Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Separation of Close-Boiling Components Using a New Chromatographic Method

K. H. Row[a]; W. K. Lee[a]
[a] Department of Chemical Engineering, Korea Advanced Institute of Science and Technology Dongdaemun, Seoul, Korea

To cite this Article Row, K. H. and Lee, W. K.(1987) 'Separation of Close-Boiling Components Using a New Chromatographic Method', Separation Science and Technology, 22: 7, 1761 — 1777
To link to this Article: DOI: 10.1080/01496398708058433
URL: http://dx.doi.org/10.1080/01496398708058433

SEPARATION SCIENCE AND TECHNOLOGY, **22(7)**, pp. 1761-1777, 1987

Separation of Close-Boiling Components Using a New Chromatographic Method

K. H. ROW and W. K. LEE*

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

Abstract

A combined continuous and preparative system of gas-liquid chromatography was developed and used for the separation of the close-boiling components diethyl ether and dichloromethane. In this system the less-absorbed component in the mixture can be obtained continuously in an almost pure state in one section and the remaining components can be separated in the other section of the column. Several experimental conditions (e.g., column length, particle size, feed concentration, and flow rates of carrier gas and desorbent) were varied in order to evaluate their effects on the performance of the chromatographic system. From the results of the experiments, additional column length and desorbent velocity were found to be the most important factors in separating the feed mixture continuously. The optimum switching time for good separation was experimentally measured, and it was mainly affected by column temperature and column length if the feed mixture and stationary phase were fixed. Throughputs of between 5 to 10 cm^3/h resulted in good purity under certain experimental conditions.

INTRODUCTION

In response to the need for fast and accurate separation, various methods have been developed. One of the most powerful processes among them is chromatography.

In 1952, James and Martin (*1*) introduced gas-liquid chromatography which is based on differences in the partition coefficients of substances

*To whom correspondence should be addressed

distributed between a stationary liquid phase and a mobile phase (*2*). The advantages of conventional gas chromatography are the speed of analysis and the simplicity of detection (*3*), but it is inherently difficult to scale up to industrial size because conventional chromatography uses the batch method for handling the feed mixture as a pulse and requires substantial dilution of the components with the mobile phase (*4*).

After the introduction of the UOP process (*5*), however, considerable progress has been made toward separation using continuous chromatography. Barker et al. (*6*) developed a semicontinuous countercurrent refiner (SCCR) for dextran fractionation. In previous papers (*7, 8*), we investigated moving feed-injection chromatography. Reviews of chromatography as a preparative process or on a production scale have been made by Barker (*9*) and Sussman (*10*).

In this paper a new separation method is introduced in which feed mixtures (binary) are separated continuously by the combined operation of continuous and preparative chromatography in two sections (partition and desorption). Although the system is equipped with segmented columns and the less-absorbed (less-adsorbed) component can be obtained in pure form in the partition (adsorption) section as well as in other continuous systems, the remaining components can also be separated in the desorption section by changes of such operating conditions as column length and desorbent velocity. In the UOP process, part of the more-absorbed component was directed from the desorption zone into the rectification zone in which displacement of the less-adsorbed component occurred. The displacement method has limited applicability compared to the much greater flexibility offered by the gas-liquid technique. A purge section was used in the SCCR unit to obtain the more-absorbed component, while in this system several columns are added in the desorption section to separate the noneluted components. The effects of various experimental conditions on the performance of the system are discussed.

OPERATIONAL PRINCIPLES OF THE SYSTEM

As a feed mixture is injected into the column, the less-absorbed component is eluted initially by the solubility difference of the feed mixture and the stationary liquid phase. After a while, as the more-absorbed component begins to be eluted, components whose compositions are the same as the feed mixture come out of the column. As seen in Fig. 1, the less-absorbed component exists as a pure product for a time (the shaded section of the figure).

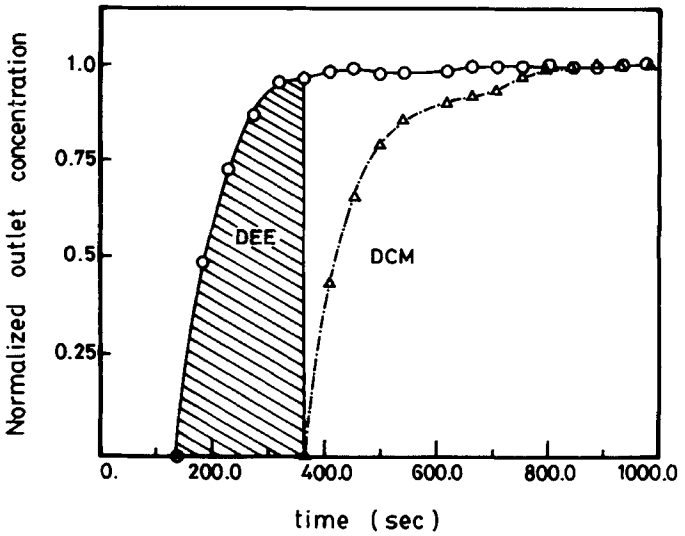

FIG. 1. Elution profile in case of step input. 45/60 mesh; 35°C; average gas velocity = 7.69 cm/s; column length = 150 cm; feed concentration, DEE = 0.72×10^{-3} mol/L, DCM = 0.69×10^{-3} mol/L.

If the column in the system is divided into two sections, the less-absorbed component can be obtained in pure form before the elution of the more-absorbed component in one of the partition section. During that time, in the desorption section, the less-absorbed component remaining in the column with the more-absorbed component can be separated by adjusting the column length and the desorbent velocity.

If the above two steps can be completed simultaneously within a certain time (switching time), the feed mixture can be separated continuously. The switching time is varied by combinations of the stationary liquid and the feed mixtures. In the desorption section the remaining components are separated within the switching time by changes of the operating conditions.

Figure 2 shows the arrangement of segmented columns and solenoid valves in the equipment. During operation, two streams, carrier gas with feed and desorbent, enter the system, and are withdrawn through the partition and desorption sections.

For example, the partition section consists of four columns and the desorption section of eight columns. During the first switching time, the feed mixture is continuously injected into the inlet of Column 1, and the less-absorbed component is obtained in pure form at the outlet of

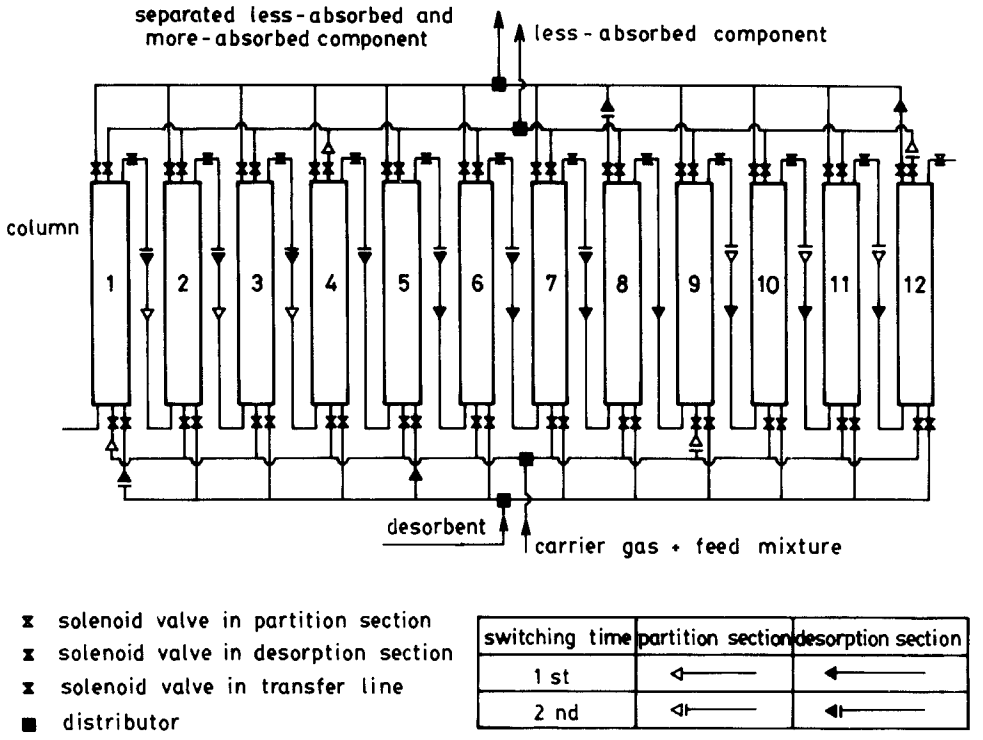

FIG. 2. Schematic diagram of flow path in partition section and desorption section.

Column 4. Just before the elution of the more-absorbed component, within the second switching time the feed mixture is injected in the inlet of Column 9. Columns 1–8 are the desorption section, and at the outlet of Column 8 the remaining less-absorbed component and the more-absorbed components are obtained separately within the switching time.

The system is a binary separation process which, by careful selection of stationary liquid phase and operating conditions, can be extended to various feed mixtures.

EQUIPMENT

A general view of the system is shown in Fig. 3. A schematic diagram of the overall experimental apparatus is shown in Fig. 4. Nitrogen was used

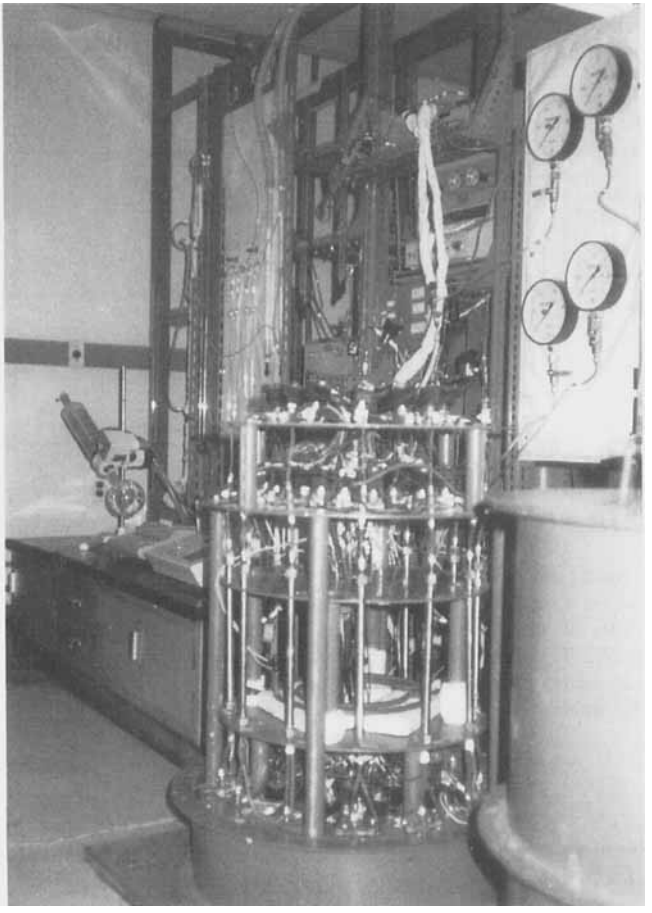

FIG. 3. Photograph of the chromatographic unit.

as the carrier gas and the desorbent, and the flow rates were controlled by microneedle valves (A_4, A_5).

The feed reservoir C was made of stainless steel, 6 cm i.d., 50 cm high, and filled with ⅛ and ½ in. ceramic Raschig rings to enlarge the interfacial area between the carrier gas and the liquid feed mixtures.

Twelve columns were arranged in a circle. Each column was made of stainless steel, 1 cm i.d., 30 cm high, with a packed height was 25 cm. Glass wool was used in both ends of the column to retain solid particles in place. Each column had four openings, two for entering streams and

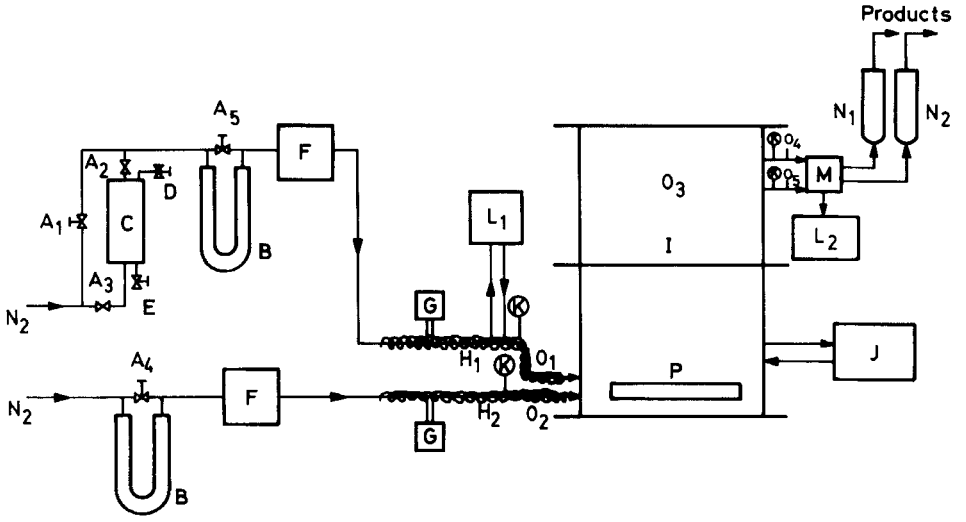

FIG. 4. Schematic diagram of experimental apparatus. A_1, A_4, A_5: microneedle valves. A_2, A_3: solenoid valves. *B*: manometers for adjustment of flow rates. *C*: feed reservoir. *D*: inlet of feed. *E*: outlet of feed. *F*: preheaters for carrier gas and desorbent. *G*: temperature controllers. H_1, H_2: heating wires. *I*: main chromatographic system. *J*: programmable controller. *K*: pressure gauges. L_1, L_2: gas chromatographs. *M*: multifunctional sampling valve. N_1, N_2: bubble flow meters for carrier gas and desorbent. O_1-O_5: thermocouples. *P*: electric heater.

two for leaving streams. The system was covered with ceramic insulation to keep the column temperatures constant.

Five solenoid valves (CKD, AB 31-01-4) were used per column. The detailed arrangement of the main chromatographic columns (*I*) is shown in Fig. 2. A supporter was made to fix the 12 columns, 60 solenoid valves, and four distributors, and it was enclosed to maintain the desired temperature. Two distributors were for entering streams and two for leaving streams. The upper side of each distributor has one central bore, and the side of each distributor has 12 openings. The entering stream passes through the central bore and into one of the openings in the distributor.

An electric heater (*P*) in circular form was set in the inner side of the main system for easy temperature control. Two outlet streams and inlet feed mixtures were analyzed by conventional gas chromatography (Gow Mac 550P thermal conductivity detector, L_1 and L_2) with a syringe (Hamilton Co.) and a 10-port multifunctional sampling valve (Valco

Instruments Co., *M*). The signals were analyzed by a HP 3390A integrator. A programmable controller (*J*) was used to control the solenoid valves used for the main chromatographic system.

EXPERIMENTAL

The column was packed with Chromosorb A (Alltech Associates) whose particle sizes were 60/80, 45/60, and 20/30 mesh. A rotavapor (Brinkmann Co.) was used to coat dinonylphthalate on the particles, and the ratio of the stationary liquid to the solid support was 0.20 for all particle sizes.

Diethyl ether (DEE) and dichloromethane (DCM) were used as feed materials. Their boiling points are 37.8 and 34.6°C, respectively. One of the advantages of the chromatography over simple distillation is that separation can be done even in the case of small boiling point differences.

The feed mixture was put into the reservoir through the inlet valve (*D*) and drained through the outlet valve (*E*). With the solenoid valves A_2 and A_3 on, part of the nitrogen was passed into the feed reservoir (*C*). The concentration of the inlet feed mixture was controlled by adjusting the microneedle valve (A_1). Outlet flow rates were measured by the bubble flowmeters N_1 and N_2.

Lines of ⅛ in. copper tubing to the main system were wrapped with the heating wire (H_1) to prevent condensation of the feed materials in the carrier gas.

By the use of the programmable controller (*J*) the flow paths of the partition and desorption sections were programmed, and the paths automatically turned to the next stage after each switching time. The temperatures of several positions were read on the temperature indicator connected to the thermocouples (O_1-O_5). Pressure gauges (*K*) were set at the inlet and outlet of the main system.

The dead volume of the system was determined from measurement of the retention time of a helium sample. The results showed that the dead volume per column was about 31 cm^3 and that of the inlet and outlet lines was 10 cm^3. The elution profile from the data points in each experimental run was corrected for the total dead volume.

RESULTS AND DISCUSSION

The pressure drop sharply increased in the longer column with particles of 60/80 and 20/30 mesh; smaller particles caused a larger

pressure drop (Fig. 5). The velocity was changed as a consequence of pressure changes in the column. The average velocity indicated by the abscissa of Fig. 5 means the velocity corrected by the compressibility factor, $j = 3\{(P_i/P_o)^2 - 1\}/2\{(P_i/P_o)^3 - 1\}$, of James and Martin (*1*), where P_i and P_o denote the inlet and outlet pressures, respectively. A pressure drop of 30–90 cmHg was observed in the experimental range of this system.

The total elution volumes of the DEE and DCM mixture are plotted with the feed concentration and the column temperature in Fig. 6. The volume is the quantity of the gas which can elute the components completely in the column. Although the slope of the elution curve of DEE was low and that of DCM was high, the bandwidth of both components was observed to be wider with increasing feed concentration and decreasing column temperature.

In order to examine the applicability of this system over a wide range of operating conditions, the outlet concentrations of DEE and DCM were measured and the concentration profiles of the components in each experimental run were obtained. Experimental conditions of some runs in the partition section are listed in Table 1, in which the peak width (in seconds) is defined as the time from start to feed concentration.

Three different elution profiles with the three particle sizes in a

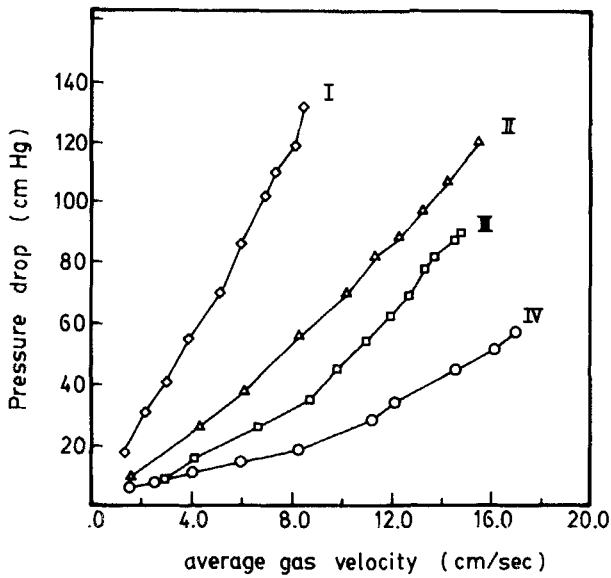

FIG. 5. Effect of average gas velocity on pressure drop. I = 60/80 mesh, column length = 200 cm; II = 60/80 mesh, 100 cm; III = 20/30 mesh, 200 cm; IV = 20/30 mesh, 100 cm.

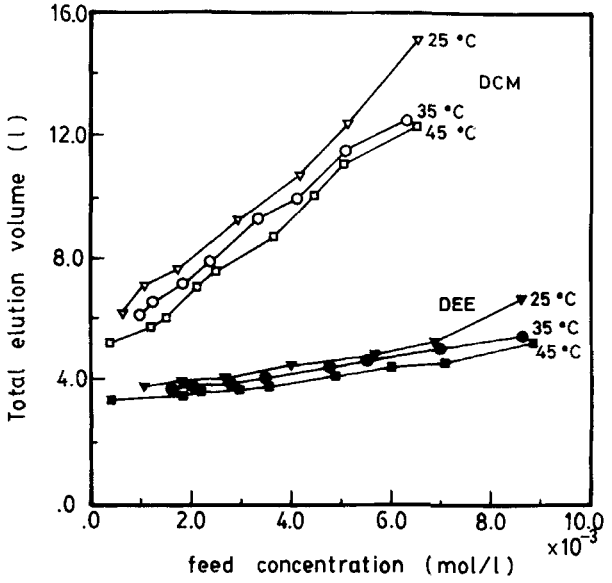

FIG. 6. Effect of feed concentration on total elution volume with column temperature. 20/30 mesh; average gas velocity = 9.53 cm/s; column length = 100 cm; 5 min of feed-injection time.

TABLE 1
Experimental Conditions in the Partition Section

	Run									
	1	2	3	4	5	6	7	8	9	10
Mesh size	20/30	45/60	60/80	60/80	60/80	60/80	20/30	20/30	20/30	20/30
Column temperature (°C)	45	45	45	45	45	45	45	35	35	35
Column length (cm)	100	100	100	150	150	150	150	150	150	150
Average carrier velocity (cm/s)	9.53	8.76	7.70	8.47	7.35	5.23	9.09	9.09	9.09	9.09
Feed concentration ($\times 10^{-3}$ mol/L):										
DEE	0.99	0.98	0.99	1.35	1.35	1.34	0.90	3.40	0.90	0.88
DCM	0.89	0.91	0.88	1.28	1.29	1.31	0.88	0.90	0.91	0.89
Peak width (s)	113.8	98.9	87.2	97.0	110.6	112.2	100.0	63.0	169.6	265.2

constant outlet velocity of 10.61 cm/s of carrier gas are shown in Fig. 7. The ordinate is the ratio of outlet to feed concentration. The compressibility factors for 20/30, 45/60, and 60/80 mesh sizes are 0.898, 0.826, and 0.726, respectively. It is also shown that the smaller particle had good column efficiency, but the larger pressure drop caused by them placed a limitation on the use of a high gas velocity.

Figures 8 and 9 show the effects of average carrier velocity and column temperature in the partition section, respectively. As the velocity increased, the slope of the leading edge in the profile became sharper. The column temperature is an important factor to be considered in the partition section because the partition coefficient is a function of temperature. The values of DEE were 184.2, 126.3, and 88.7, and for DCM were 437.1, 297.1, and 206.8 at 25, 35, and 45°C, respectively (*11*). Therefore, the separation factor of the two components was about 2.35. As the column temperature increased, the gas volume required for eluting the components became smaller. That is, as the products exit faster from the column, they are not completely separated. Figure 9 shows that in a higher concentration of DEE (3.40×10^{-3} mol/L) than of DCM ($0.20 \times$

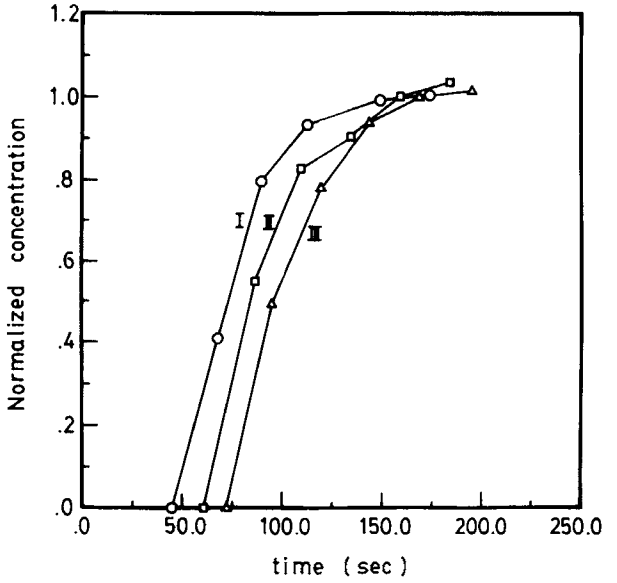

FIG. 7. Effect of particle size on elution profile in partition section. I = 20/30 mesh (Run 1); II = 45/60 mesh (Run 2); III = 60/80 mesh (Run 3); DEE.

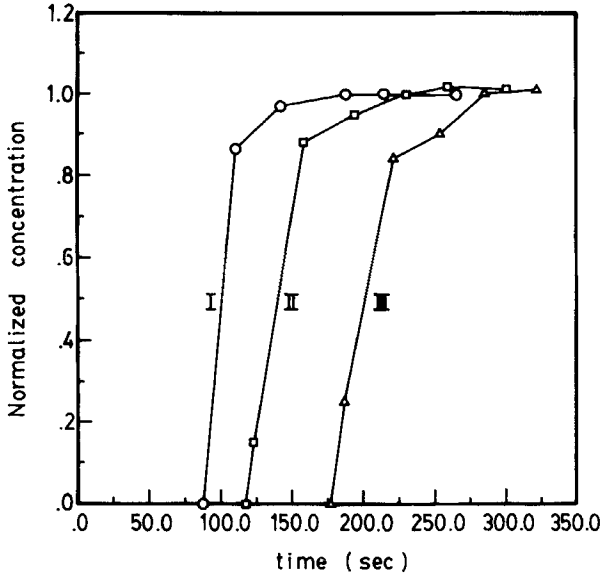

FIG. 8. Effect of average carrier velocity on elution profile in partition section. I = 8.47 cm/s (Run 4); II = 7.35 cm/s (Run 5); III = 5.23 cm/s (Run 6); DEE.

10^{-3} mol/L), the outlet concentration of DEE exceeded its inlet feed concentration.

The stationary liquid should generally be chosen to be as highly selective with the feed materials as possible. Once the system was determined, the switching time was measured as the elapsed time from start to just before the elution of the more-absorbed component, DCM. As seen in Table 2, the column temperature and the column length mainly affected the switching time. The experimental conditions of some runs in the desorption section are listed in Table 2 in order to understand the effects of unseparated DEE and DCM in the section. The impurity in the desorption section is defined by the ratio of the overlapped section to the total areas of two chromatograms.

The desorption section can be classified by whether or not an additional column length was used. Figures 10 and 11 show elution profiles in the desorption section without additional column lengths. Upon increasing the column length, the elution profile of DCM was more skewed. This is attributed to the larger pressure drop caused by a longer column length (*12*). Smaller particle size also shows lower impurity, as in Fig. 11. In the case of no additional column length, the impurities are

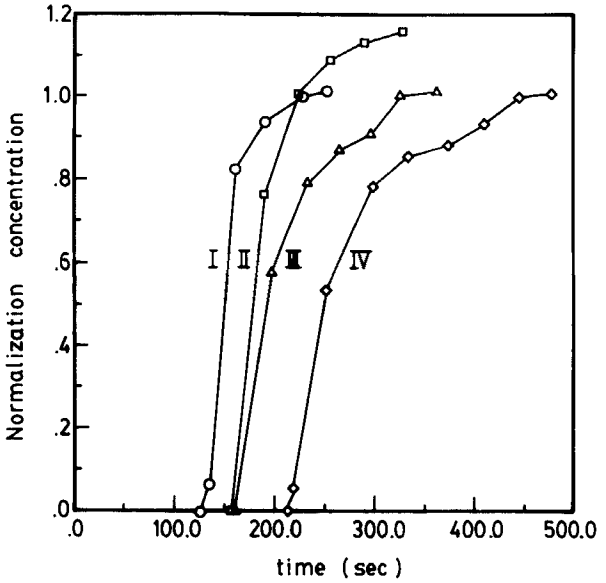

FIG. 9. Effect of column temperature on elution profile in partition section. I = 45°C (Run 7); II = 35°C (Run 8); III = 35°C (Run 9); IV = 25°C (Run 10); DEE.

rather serious. The additional column length is a unique factor to improve purity in the system. As shown in Fig. 12 with an increase in column length, better resolution was achieved but the process time exceeded the switching time of 240 s. The desorbent velocity was adjusted to overcome this difficulty. By increasing the desorbent velocity, the operation was continued with a switching time of 240 s (Fig. 13).

Based on the results of the experimental conditions in Run 18, a quantity of feed mixture between 5–10 cm^3/h was injected continuously into the system and pure DEE was obtained in the partition section, and DEE and DCM were almost completely separated in the desorption section.

The usefulness of the system depends mainly on a good selection of experimental conditions in the desorption section, i.e., the additional column length and the desorbent velocity. In the partition section the effect of the column temperature is important because the period when the less-absorbed component, DEE, exists in a pure state is determined by the temperature. Figure 14 shows that impurity was decreased by a lower temperature in the desorption section (see also Table 2).

One of the obvious advantages of this system is that the less-absorbed

TABLE 2
Experimental Conditions in the Desorption Section

	Run											
	11	12	13	14	15	16	17	18	19	20	21	22
Mesh size	45/60	45/60	60/80	45/60	20/30	20/30	20/30	20/30	20/30	20/30	20/30	20/30
Column temperature (°C)	35	35	45	45	35	35	35	35	45	35	35	35
Column length (cm)	100	150	100	100	100	100	100	100	150	150	150	150
Additional column length (cm)	0	0	0	0	25	75	100	100	50	50	50	50
Average desorbent velocity (cm/s)	12.41	10.22	13.03	12.62	19.40	19.83	18.53	21.87	14.46	16.65	14.97	17.92
Feed concentration ($\times 10^{-3}$ mol/L): DEE	0.92	0.94	0.94	0.98	0.61	0.45	0.85	0.84	0.64	0.68	3.40	3.40
DCM	0.70	0.75	0.78	0.82	0.57	0.46	0.78	0.82	0.73	0.77	0.20	0.20
Switching time (s)	240	360	180	180	240	240	240	240	270	240	360	360
Impurity (%)	28.7	18.3	13.1	18.6	12.0	3.9	1.6	1.87	12.6	8.64	8.75	15.24

component can be obtained as an almost pure product. Figure 15 shows that in the case of a higher concentration of DEE than of DCM, as the trailing edge of the less-absorbed component in the concentration profile was decreased, the leading edge of DCM in the profile was abruptly increased.

CONCLUSIONS

The combined continuous and preparative chromatographic separation of the close-boiling components diethyl ether (DEE) and dichloromethane (DCM) was experimentally performed. This system was characterized by segmented columns and solenoid valves controlled with a programmable controller.

The most important factors were additional column length and desorbent velocity. Rather larger particle sizes were preferred in order to

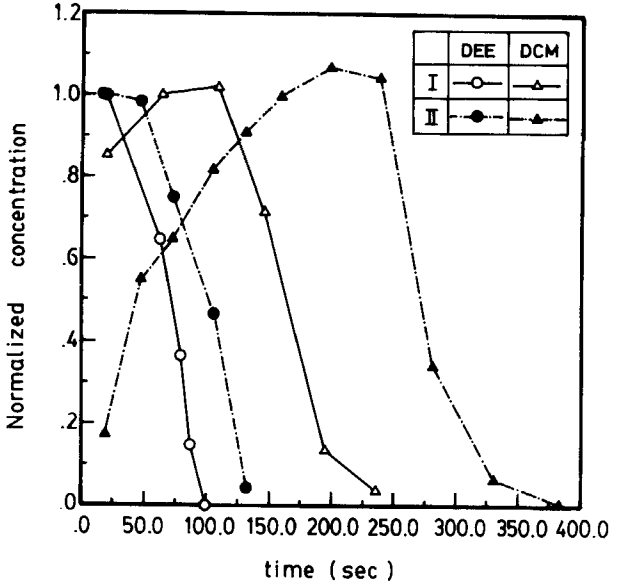

FIG. 10. Effect of column length on elution profile in desorption section. I = 100 cm (Run 11); II = 150 cm (Run 12).

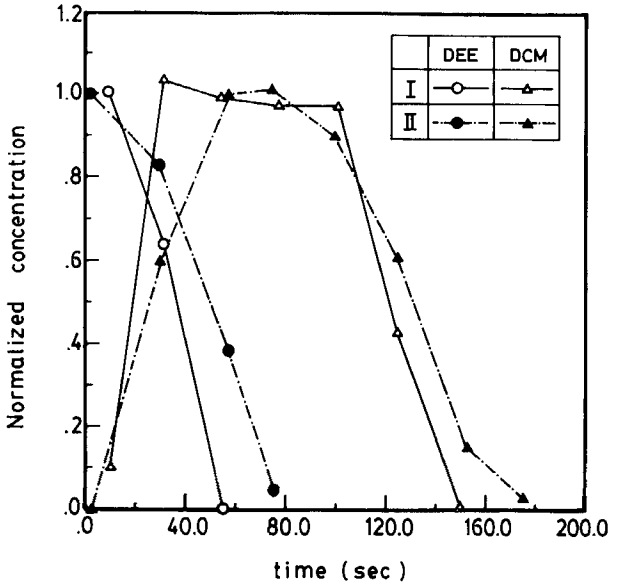

FIG. 11. Effect of particle size on elution profile in desorption section. I = 60/80 mesh (Run 13); II = 45/60 mesh (Run 14).

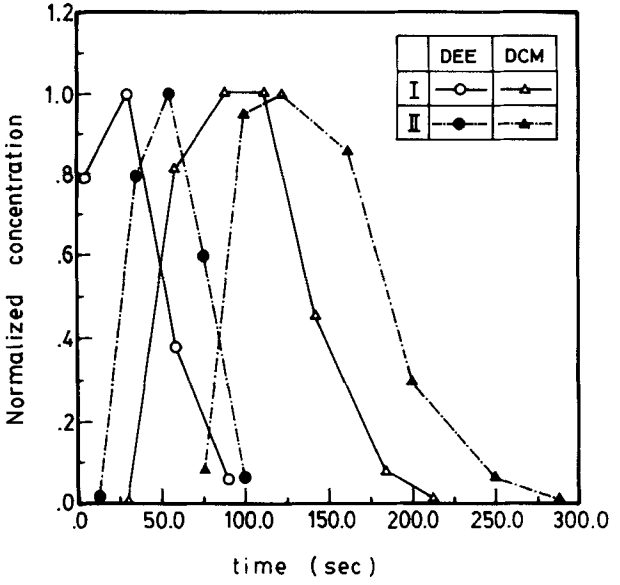

FIG. 12. Effect of additional column length on elution profile in desorption section. I = 25 cm (Run 15); II = 75 cm (Run 16).

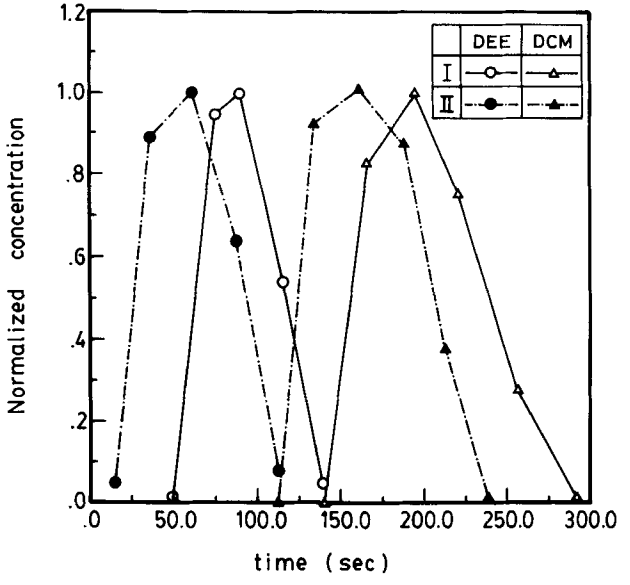

FIG. 13. Effect of desorbent velocity on elution profile in desorption section. I = 18.53 cm/s (Run 17); II = 21.87 cm/s (Run 18).

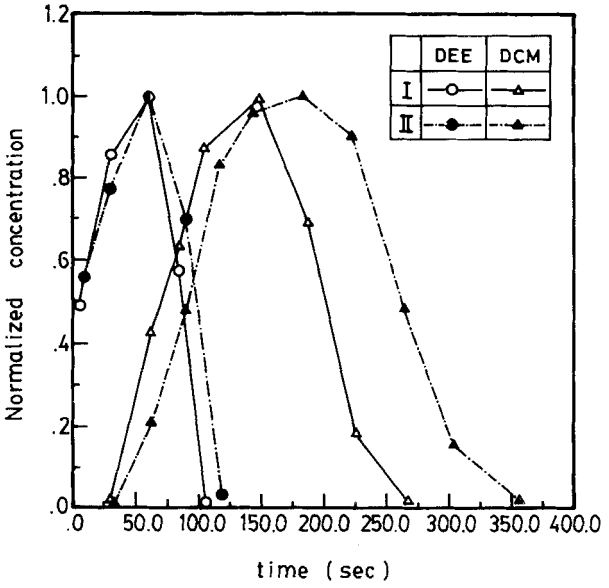

FIG. 14. Effect of column temperature on elution profile in desorption section. I = 45°C (Run 19); II = 35°C (Run 20).

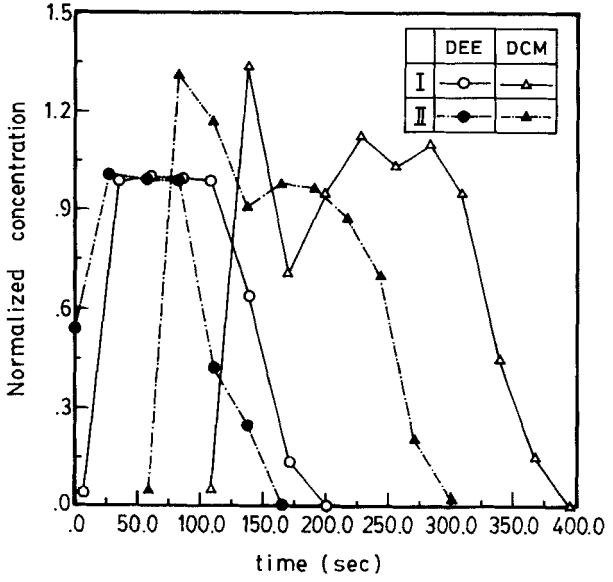

FIG. 15. Elution profile for higher feed concentration of DEE than of DCM in desorption section. I = 14.97 cm/s (Run 21); II = 17.92 cm/s (Run 22); feed concentration of DEE = 3.40 $\times 10^{-3}$ mol/L, feed concentration of DCM = 0.90 $\times 10^{-3}$ mol/L.

compensate for the increased pressure drop of the longer column length and the greater velocities of the carrier gas and desorbent.

The switching time was determined by the choice of the stationary liquid and the materials to be separated. Therefore, the stationary liquid should be chosen with as high a selectivity as possible for the feed mixture. Throughputs between 5-10 cm^3/h yielded pure DEE and almost completely separated DEE and DCM with column lengths of 100 cm in the partition and the desorption sections, 20/30 mesh particle size, and 35°C column temperature.

REFERENCES

1. A. T. James and A. J. P. Martin, *Biochem. J., 50,* 679 (1952).
2. K. H. Row and W. K. Lee, *Korean J. Chem. Eng., 3,* 7 (1986).
3. H. M. McNair and E. J. Bonelli, *Basic Gas Chromatography,* Varian Aerograph, Berkeley, California, 1969, Chap. I, p. 4.
4. C. J. King, *Separation Processes,* McGraw-Hill, New York, 1980, Chap. 4, p. 191.
5. D. B. Broughton, *Chem. Eng. Prog., 64,* 60 (1969).
6. P. E. Barker, G. Vlachogiannis, and R. M. Alsop, *Chromatographia, 17,* 149 (1983).
7. H. Y. Ha, K. H. Row, and W. K. Lee, *Sep. Sci. Technol., 22*(1), 141 (1987).
8. H. Y. Ha, K. H. Row, and W. K. Lee, *Ibid., 22*(4), 1281 (1987).
9. P. E. Barker and C. H. Knapman (eds.), *Developments in Chromatography,* Applied Science Publisher, London, 1978, Chap. 2, p. 41.
10. M. V. Sussman, *Chemtech,* p. 260 (April 1976).
11. I. Moon, K. H. Row, and W. K. Lee, *Korean J. Chem. Eng., 2,* 155 (1985).
12. K. H. Row and W. K. Lee, *J. Chem. Eng. Jpn., 19,* 173 (1986).

Received by editor August 12, 1986