed ports on resolution for a total feed time of 12 min ($V_{feed} = 7.692 \times 10^{-3}$ m/min).

The effect of the number of feed injection ports on resolution when the total feed time was fixed is shown in Fig. 9. Resolution is commonly defined as resolution = $2d/(W_A + W_B)$, where d is the gap between the maxima of two peaks for Components A and B, and W_A and W_B are the lengths of the base lines cut by the two tangents of each peak. Since resolution generally increases with column length and decreases with injection time, the maximum resolution is a balance between column length and injection time (see Fig. 9). When the total feed time is fixed, the injection times (Δt) at each feed port and the distances for the solute to travel in the column are decreased with NP, since Δt is t_f/NP and the column lengths used for separation decrease with NP. Thus, an optimum NP to obtain maximum resolution exists when the total feed time (t_f) is fixed. This implies that there is an optimum column length for feed injection, i.e., L_{NP}, in order to obtain maximum resolution at a fixed total feed time.

CONCLUSION

Moving feed port chromatography was studied by a rate model with a mass transfer effect, and the solution was obtained by summing up a

series of solutions for individual pulses of feed which were calculated by the orthogonal collocation method.

Two criteria were introduced for the selection of the moving feed port velocity required to obtain the best separation. One was used to obtain the minimum intermixing zone in the column, and the other was used to obtain the region in which the two feed pulse inputs at two adjacent feed ports overlapped. When the moving feed port velocity was satisfied simultaneously by the two criteria, the elution profiles for MFPC had a narrower bandwidth, a higher outlet concentration, and an improved resolution than those for conventional chromatography.

There is an optimum number of feed ports needed to give maximum resolution at a fixed total feed injection time, and it is suggested that the optimum column length for feed injection is required to obtain maximum resolution at a fixed total feed injection time.

SYMBOLS

A	cross-sectional area of column (m^2)
C	concentration of solute in fluid phase (mol/m^3)
C_m	individual solution for a pulse input at mth port (mol/m^3)
C_0	input concentration of solute in fluid phase (mol/m^3)
C_T	solution of the elution profile for MFPC (mol/m^3)
d	gap between the maxima of two peaks (min)
F_R	flow rate of solvent (m^3/min, cm^3/min)
K	equilibrium constant (m^3/kg)
k_{so}	overall mass transfer coefficient (m/min)
L	column length (m)
L_m	column length up to mth feed port (m)
L_{NP}	column length for feed injection (m)
L_t	total column length (m)
NP	number of feed ports used (—)
q	concentration of solute in solid phase (mol/kg)
R	particle radius (m)
t	time (min)
t_f	total feed injection time (min)
t_{in}	injection time of a pulse (min)
t_{2m-1}	ending time of injection at mth feed port (min)
t_{2m-2}	starting time of injection at mth feed port (min)
t_{2m-4}	starting time of injection at $(m-1)$th feed port (min)
u_c	component velocity (m/min)

u_c^h highest value for Criterion II expressed in Eq. (13) (m/min)
u_c^l lowest value for Criterion II expressed in Eq. (13) (m/min)
V_{feed} moving velocity of feed port (m/min)
v interstitial velocity of fluid phase in the column (m/min)
W lengths of the base lines cut by the two tangents of each peak (min)
x axial distance (m)
μ_1 first absolute moment expressed as Eq. (7) (min)
ρ_p particle density (kg/m^3)
ε void fraction of column (—)
ΔL distance between two adjacent feed ports, $L_m - L_{m-1}$ (m)
Δt injection time at each port, t_f/NP (min)

Subscripts

A Component A
B Component B

REFERENCES

1. D. B. Broughton, R. W. Neuzil, J. M. Pharis, and C. S. Breasley, *Chem. Eng. Prog., 66*(9), 70 (1970).
2. P. C. Wankat, *Ind. Eng. Chem., Fundam., 16*(4), 468 (1977).
3. P. C. Wankat and P. M. Oritz, *Ind. Eng. Chem., Process Des. Dev., 21*(3), 416 (1982).
4. R. S. McGary and P. C. Wankat, *Ind. Eng. Chem., Fundam., 22*(1), 10 (1983).
5. W. K. Lee, K. H. Row, and H. Y. Ha, *Sep. Sci. Technol., 22*(1), 141 (1987).
6. J. C. Giddings, *Dynamics of Chromatography,* Part I, Dekker, New York, 1965.
7. P. Schneider and J. M. Smith, *AIChE J., 14*(5), 262 (1968).
8. H. W. Haynes and P. N. Sarma, *Ibid., 19,* 1043 (1973).
9. M. Windholz, S. Budavari, R. F. Blumetti, and E. S. Otterbein, *The Merck Index,* 10th ed., Merck, 1983, p. 345.
10. B. A. Finlayson, *The Method of Weighted Residuals and Variational Principles,* Academic, New York, 1972.

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