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A Plate Model for Moving Feed-Injection Chromatography. I. Simulation Results

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Abstract

The plate model was used to clarify the characteristics of a moving feed-injection system. The selected sample system was gas–liquid chromatography for the separation of close-boiling components such as diethyl ether and dichloromethane. The solution of the model for the moving feed-injection system with simplified assumptions was obtained by summing up a series of solutions for a single pulse of feed. The results of the simulation showed that the efficiency of a chromatographic column could be improved by using the moving feed-injection system: the system had narrower bandwidths, higher outlet concentrations, and better resolutions when these were compared to those of preparative chromatography. Moreover, the system had much flexibility in its operation so that the retention times and the bandwidths of the components to be separated could be controlled by changing the feed port velocities. The velocity had optimum values; beyond the optimum value, the resolution became worse. An increased number of ports for feed-injection improved the resolution.

INTRODUCTION

Much interest has been aroused over the years in the use of chromatography as a method for handling large preparative-scale separations (*1*).

The most direct approach to scale-up is to increase the size of the column in diameter and length. Research and development work has

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concentrated on column design and packing techniques (*2, 3*). However, as the dimensions of the column are increased, the efficiency is decreased sharply (*4*). Another approach is to achieve continuous separation of a feed mixture into each component by a countercurrent flow of mobile phase and stationary phase. Based on countercurrent flow, simulated moving beds (UOP process) have been developed (*5*).

Wankat (*6–8*) proposed a moving feed point system which retained characteristics of both elution chromatography and the simulated countercurrent system. This method was reported to reduce irreversible mixing of components and to be thermodynamically more efficient than conventional preparative chromatography.

To achieve a mathematical model of the chromatographic process, the theoretical plate concept has been widely used. The chromatographic column in the model is conceived in the form of consecutively united equilibrium steps, upon each of which, by definition, thermodynamic equilibrium exists between the gas and the stationary phase (*9, 10*).

In spite of the somewhat inadequate aspects of this concept in describing the chromatographic processes (*11*), it has definite advantages that are particularly important in practical work. That is, the plate model is simple and all the parameters of the equations, including the height equivalent to a theoretical plate, are readily determined by measuring experimental elution curves.

In this paper the theoretical plate model was used to predict the elution profile. Separations of diethyl ether (DEE) and dichloromethane (DCM) were simulated by moving feed-injection chromatography which had segmented columns with feed ports at distinct locations. The purpose of this work is to investigate the characteristics of moving feed-injection chromatography by using the theoretical plate model.

PRINCIPLES OF MOVING FEED-INJECTION CHROMATOGRAPHY

Figure 1 schematically shows the operating patterns of conventional preparative and moving feed-injection chromatography. The carrier gas is continuously fed to the inlet end of each column, and the total amount of feed is assumed to be equal for each type.

In the conventional preparative system shown in Fig. 1(a), a pulse of feed is fed to the inlet end of the column. Therefore, all the solute introduced must travel the full length of the column.

For the moving feed-injection system shown in Fig. 1(b), however, the feed pulse is broken into parts, in this case two equal parts, and is fed sequentially into the two feed ports. The input position of the second feed

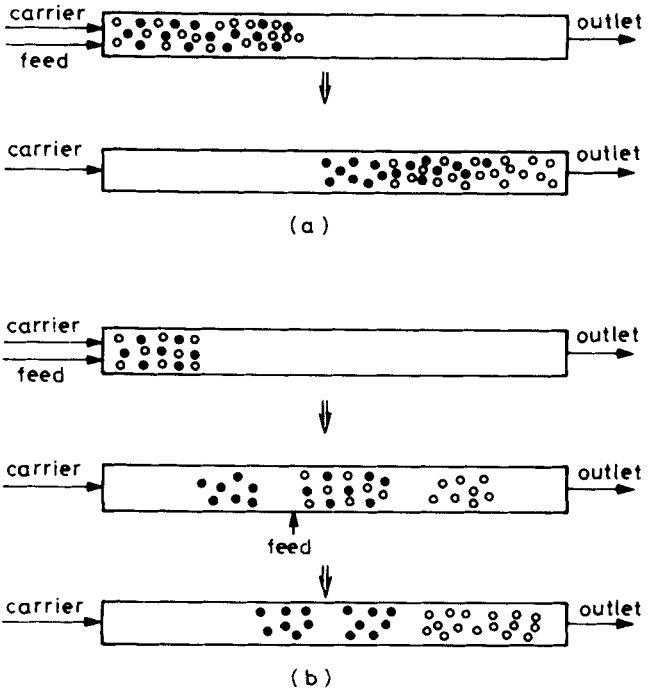

FIG. 1. Schematic diagrams of (a) conventional preparative chromatography and (b) moving feed-injection chromatography.

pulse is chosen so that the pulse is introduced between the two separate bands of the first pulse. This mode of operation gives a reduced intermixing region between the two components and a decreased total migration distance for the solute to travel in the column. Because the solute fed at different times and positions overlaps, the outlet concentration is very high. When the feed port velocity U_F, illustrated in Table 2, lies between the velocities of the two components, i.e.,

$$U_B < U_F < U_A \tag{1}$$

where U_A and U_B are the average velocities of the two components A and B in the column, respectively, better separation and more product will be obtained.

THEORETICAL PLATE MODEL

In developing the theoretical plate model, it is assumed that the carrier gas is incompressible, the variation in velocity of the gas through the column due to phase change of a solute is negligible, and the components move independently.

A material balance over plate n gives

$$Y_{n-1}dV - Y_n dV = d(v_m Y_n + v_s X_n) \tag{2}$$

where Y_n and X_n are the concentrations of solute in the mobile and in the stationary phases, respectively, and v_m and v_s are the volumes of the gas and stationary liquid phases of one plate, respectively, and V is the volume of the gas that has passed through the column (Fig. 2).

Assuming a linear isotherm,

$$K = X_n/Y_n \tag{3}$$

and substituting into Eq. (2) gives

$$\frac{dY_n}{dV} + aY_n = aY_{n-1} \tag{4}$$

where a is a constant, $1/(v_m + Kv_s)$.

In the development of the deposition process, the mobile phase enters Plate 1 with a solute concentration of Y_0, and the concentration of solute in each plate at the start is zero, so that

$$Y_1^\circ = Y_2^\circ = \ldots = Y_N^\circ = 0 \text{ at } V = 0 \tag{5}$$

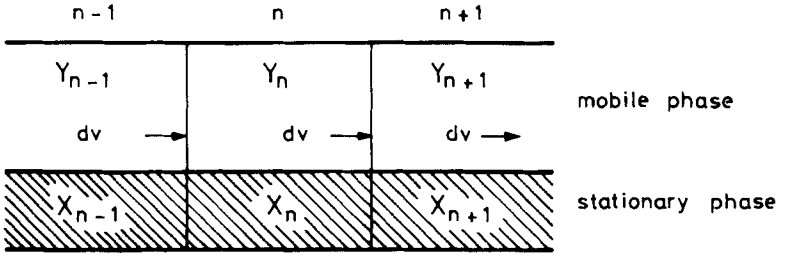

FIG. 2. Distribution of solute concentration on the nth theoretical plate.

$$Y_0 = \text{constant (feed concentration)} \tag{6}$$

Substituting the boundary condition of $Y_1^\circ = 0$ at $V = 0$, and solving for Y_i from Plate 1 to Plate N for each plate, the following deposition equation is obtained:

$$Y_N = Y_0\left(1 - \sum_{r=0}^{N-1} \frac{(aV)^r}{r!} e^{-aV}\right) \tag{7}$$

At the beginning of the elution process, the initial concentration of the solute on the nth plate is Y_n° and the mobile phase enters Plate 1 without solute. With these boundary conditions, solving Eq. (2) gives

$$Y_N = \sum_{r=1}^{N} Y_r^\circ \frac{(aV)^{N-r}}{(N-r)!} e^{-aV} \tag{8}$$

The following assumptions should be added for the moving feed-injection system in addition to the assumptions made for the preparative case.

1. The feed pulse injected to the column at one feed port moves independently from those injected at other feed ports.
2. The height equivalent to a theoretical plate (HETP) remains constant regardless of the position of the feed-injection port.

With these assumptions, the outlet concentration can be calculated by summing a series of solutions obtained for a single pulse of feed as shown in Fig. 3. The numbers 1, 2, and 3 in the figure indicate sequential feed ports.

The theoretical plate model can then be used to predict the concentration profile and to determine the operating conditions for the moving feed-injection system.

RESULTS AND DISCUSSION

The chromatographic system for simulation had a total column length of 260 cm and the feed-injection ports were positioned 26 cm apart. The partition coefficients for the two components, DEE and DCM, were obtained from Moon et al. (*12*).

In elution chromatography, the number of theoretical plates N is defined as (*13*)

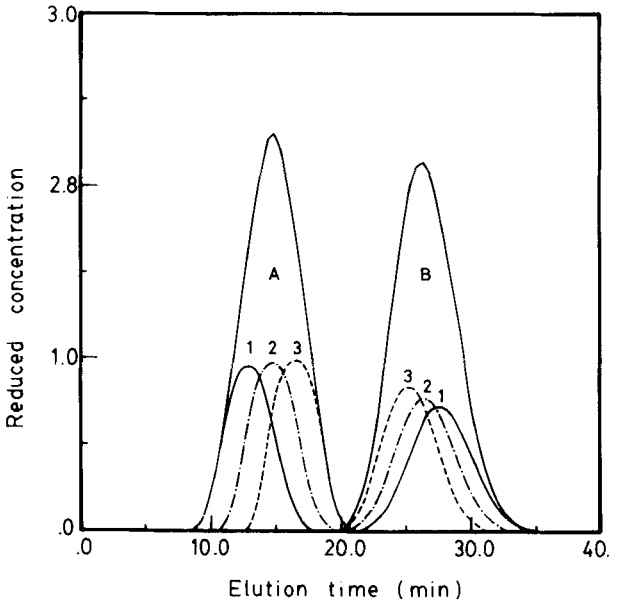

FIG. 3. Solution of the model for moving feed-injection chromatography. (1, 2, and 3 indicate the numbers of sequential feed ports.)

$$N = 16(t_R/w)^2 \tag{9}$$

where t_R is the distance from injection to peak maximum and w is the length of the base line cut by the two tangents of the peak.

Concentration profiles for preparative and moving feed-injection chromatography were obtained by using Eqs. (7) and (8). Figure 4 illustrates concentration profiles for preparative cases with different feed-injection durations. As the feed-injection time becomes larger, the top of the elution profile becomes flatter at a reduced concentration value of 1.0. This seems to be the result of the plug-wise feed injection profile and the simplified assumptions used for the model. In the moving feed-injection case, however, the flattened top does not occur.

A comparison between the elution profiles of the preparative and moving feed-injection caess is shown in Fig. 5. The advantages of the latter can be clearly seen in that it has narrower bandwidths, better resolution, and a higher peak maximum. Improvements in the moving feed-injection system are due to such operation characteristics as a

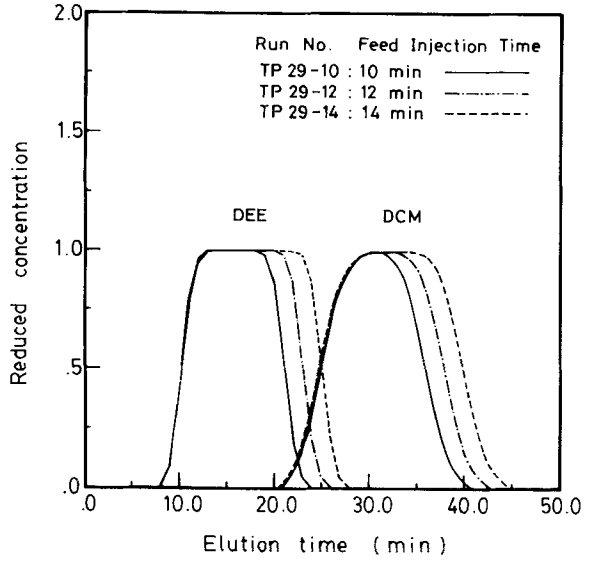

FIG. 4. Comparison of chromatograms for conventional preparative chromatography with sample sizes.

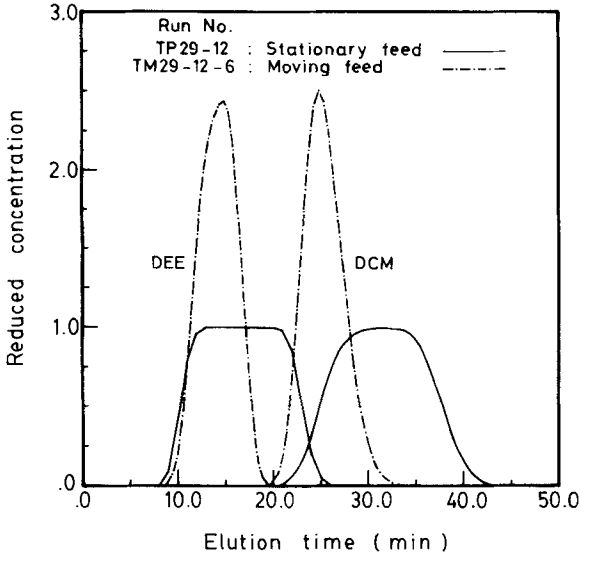

FIG. 5. Comparison between elution profiles of conventional preparative and moving feed-injection systems with equal feed time of 12 min.

smaller intermixing zone of the components, a shorter distance for the solutes to travel in the column, and the superposition of pulses injected to the column at each feed port which leads to a higher outlet concentration.

In Fig. 6, for Run TM29-12-4 in which U_F approaches the velocity of the slower component DCM, the component has a narrower bandwidth and a higher peak maximum than does DEE. For Run TM29-12-8, the situation is reversed. As shown in Figs. 6 and 7 (see also Table 1), this system is very flexible in its operation; that is, the outlet concentrations, bandwidths, and resolution of the components can be controlled by changing the velocities of the moving feed ports.

Resolution and impurity were used as measures of separation of the two components. Resolution is commonly defined as (*14*)

$$R = \frac{2d}{w_1 + w_2} \tag{10}$$

where d is the distance between the maxima of two adjacent peaks, and w_1 and w_2 are the lengths of the base lines cut by the two tangents of each

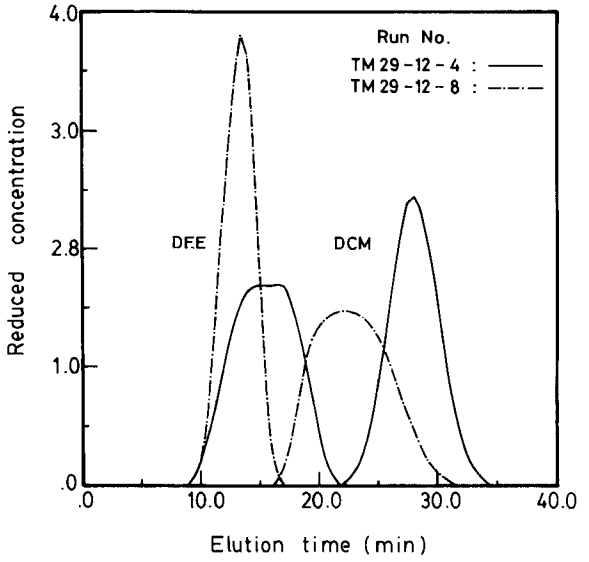

FIG. 6. Effect of U_F on elution profiles for the moving feed-injection system. (TM29-12-4; U_F = 8.7 cm/min, TM29-12-8; U_F = 17.3 cm/min.)

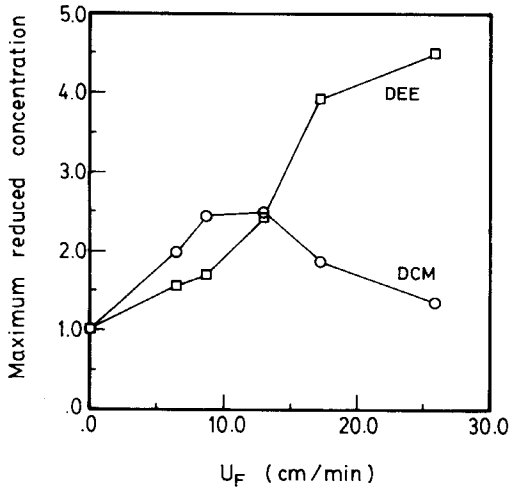

FIG. 7. Effect of U_F on maximum reduced concentration for total feed time of 12 min (column temperature = 29°C).

TABLE 1
Feed Injection Time to Each Port (in minutes)

Run[a]	U_F (cm/min)[b]	Number of feed ports							
		1	2	3	4	5	6	7	8
TP29-12	0	12							
TM29-12-3	6.5	4	4	4					
TM29-12-4	8.7	3	3	3	3				
TM29-12-6	13.0	2	2	2	2	2	2		
TM29-12-8	17.3	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

[a]The run number consists of four or five groups of letter: the first character, "T," means "theoretical" calculation; the second character, "P" or "M," represents "conventional preparative" or "moving feed-injection system"; the third and fourth groups indicate the temperature (°C) and the total feed-injection time (minute); and the fifth group, if any, denotes the number of feed ports or the number of divided feed pulses. For example, TM29-12-3: T = theoretical, M = moving feed-injection system, 29 = column temperature of 29°C, 12 = total feed-injection time of 12 min, 3 = number of feed ports.

[b]The velocity of the feed port, U_F, is calculated as follows for Run TM29-12-3:

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

peak. The extent of the superposition of the two elution profiles is not shown clearly by resolution alone. Impurity may be introduced as a measure of separation when the two adjacent peaks are superposed and is defined as (see Fig. 8)

$$\eta = \frac{\Delta A_1 + \Delta A_2}{A_1 + A_2 - \Delta A_1 - \Delta A_2} \times 100\,(\%) \tag{11}$$

where A_1 and A_2 are the areas of the peaks of Components 1 and 2, respectively. Figure 9 shows that there is a optimum feed port velocity around the average value of the velocities of the two components with respect to the resolution and the impurity. These values, however, do not always have the same trend with changes in U_F. For Run TM29-12-4 (U_F = 8.7 cm/min) and Run TM29-12-6 (U_F = 13.0 cm/min), the impurity of the latter is zero, but its resolution is worse than that of the former. This is because the increase in U_F around these values shortens the distance between the two peak maxima and hence results in decreased resolution, regardless of the impurity. When U_F becomes too high, the resolution and the impurity get worse again. Lower values of U_F have the same results.

The effect of the number of feed-injection ports at a given U_F should also be considered. The efficiency of the system is improved as the number of feed ports increases (see Fig. 10 and Table 2). Ultimately, when the feed port is moved continuously up the column as feed is added, the best separation is achieved.

The effects of column temperature are illustrated in Figs. 11 and 12. The impurity increases sharply with temperature. The velocities of the

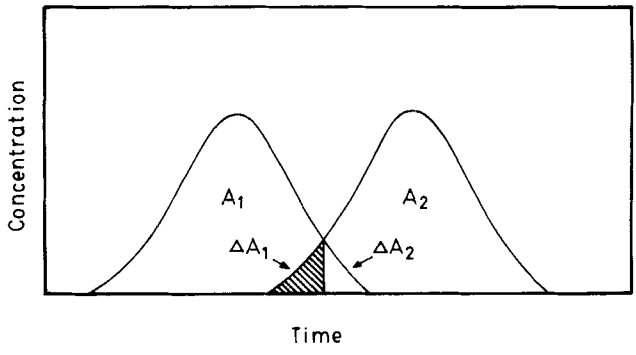

FIG. 8. Overlap of elution profiles.

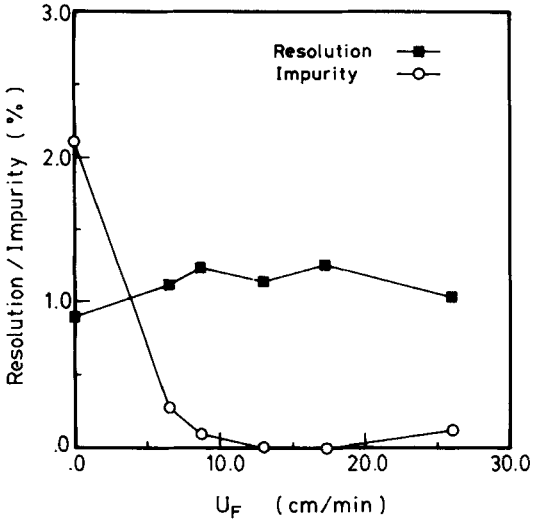

FIG. 9. Effect of U_F on resolution and impurity for total feed time of 12 min (column temperature = 29°C).

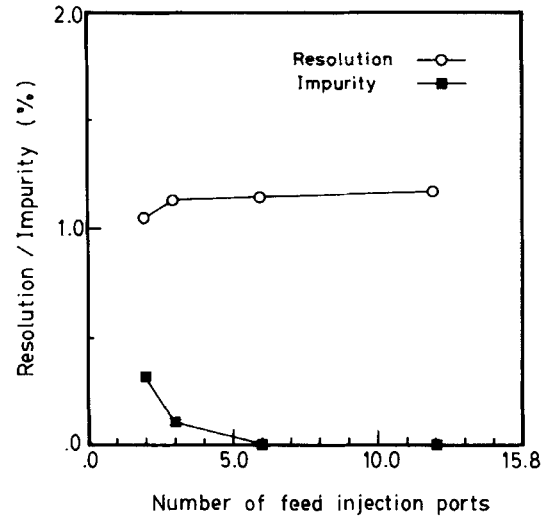

FIG. 10. Effect of number of feed-injection ports on resolution and impurity for total feed time of 12 min (U_F = 13.0 cm/min, column temperature = 29°C).

TABLE 2
Feed Injection Time to Each Port (in minutes)

Run	U_F (cm/min)	Number of feed ports											
		1		2		3		4		5		6	
TM29-12-2F	13.0	6						6					
TM29-12-3F	13.0	4				4				4			
TM29-12-6	13.0	2		2		2		2		2		2	
TM29-12-12[a]	13.0	1	1	1	1	1	1	1	1	1	1	1	1

[a]For Run TM29-12-12, the distance between any two adjacent feed port is reduced by half, i.e., 13 cm, compared to those of the other runs.

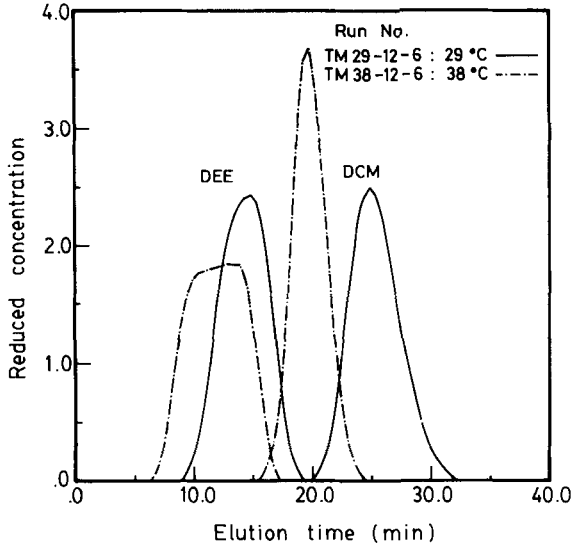

FIG. 11. Effect of column temperature on elution profiles (U_F = 13.0 cm/min).

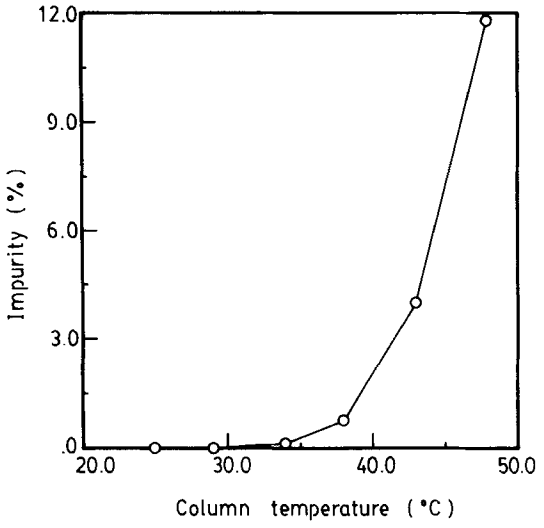

FIG. 12. Effect of column temperature on impurity (U_F = 13.0 cm/min).

components in the column increase with column temperature, as shown in Table 3. When the feed port velocity is constant, an increase in the temperature has an effect similar to decreasing U_F at a fixed temperature. At a lower temperature, retention time becomes longer with a higher resolution. However, when the temperature is above the boiling points of the components, the resolution becomes worse. Therefore, the appropriate choice of column temperature for a given chromatographic system ensures better resolution.

CONCLUSIONS

A moving feed-injection chromatographic system was compared with the conventional preparative case, and the characteristics of the system were studied by using the theoretical plate model.

Moving feed-injection chromatography proved to have some advantages over the preparative system: improved resolution and reduced impurity, narrower bandwidths, and higher outlet concentration. Moreover, the system is flexible in that the achievement of the separation can be adjusted by changing the velocities at the feed-injection port, U_F. The

TABLE 3
Average Velocities of Each Component

Temperature (°C)	Average velocity (cm/min)	
	DEE	DCM
25	22.4	9.0
29	26.7	10.6
34	32.5	13.2
38	37.8	15.0
43	47.0	18.7
48	53.4	21.8

feed port velocity has an optimum value with respect to better resolution and minimum impurity. Beyond the optimum value, resolution is worse.

Column temperature has a large effect on resolution, and the separation of mixtures was better around the temperature of the boiling points of the components. The number of ports for feed-injection also had an effect on resolution, even though the feed port velocity was constant. These predictions were confirmed by experiments, and these will be reported in a separate paper.

SYMBOLS

A_1, A_2	area of peak
a	constant equal to $1/(v_m + Kv_s)$
d	distance between the two peak maxima (cm)
K	partition coefficient
L	total length of the chromatographic beds (cm)
N	the number of theoretical plates
R	resolution defined by Eq. (10)
t_R	distance from injection to peak maximum (cm)
U_A, U_B	average solute velocity of component in the column (cm/min)
U_F	feed port velocity illustrated in Table 2 (cm/min)
V	volume of the mobile phase (cm^3)
v_m	void volume in a plate (cm^3)
v_s	volume of stationary phase in a plate (cm^3)

w	length of the base line cut by the two tangents of the peak (cm)
X_n	concentration of solute in the stationary phase (mol/L)
Y_i°	initial concentration of solute in the mobile phase on the ith plate (mol/L)
Y_n	concentration of solute in the mobile phase (mol/L)
Y_0	feed concentration (mol/L)
η	impurity defined by Eq. (11)

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