Korean J. of Chem. Eng., **4**(2) (1987) *113-119*

CHARACTERISTICS OF MOVING FEED-INJECTION CHROMATOGRAPHY

Kyung Ho ROW, Heung Yong HA and Won Kook LEE*

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, Seoul 131, Korea

(Received 11 July 1986 • accepted 13 January 1987)

Abstract—An alternate method for preparative chromatography, moving feed-injection system was studied with a modified plate model and was compared with the conventional preparative case. Experiments were performed for the separation of diethylether and dichloromethane by a gas-liquid chromatography. The moving feed technique had some advantages over the conventional preparative system; decreased bandwidths, higher peak maxima, and better resolution.

The moving feed chromatography can be optimized by variation of the feed port velocities. A plate model was used successfully to predict the experimental concentration profiles. The effects of the particle size were also studied experimentally.

INTRODUCTION

The high resolution and versatility of analytical batch chromatography using both gas and liquid mobile phases has been concentrated in considerable attentions for years to convert the technique into a preparative method.

The most obvious approach is to scale up an analytical chromatography by using large diameter columns. Scale up of these batch systems has been studied by many researchers [1, 2, 3].

The conventional elution chromatography or batch system is thermodynamically inefficient and its throughput capability is not large. To overcome the problem in batch system, the continuous mode was introduced and has taken several forms: vertical moving bed [4], rotating-circular column [5], and simulated moving bed (SMB) [6]. Significant industrial applications have been found by the simulated moving bed of Universal Oil Products [7]. Baker et al. [8] developed a simulated counter-current refiner for the fractionation of dextran. Row and Lee [9] showed experimentally that moving feed-injection and product-withdrawal enabled to separate the binary feed mixtures continuously. Later, as a scaled-up system, combined continuous and preparative chromatography has been proposed [10].

Wankat [11] proposed an alternate method of improving the efficiency of a preparative system, moving feed point system and demonstrated the advantages of using a moving feed with the local equilibrium model. He and his colleagues[12, 13] found a method to have better resolution and higher throughput compared to a conventional preparative system.

In this work, a theoretical plate model was used to investigate the characteristics of the moving feed-injection chromatography (MFIC) and the theoretical results were compared with those of experiments for the separation of diethylether (DEE) and dichloromethane (DCM) by gas-liquid chromatography. The effects of the operating variables on the performance of this system was also discussed experimentally.

MOVING FEED-INJECTION CHROMATOGRAPHY

The conventional operating method of fixed beds for preparative chromatography is to use a large pulse of feed followed by a carrier gas or solvent in a long period. The pulse of feed is fed to the bottom of the column and the carrier is also continuously fed to the bottom of the column. Therefore, the region in which all the components are intermixed is very wide because the total of the feed is introduced to the column at the same position.

The moving feed-injection technique uses a feed injection point which moves at a velocity U_F up the column during the time the feed containing two or more solutes is injected. The carrier gas is continuously fed to the bottom of the column. In actual practice a segmented column with feed ports at distinct locations is used and movement of the feed port can be attained by switching the feed port locations. The arrangement

* To whom all correspondence should be addressed.

of the segmented column used in this study is shown in Fig. 1. In the moving feed-injection system the feed is introduced as a long pulse. The first portion of this pulse is put into number 1 of the column while the second portion of the feed pulse is put into number 2 of the column, and so on. By use of this technique of feed-injection, the region of intermixing can greatly be reduced in the system. Because only the first portion of the feed pulse travels the total length of the column and the other portions travel the smaller distances than the first, the total migration distance of the solutes is less than that of the preparative case. This may reduce zone spreading which is proportional to the total migration time. The solute bands fed at different times and positions superpose in the column and consequently the outlet concentration becomes very high.

The feed port velocity, U_f, is defined as the velocity with which the position of feed-injection moves up the column, and it is calculated as in Table 2. The separation condition of the moving feed-injection system is that the feed port velocity should be lied between the *velocities of the two components in the column.

THEORETICAL PLATE MODEL

In the theoretical plate model, a chromatographic column is conceived in the form of consecutively united equilibrium steps, upon each of which thermodynamic equilibrium exists between the gas and liquid phase. It is assumed that complete mixing of the gas do not vary throughout the column and the components are independent of each other.

A material balance equation for the first step is as follows

$$v_m dY_1 - v_s dX_1 + Y_1 dV = Y_o dV \quad 0 \leqq V \leqq V_f$$
$$v_m dY_1 - v_s dX_1 + Y_1 dV = 0 \quad V \geqq V_f \qquad (1)$$

where Y and X are concentrations of solute in the gas and the liquid phase, v_m and v_s are volumes of the gas and liquid phase of one plate, V is the volume of the gas that has passed through the column, and V_f is the volume of feed with a concentration of Y_o.

For all other steps, the following equation is valid:

$$v_m dY_n + v_s dX_n + Y_n dV = Y_{n-1} dV \quad (n=2, 3, \cdots, N) \qquad (2)$$

Assuming a linear isotherm,

$$K = X_n / Y_n \qquad (3)$$

the systems of equations 1 and 2 can be reduced to

$$\frac{dY_n}{dV} = a(Q - Y_n) \qquad (4)$$

where $Q = Y_o$ at $0 \leqq V \leqq V_f$
$Q = 0$ at $V \geqq V_f$ $n = 1$
$Q = Y_{n-1}$ $(n=2, 3, \cdots, N)$
$a = 1/(v_m + Kv_s)$.

With the initial conditions

$$Y_1 = Y_2 = \cdots = Y_n = 0 \qquad (5)$$

the equation (4) gives a full mathematical description of the plate model of the chromatographic process.

To apply the model to the moving feed-injection system, several simplifying assumptions may be added: the feed pulses at different positions independent of one another and constant HETP regardless of the feed positions. With these assumptions, the outlet concentration can be calculated by summing a series of solution obtained for a single pulse of feed as shown in Fig. 2, and 1, 2, and 3 in the figure indicate the numbers of sequent feed ports.

EXPERIMENTAL

The schematic diagram of the moving feed-injection system is shown in Fig. 1. The chromatographic beds consisted of 10 small columns made of stainless steel with 10 mm I.D. and 26 cm packed height. From one (conventional chromatography) to 8 feed ports could be used in the experiments. Switching of the feed-injection position was done automatically with solenoid valves controlled by a specially-designed microprocessor. The materials used and their properties are listed in Table 1. Outlet products were analyzed by an analytical gas chromatograph (GOW MAC 550 P

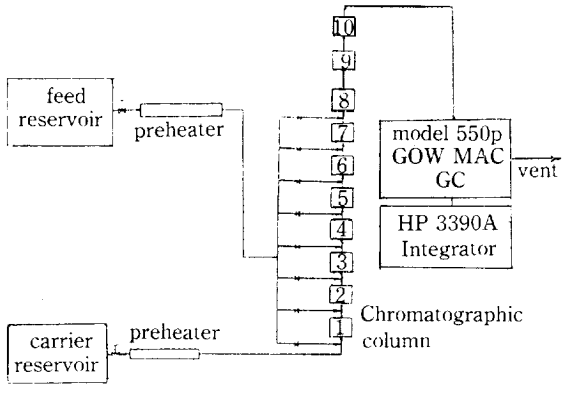

Fig. 1. Schematic diagram of apparatus for moving feed-injection chromatography.

*: The velocity of a component or the solute velocity is the velocity at which the solute moves through a column and its average value can be calculated by dividing the total length of the column with the retention time of the component.

Table 1. Materials used and their properties.

carrier gas	N_2
solid support	Chromosorb A
particle size	20/30, 45/60 mesh
liquid phase	dinonylphthalate
liquid loading	20% by wt. %
feed component	diethylether(DEE), dichloromethane(DCM)

typical properties of the materials

material	formula	molecular weight	b.p. (°C)
DEE	$C_2H_5OC_2H_5$	74.12	34.6
DCM	CH_2Cl_2	84.93	39.0
DNP	$C_6H_4(COOC_9H_{19})_2$	418.62	175.0*

*: recommended maximum temperature

TCD) through ten port sampling valves (Valco Instrument Co.). In this experiments, two stream of N_2 were used, one for a carrier gas, and the other for a feed stream which passed through a saturator containing liquid feed mixture and then entered into the chromatographic column. The chromatographic beds were confined in an enclosure of steel with an electric heater inside it.

RESULTS AND DISCUSSION

The plate model is very simple and hence, is easily applied to the moving feed-injection system. The characteristics and advantages of the system over the conventional preparative case can be clearly shown with this model.

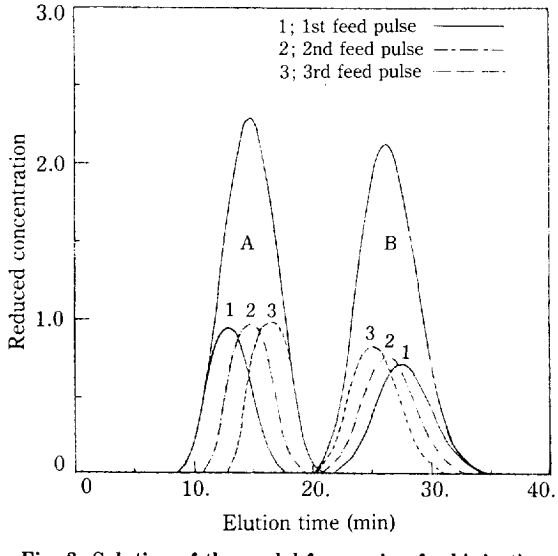

Fig. 2. Solution of the model for moving feed-injection chromatography.
(A, B: components)

Table 2. Feed injection time to each port.

(unit = minute)

Run No.	U_F* (cm/min)	Number of Feed Ports 1	2	3	4	5	6	7	8	9	10
SIM-1	0.	12									
SIM-2	6.5	4	4	4							
SIM-3	8.7	3	3	3	3						
SIM-4	13.0	2	2	2	2	2	2				
SIM-5	17.3	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5		
SIM-6	21.7	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
SIM-7	13.0	6			6						
SIM-8	13.0	4		4			4				
SIM-9**	13.0	1	1	1	1	1	1	1	1	1	1

*: The velocity of feed port, U_F, is calculated as follows: for Run No. SIM-2

$$U_F = \frac{L_1 + L_2}{t_1 + t_2} = \frac{26+26}{4+4} = 6.5 \text{ (cm/min)}$$

**: For Run No. SIM-9, the distance between any two adjacent feed ports is reduced by half, i.e. 13 cm.

The fundamental difference between the two chromatographic system lies in the mode of feed injection to the column. In the moving feed-injection system, the outlet concentration profiles are directly dependent on the velocity of moving feed port, whereas in the conventional preparative system this is not the case because the feed port is fixed.

Simulation was done with respect to a real system used in this work where the total length of the column was 260 cm and feed-injection ports were located distinctively 26 cm apart from adjacent ports, and the conditions were listed in Table 2.

The concentration profiles of the preparative and moving feed-injection systems are compared in Fig. 3. The latter has better resolution with sharper bandwidth and trailing edge of more-absorbed component, DCM, comes out faster. The moving feed-injection system is very flexible in its operation and the bandwidths and resolution can be varied somewhat at will by changing the feed port velocities.

The resolution, which is used as a measure of separation of the two components, is commonly defined as

$$R = \frac{2d}{w_1 + w_2} \quad (6)$$

where d is the distance between maxima of the two adjacent peaks, w_1 and w_2 are the lengths of the base

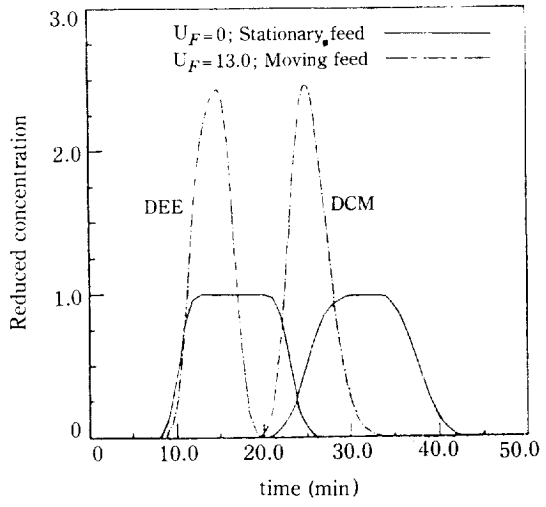

Fig. 3. Comparison between the elution profiles of conventional preparative and moving feed-injection systems with equal feed-injection time of 12 min.

(Stationary feed = Run No. SIM-1, Moving feed = Run No SIM-4, column temperature = 29°C)

lines cut by the two tangents of each peak.

The effects of the feed port velocity on bandwidth and resolution are shown in Figs. 4 and 5, respectively, and it is clear that there is an optimum average feed port velocity or range of feed port velocities. As shown

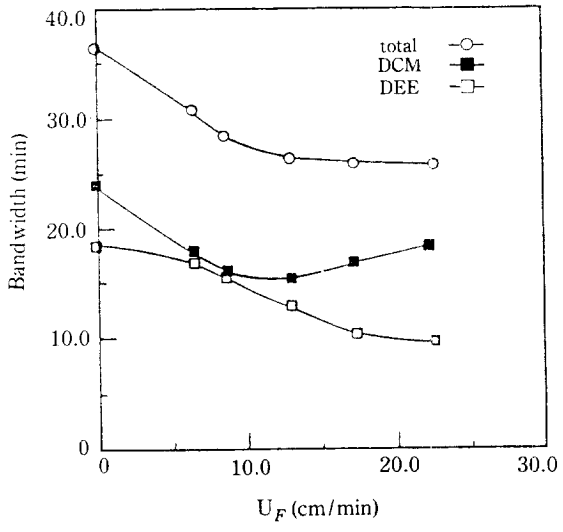

Fig. 4. Effect of U_F on bandwidth for total feed-injection time of 12 min.

(Run No SIM-1 -- SIM-6, column temperature = 29°C)

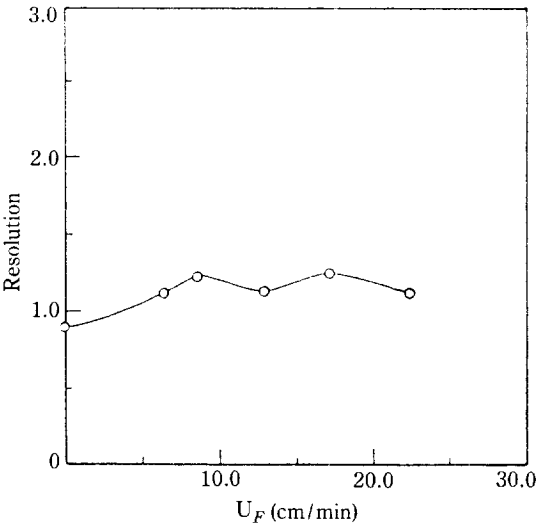

Fig. 5. Effect of U_F on resolution for total feed-injection time of 12 min.

(column temperature = 29°C)

in the figures, a peak of one component can be made very sharp by appropriately adjusting the feed port velocity while that of the other is broadened. The bandwidth of each component shows a minimum point with respect to the feed port velocity. This is clearly shown for the component of DCM in Fig. 4. For DEE, however, the minimum point is not clear in this range of feed port velocity, U_f.

The temperature has great effect on the resolution. The velocities of the components in the column increase with the column temperature. For a given system, however, the attainable maximum feed port velocity, U_{FM}, is limited to the value expressed as follwos:

$$U_{FM} = \frac{L_f}{t_T - t_f} \tag{7}$$

where L_f is the distance from the origin of the column to the last feed port, t_T is the total feed injection time and t_f is the time of feed-injection to the last port. Therefore, when the column temperature increases, the maximum feed port velocity may be exceeded by the solute velocities even with a constant carrier velocity, which greatly deteriorates the resolution as shown in Fig. 6. The column temperature as well as the carrier velocity should be adjusted so that the separation condition may be satisfied, or the attainable maximum feed port velocity may lie between the velocities of the two components. In addition, the number of ports for feed-injection has effect on the resolution even with the same value of U_F, This is illustrated in Fig. 7 where the resolutions are increased with the number of feed

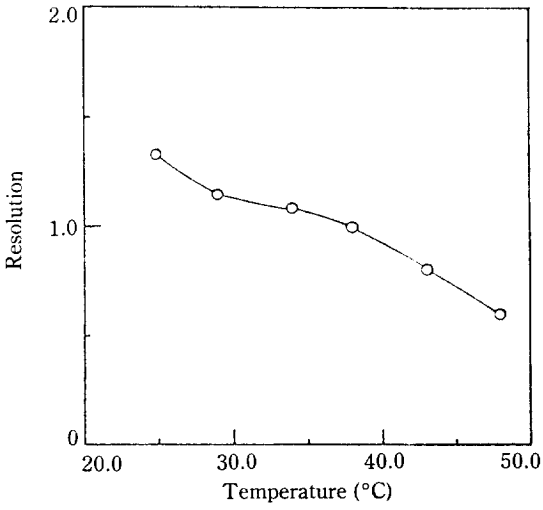

Fig. 6. Effect of temperature on resolution for total feed-injection time of 12 min.
(Run No SIM-4, U_F=13.0 cm/min)

ports.

As already shown in the previous work [14, 15] the plate model was in relatively good agreement with the experimental data. The operating conditions of the experiments are listed in Table 3. Comparisons between the profiles of the simulation and experiment are shown in Figs. 8 and 9 for the preparative and the moving feed case, respectively. The discrepancies between the profiles may be ascribed to the assumptions

Table 3. Experimental conditions.

particle size: 45/60 mesh
carrier flow rate
: with feed = 464.10 cm^3/min
: without feed = 427.35 cm^3/min
feed concentration
: DEE = 2.829×10^{-4} mol/l
: DCM = 1.950×10^{-4} mol/l
time of feed-injection to each port (unit: min)

Run No.	Temp. (°C)	U_F (cm/min)	Number of feed ports 1	2	3	4	5	6
Run 1	29	0	12					
Run 2	29	13.0	2	2	2	2	2	2

in the model which fail to meet the real system. However, with some inappropriate aspects, the model is very useful to interpret the moving feed-injection system and predict its optimum operating conditions.

Experimental results obtained with the particle size of 20/30 and 45/60 mesh sizes were compared. The size of the solid supports has some effects on the column performance. Generally column efficiency increases with decrease in particle size. However, pressure drop considerably increases with decreasing the size thus limiting the reduction of the particle size. Therefore any increase in efficiency gained by reduced particle size is obtained only at the expense of a greatly

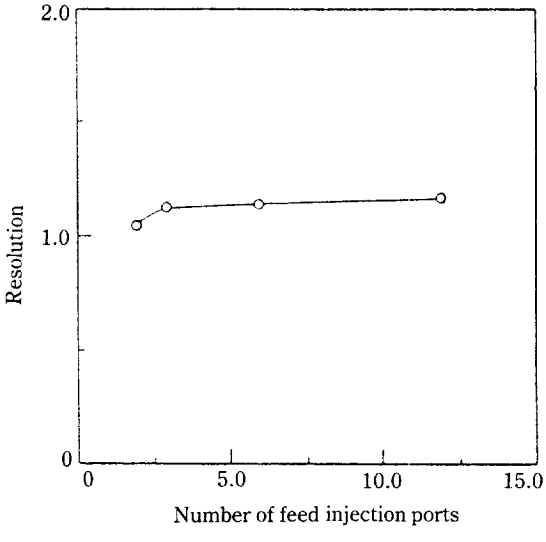

Fig. 7. Effect of the number of feed ports on resolution for total feed-injection time of 12 min.
(Run No SIM-4,7,8, and 9, U_F = 13.0 cm/min)

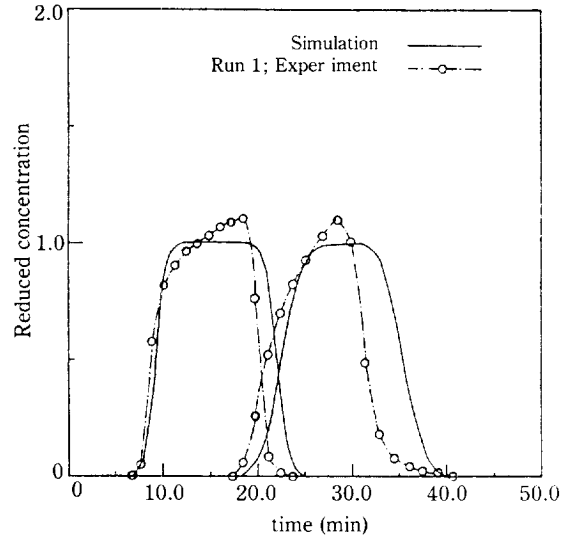

Fig. 8. Comparison between experimental and calculated elution profiles for conventional preparative chromatography.

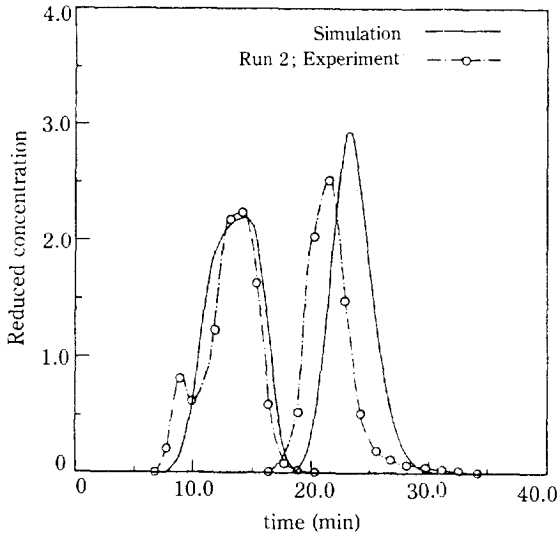

Fig. 9. Comparison between experimental and calculated elution profiles for moving feed-injection system.

increased flow resistance [16].

Figures 10 and 11 shows the effects of the change in particle size on the elution profiles of the conventional preparative and the moving feed system, respectively. As can be seen, the change in the particle size has little effect on the less absorbed component, DEE, while for the DCM the increased retention times and bandwidths are resulted with the smaller particles. As a whole, the separation is better for the case of the smaller supports of 45/60 mesh size, but the effects of

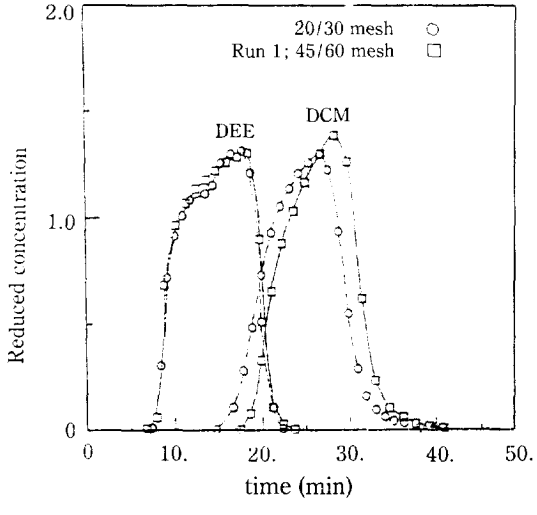

Fig. 10. Effect of the particle size on the elution profiles of the conventional preparative system.

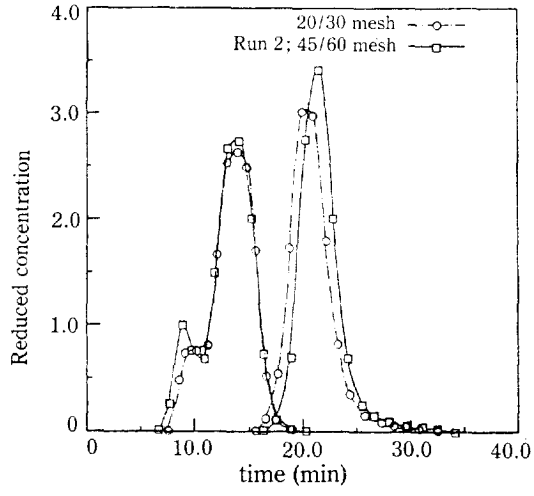

Fig. 11. Effect of the particle size on the elution profiles of the moving feed-injection system.

the particle size are not so great. This is because in the preparative work, as the sample size increases the effect of the partcle size is small and the penalty accompanying the reduction of the support size becomes very slight [17, 18].

CONCLUSIONS

The results of simulation and experiments show that the moving feed-injection technique offers improved separation and flexibility over the conventional preparative system. Products can be obtained with faster separation and better resolution by using a moving feed. In this system the extent of the separation depends on the velocities of the moving feed ports, in which the resolution of two adjacent components in a chromatogram cna be improved by choosing the feed port velocity between the velocities of the two components which vary with carrier velocity and column temperature. Therefore the operating conditions should be carefully chosen so that the separation condition may be fulfilled. The plate model with some simplifying assumptions was in good agreement with the experimental data and can be used to predict the optimum operating conditions of the moving feed-injection system. For a given set of experimental conditions, the smaller size of solid support gave a slightly better resolution with increased bandwidth.

NOMENCLATURE

a : constant, $1/(v_m + Kv_s)$
d : distance between the two peak maxima, min
K : partition coefficient

L : total length of the chromatographic beds, cm
L_f : distance from the origin of the column to the last feed-injection port, cm
L_i : length of the i-th feed column, cm
Q : value defined by Eq. (4)
R : resolution
t_f : time of feed-injection to the last feed port, min
t_i : time of feed-injection to the i-th port, min
t_T : total feed-injection time, min
U_F : feed port velocity, cm/min
U_{FM} : attainable mixiumum feed port velocity, cm/min
V : volume of the gas that has passed through the column, cm^3
V_f : volume of feed with concentration of Y_o, cm^3
v_m : void volume in a plate, cm^3
v_s : volume of stationary phase in a plate, cm^3
w : distance of the base line cut by the two tangents of the peak, min
X_n : concentration of solute in the stationary phase, mol/*l*
Y_n : concentration of solute in the mobile phase, mol/*l*
Y_o : feed concentration, mol/*l*

REFERENCES

1. Sakodynskii, K.T.: *J. Chromatogr.*, **204,** 167 (1981).
2. Albrecht, J. and Verzele, M.: *J. Chromatog. Sci.*, **8,** 586 (1970).
3. Bonmati, R.G., Chapelet-Letourneux, J. and Margulis, J.R.: *Chem. Eng.*, **86,** 70 (1980).
4. Fitch, G.R., Probert, M.E. and Tiley, P.E.: *J. Chem. Soc.*, 4875 (1962).
5. Barker, P.E. and Al-Madfai, S.: *J. Chromatog. Sci.*, **1,** 425 (1969).
6. Broughton, D.B.: *Chem. Eng. Progr.*, **64,** 60 (1968).
7. Broughton, D.B, Neuzil, R.W., Pharis, J.M. and Breasly, C.S.: *Chem. Eng. Progr.*, **66,** 70 (1970).
8. Barker, P.E., Ellison, F.J. and Hatt, B.W.: Ind. Eng. Chem. Process Des. Dev., **17,** 302 (1978).
9. Row, K.H. and Lee, W.K.: *Korean J. Chem. Eng.*, in press (1986).
10. Row, K.H. and Lee, W.K.: Ind. Eng. Chem. Fundamen., submitted (1986).
11. Wankat, P.C.: *Ind. Eng. Chem. Fundamen.*, **16,** 468 (1977).
12. Wankat, P.C. and Oritz, P.M.: Ind. Eng. Chem. Process Des. Dev., **21,** 416 (1982).
13. McGary, R.S. and Wankat, P.C.: *Ind. Eng. Chem. Fundamen.*, **22,** 10 (1983).
14. Ha, H.Y., Row, K.H. and Lee, W.K.: Sep. Sci. and Technol., **22**(1), 141 (1987).
15. Ha, H.Y., Row, K.H. and Lee, W.K.: Sep. Sci. and Technol., **22**(4), 1281 (1987).
16. Pescar, R.E.: "Preparative Gas Chromatography", A. Zlatkis and V. Pretorious, Ed., Wiley & Sons, London P102, (1971).
17. Reiser, R.W.: *J. Gas Chromatog.*, **4,** 390 (1966).
18. Verzele, M. and Verstapper, M.: *J. Chromatogr.*, **19,** 504 (1965).