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A Plate Model for Moving Feed-Injection Chromatography. II. Experimental Results

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Abstract

Operational characteristics of a moving feed-injection system were studied for separation of diethyl ether (DEE) and dichloromethane (DCM) by gas-liquid chromatography. The experimental data were compared with the results obtained by the theoretical plate model. As anticipated from the theoretical work, moving feed-injection chromatography had some advantages over the conventional preparative case. Its operation was flexible, the bandwith was decreased by 20%, and peak maximum was increased as much as two times. The theoretical plate model, which assumed linear partition isotherm, instantaneous equilibrium, and constant flow rate through the column, was observed to be in relatively good agreement with the experimental results, and it could be used as a powerful predictive tool for determining optimum operating conditions of the moving feed-injection system.

INTRODUCTION

Chromatographic separation is a good method to obtain materials of high purity. Over the past 30 years much effort has been made to increase the throughput capabilities of chromatographs.

To date, scale-up of chromatographic systems has consisted mainly in using large diameter columns and injecting proportionally large samples into these columns. However, a number of factors restrict the usefulness of this mode of operation (*1*). Another approach is to have a continuous

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chromatography based on countercurrent flow (*2, 3*). The most popular continuous chromatographic process is the SORBEX process (*4*). More recently, Barker and Chuah (*5*) reported a semicontinuous chromatographic separation technique for the two monosaccharides.

An alternate method for improving the efficiency of preparative chromatography is the moving feed point system developed by Wankat (*6*). The technique uses a feed-injection port which moves at a velocity U_F up the column during the time of feed injection while solvent or carrier gas is continuously fed at the same port of the column.

This work reports on a moving feed-injection system of gas-liquid chromatography used for the separation of a mixture of diethyl ether (DEE) and dichloromethane (DCM). Experimental results are discussed and compared with the simulation results obtained from previous work (*7*).

EXPERIMENTAL

Figure 1 is a schematic diagram of the moving feed-injection system used. The chromatographic column consisted of 10 segments connected in series. Each segment was made of stainless steel and had a 10-mm inner diameter and a 26-cm packed length. The packing material was 20/30 mesh Chromosorb A loaded with 20% dinonylphthalate as a stationary liquid phase.

The operating conditions are listed in Table 1. Switching of the feed-injection position was done automatically with solenoid valves controlled by a specially designed microprocessor.

The feed was a mixture of DEE and DCM, whose boiling points are 34.6 and 39.8°C, respectively. Nitrogen was used as the carrier gas, and the outlet products were analyzed by analytical gas chromatography (Gow Mac 550P TCD) through 10 port sampling valves (Valco Instrument Co.).

In this experiment the liquid feed mixture was placed in a chamber and a stream of N_2 was passed through the chamber. The mixture was then vaporized with the carrier gas, and they were fed into the column. This method resulted in an approximately plug-wise injection profile. The carrier gas and the feed stream passed through preheaters in order to prevent condensation and to attain the desired temperatures. The chromatographic beds were confined in a steel enclosure with an interior electric heater so the column temperature could be controlled.

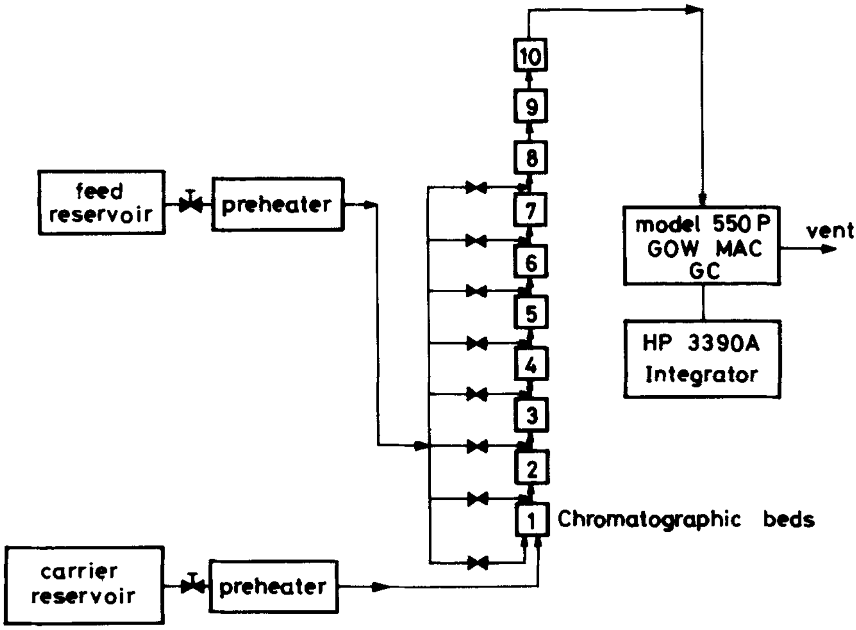

FIG. 1. Schematic diagram of experimental apparatus.

RESULTS AND DISCUSSION

In Part I of this series (*7*) the theoretical plate model was developed with the assumptions of instantaneous equilibrium of the solutes between the gas and liquid phases, a linear partition isotherm, and a constant flow rate of the mobile phase, and the characteristics and separation conditions of the moving feed-injection chromatography were investigated. Experiments on the moving feed-injection and conventional preparative system were performed for this paper, and these were compared with the theoretical results.

The number of theoretical plates of the chromatographic column used in this work are listed in Table 2. They were calculated from the equation in the table footnote. The number of plates decreased with sample size and column temperature.

Figures 2 and 3 show chromatograms for moving feed and conventional preparative cases with equal times of feed injection. The feed port velocity of the conventional system is equivalent to $U_F = 0$. The superiority of the moving feed-injection system to the conventional case is well demonstrated in these figures; that is, the former has much higher peak

TABLE 1
Experimental Conditions[a]

Run	Temperature (°C)	U_F (cm/min)	Number of feed port[b] 1	2	3	4	5	6	7
EP29-10	29	0	10						
EP29-10-7	29	17.3	1.5	1.5	1.5	1.5	1.5	1.5	1
EP29-14	29	0	14						
EM29-14-7	29	13.0	2	2	2	2	2	2	2
EP29-12	29	0	12						
EM29-12-6	29	13.0	2	2	2	2	2	2	
EM29-12-4F	29	17.3	3		3		3		
EP34-12	34	0	12						
EM34-12-6	34	13.0	2	2	2	2	2	2	
EP43-12	43	0	12						
EM43-12-6	43	13.0	2	2	2	2	2	2	

[a]Carrier velocity during deposition process = 464.10 cm/min; during elution process = 427.35 cm/min. Feed concentration: For DEE = 2.829×10^{-4} mol/L; for DCM = 1.950×10^{-4} mol/L.
[b]Time of feed injection to each port is in minutes.

TABLE 2
Number of Theoretical Plates

Run	Feed time (min)	Temperature (°C)	Number of plates[a]	
			DEE	DCM
EP29-04	4	29	113	170
EP29-10	10	29	31	69
EP29-12	12	29	18	42
EP34-12	12	34	18	42
EP43-12	12	43	15	28
EP29-14	14	29	17	37

[a]The number of theoretical plates is commonly defined as $N = 16(t_R/w)^2$, where t_R is the distance from injection to peak maximum, and w is the length of the baseline cut by two tangents.

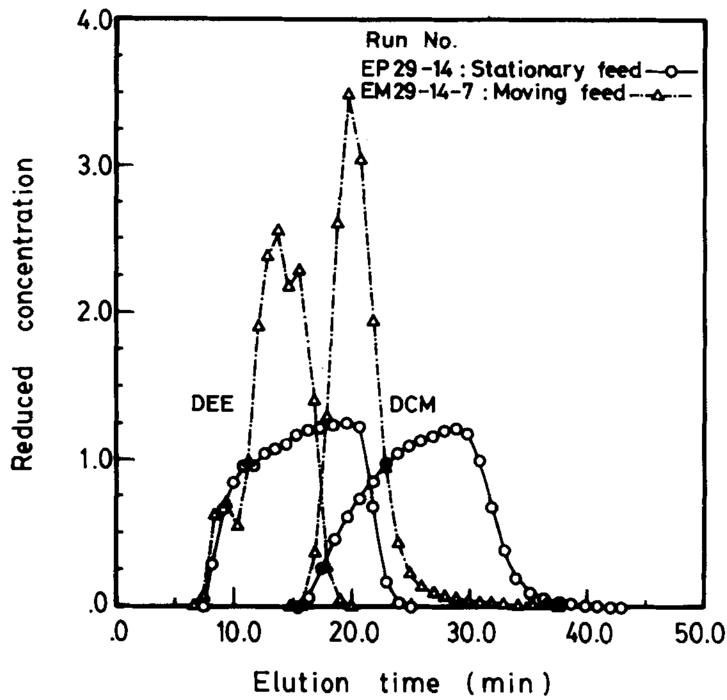

FIG. 2. Comparison of elution profiles for conventional preparative and moving feed-injection systems with a total feed time of 14 min.

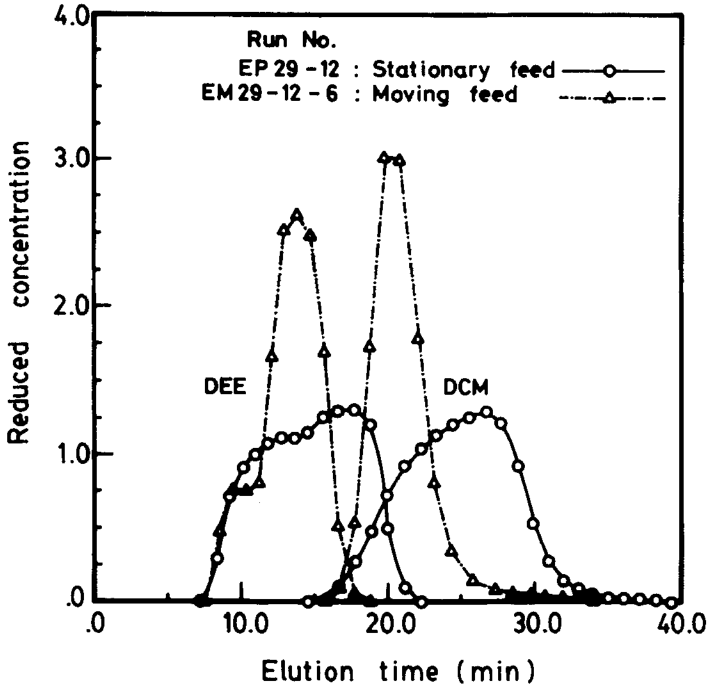

FIG. 3. Comparison of elution profiles for conventional preparative and moving feed-injection systems with a total feed time of 12 min.

maxima, better resolution, and narrower bandwidths. The decrement in total bandwidth of the moving feed system compared to the conventional case is no more than 20%, which is a little less than the value predicted by the theoretical model. This is because the elution peak of the slower component, DCM, has a large trailing edge, due mainly to the effects of the large sample size and temperature change in the column (*8, 9*). Even so, the decrement in total bandwidth ensures the increased throughput capability of this system.

To achieve better separation, the feed port velocity should be between the velocities of the two components in the column. With this limitation in U_F, however, the moving feed-injection system has an operational flexibility such that the shape of the elution profile of each component (i.e., bandwidths, maximum concentrations, and retention times) can be easily controlled by adjusting the feed port velocity as shown in Fig. 4. This was also predicted in Part I of this work.

It was theoretically shown that better resolution would be obtained by using a larger number of feed ports. In the actual system there are some

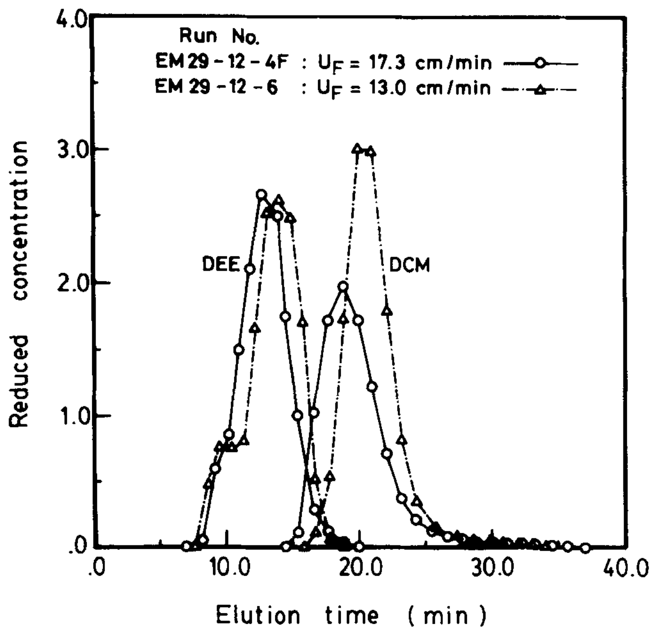

FIG. 4. Comparison of elution profiles for a total feed time of 12 min.

problems in increasing the number of feed ports because of increasing the undesirable dead volume between segments of the column, which might lessen column efficiency. Therefore, an optimum number of the feed ports with respect to column efficiency might exist.

When the column temperature was increased, the partition coefficients of the components had lower values and the components moved faster in the column. Therefore, increasing the column temperature at a fixed U_F and carrier velocity, as shown in Fig. 5, resulted in a relatively sharp peak in the chromatogram for the slower moving component, DCM.

The velocity of each component in the column was directly related to column temperature and carrier velocity for a given system. When feed is injected into the column through only one feed port at a time, there is a limit to the increase of feed port velocity. Therefore, the column temperature and the carrier velocity should be carefully chosen so that the feed port velocity is between the velocities of the two components.

According to the results obtained by Moon et al. (*10*) who used an analytical gas chromatographic column (1/8 in. × 2 m) packed with the same material used in this work, DEE and DCM have Langmuir-type

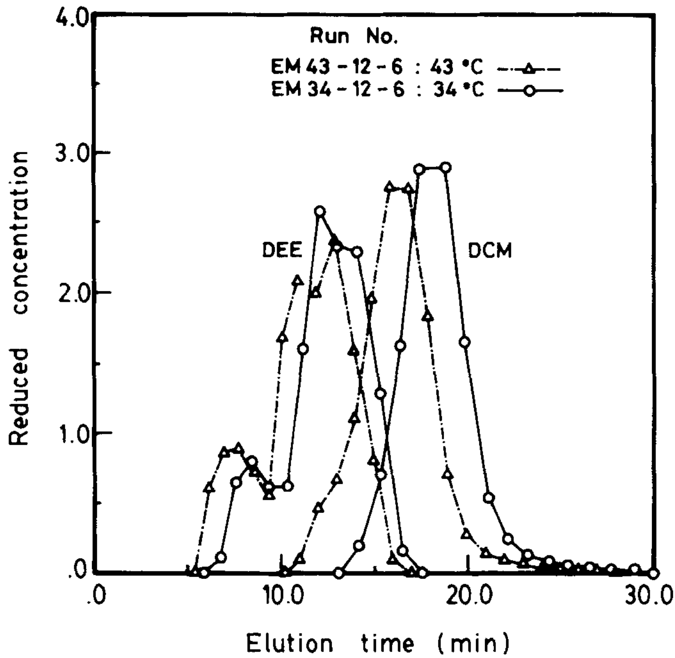

FIG. 5. Effect of column temperature on elution profiles (U_F = 13.0 cm/min).

concentration profiles for large sample sizes. However, as shown in Figs. 2, 3, and 6, elution profiles for conventional preparative case differed from those of Moon's experiment. The differences may arise from the type of feed injection profile used, which in this work was plug-wise.

Figure 6 compares the experimental profiles for the conventional case with the results of simulation. The simulated profiles of the two components have flattened tops at reduced concentrations equal to 1.0, which may occur for a large plug-wise sample charge due to the linear partition coefficient and instantaneous equilibrium in the model. The corresponding experimental profiles, however, do not have flattened tops, and their peak maxima are larger than the reduced concentration of 1.0. The experimental and simulated elution profiles show some deviations. This is also the case for the moving feed-injection system (Fig. 7). However, in spite of the deviations found between experimental and simulated elution profiles, the theoretical results are in relatively good agreement with the experimental data. Hence, the model can be used as a fairly good estimation of optimum operating conditions for moving feed-injection chromatography.

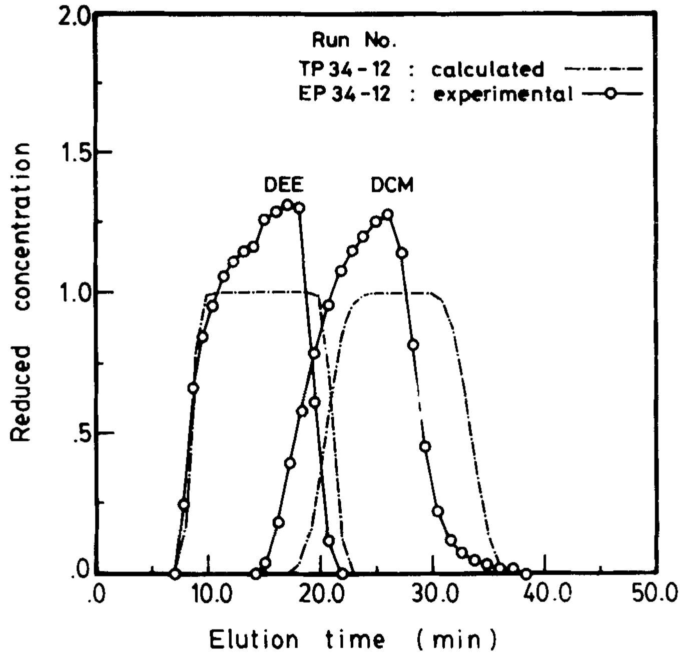

FIG. 6. Comparison of experimental and calculated elution profiles for conventional preparative chromatography.

The reason for discrepancy between experimental and simulational results could originate from the concept of a theoretical plate itself. The model cannot be intrinsically met exactly in a real chromatographic system (*11*). In addition, the assumption that mobile phase velocity remains constant throughout the column cannot be correct because variations in solute concentration along the length of the chromatographic column are necessarily accompanied by changes in the velocity of the mobile phase (*12–14*). When the solute concentration is increased, the process in the column becomes more complex, and the chromatographic behavior is determined by the interplay of three major effects: the isotherm, the sorption, and the diffusion effects (*15, 16*).

Nevertheless, for a fairly good prediction, the plate model is very useful for investigating the characteristics and the operating conditions of the moving feed-injection system. Further work is required to establish a more realistic model.

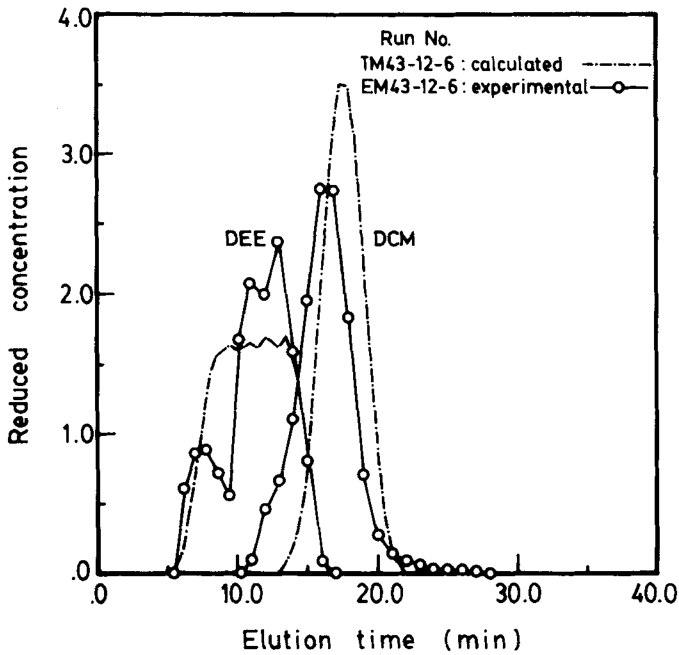

FIG. 7. Comparison of experimental and calculated elution profiles for the moving feed-injection system.

CONCLUSIONS

As expected from theoretical work with the plate model, experimental results compared with those of a conventional preparative system showed that the moving feed-injection system had up to 85% decreased impurity, a peak width as much as 20% less, a maximum concentration as much as twice as large, and operational flexibility.

However, the total retention time required for the trailing edge of the slower component to be eluted out was longer than expected, which may be reduced by variation of the carrier velocity. Operating column temperature should be chosen carefully. For a given set of operating conditions, a temperature as little as 5°C below the boiling point of the less adsorbed component, DEE, gave the best results. Elution profiles obtained by the model deviated somewhat from experiment, especially for the slower moving component, DCM. Such assumptions in this model as instantaneous equilibrium, constant mobile phase velocity, and linear partition isotherm are valid only for very dilute systems. However, because of its simplicity, our model has value for making fairly good predictions in determining the operating conditions of this system.

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