SIMULATION OF THE COMBINED CONTINUOUS AND PREPARATIVE SEPARATION OF THREE CLOSE-BOILING COMPONENTS IN A GAS-LIQUID CHROMATOGRAPHY

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Abstract—The combined continuous and preparative gas-liquid chromatographic system was considered for separating continuously three close-boiling components, diethylether, dimethoxymethane, and dichloromethane. Their concentration profiles were simulated by the methematical model, which assumed the uniform distribution of stationary liquid phase and the linearity of the equilibrium isotherm.

The operational principles of the system are that the least-absorbed component of the three components can be obtained purely before the elution of the most-absorbed components if the mixture is continuously injected into the one of the two sections (partition section) and at the same time, in the other section (desorption section), the three components remained in the column can be separated by the adjusting the experimental conditions and the column configuration. If the operations in the two sections are simultaneously finished within a time (switching time), continuous separations of the three components are feasible. The effect of the various operating conditions on the resolution is investigated. From the results of the simulations, the resolution is greatly affected by the additional column length in the desorption section and the switching time can be determined by the desorbent velocity.

INTRODUCTION

Gas-liquid chromatography is a separation method based on differences in the partition coefficients of substances distributed between a stationary liquid phase and a mobile phase. Since the introduction of the chromatography [1], over the past 30 years much efforts have been made to increase the throughput capabilities. From the start, it was recognized this technology could be used for quantitative separation on an industrial scale [2]. Until now, attempts have been made to scale up lab-sized chromatography units to treat more quantity of substances and to make the system to be continuous operation [3].

Among the some systems to meet the condition, UOP process is widely acknowledged as a useful system [4]. As an improved preparative chromatography, Wankat developed moving feed point chromatography [5], and this system was used to separate two close-boiling components in gas-liquid chromatography [6,7]. Later it was combined with moving product withdrawal chromatography, moving

port chromatography was suggested [8]. He properly used a local equilibrium model to analyze the characteristics of the system. Two mathematical models of the moving bed adsorber, an intermittent moving bed and a continuous moving bed type, were presented by Hashimoto et al. for calculating the concentration profiles of glucose and fructose [9,10].

Such mixtures as various hydrocarbons, dextran, and ssaccharoids were separated using series of the semicontinuous counter-current refiner (SCCR) [11-13] and a mathematical model based on the theoretical plate concept was used to simulate the performance of the unit [14]. For the SCCR unit and the UOP process, Ching and Ruthven have proposed the theoretical model for simulated counter-current operation as an equivalent counter-current cascade of theoretical equilibrium stage under steady state condition and obtained the analytical concentration profile [15,16].

For the combined continuous and preparative chromatographic system, mathematical models were developed and used to compare the experimental data with the calculated values in the binary mixture [17,18]. The purpose of this work is to inverstigate the feasibility and adaptation of the ternary mixture to this

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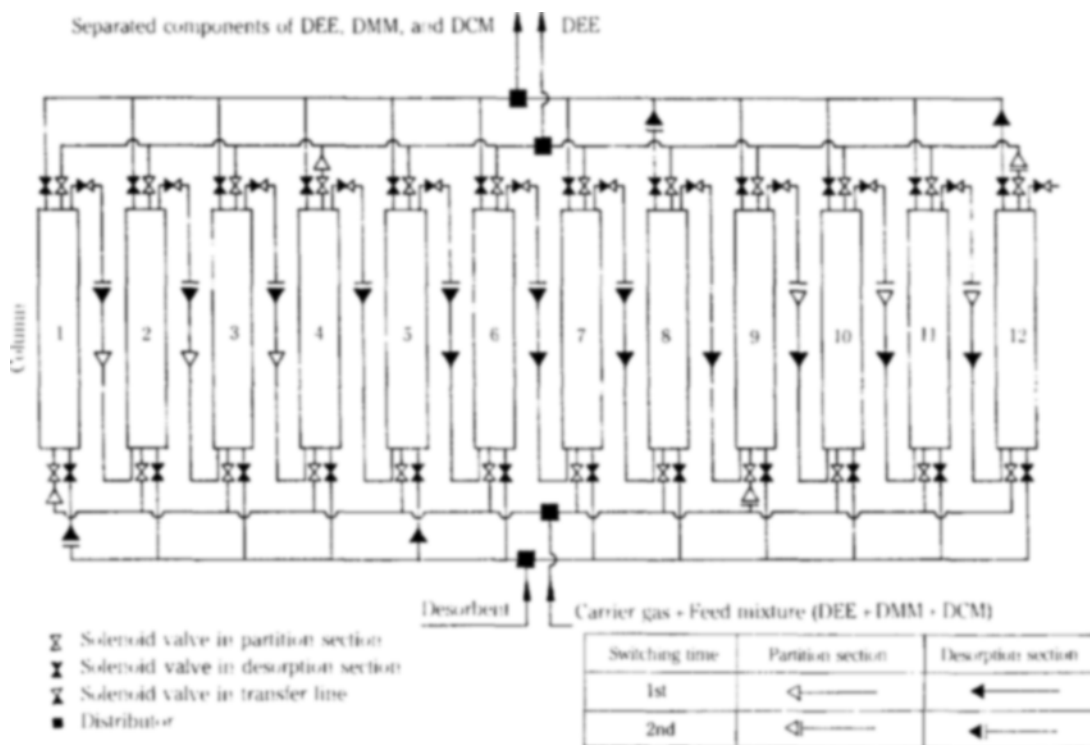*To whom all correspondence should be addressed.

Fig. 1. Schematic diagram of the combined continuous and preparative chromatographic beds.

system and the effects of operating conditions on the resolutions of the components by the prediction of the concentration profiles.

OPERATIONAL PRINCIPLES OF THE SYSTEM [17, 18]

When a mixture of diethylether (DEE), dimethoxymethane (DMM), and dichloromethane (DCM) is continuously injected into a chromatographic column, DEE is eluted first by the solubility difference with stationary liquid phase (SLP) of dinonylphthalate, and later DCM followed by DMM comes out from the column. The feed mixture is continuously injected until the only least-absorbed component (DEE) comes out from the column in partition section, and the unseparated components in the partition section can be separated with the adjustments of column length and desorbent velocity in desorption section. The experimental system was composed of 12 segmented columns and sixty solenoid valves controlled by a programmable controller (see Figure 1). The partition section is assumed to consist of 4 columns and the desorption section of 8 columns. During the first switching time, the feed is continuously injected into the column 1, and DEE is purely obtained at the outlet of column 4. Within the second switching time,

the position of feed injection is moved to the inlet of column 9. At the same time, the columns 1-8 are the desorption section, and a mixture of three components are separated at the outlet of column 8.

Separation of the components is continuously achieved if the operations in the two sections are terminated within a switching time, and the feed mixture is systematically injected into the following columns with a circular form. In the partition section, only the least absorbed component is obtained in pure state, and in the desorption sections with additional column, the remains of DEE, DMM, and DCM are separated. Each mathematical model is set up to research the feasibility of the ternary system and the performance of the chromatographic system.

BASIC EQUATIONS

The basic equations for this system are well referenced in [17-20]. The following Laplace transformed equation can be used to predict the concentration profile in the partition section for the injection time of t_0

$$C(s) = \frac{1 - e^{-st_0}}{s} \exp\left(\frac{L}{2} \left\{ \frac{u_0}{E} - \left[\left(\frac{u_0}{E} \right)^2 + 4\lambda \right]^{1/2} \right\} \right)$$

(1)

at the bed exit, z = L, where

$$\lambda = \frac{\varepsilon}{E}\left(s + \frac{3(1-\varepsilon)}{\varepsilon\, r_p} k_f \left\{ 1 - \frac{\sinh(\lambda_2 r_p)}{r_p}\lambda_1 \right\} \right) \quad (2)$$

$$\lambda_1 = \frac{r_p k_f}{D_e \lambda_2 \cosh(\lambda_2 r_p) + \left(k_f - \dfrac{D_e}{r_p}\right)\sinh(\lambda_2 r_p)} \quad (3)$$

$$\lambda_2 = \left(\frac{1}{D_e}\left[\{\varepsilon_p s + A_p k_g\} - \frac{A_p k_g^2 \cosh\lambda_3}{D_e K \sqrt{\dfrac{S}{D_1}}\lambda_3 + D_e k_g \cosh\lambda_3} \right]\right)^{1/2} \quad (4)$$

$$\lambda_3 = \delta\sqrt{\frac{S}{D_1}}. \quad (5)$$

In the desorption section, the components are assumed to be partitioned initially with the inlet concentration of the feed, c_0. Under the condition, the solution with the additional column length (L′) in the Laplace domain is

$$C(s) = \gamma\left(\exp\left\{\frac{L}{2}\left(\frac{u_0}{E} - \left(\left(\frac{u_0}{E}\right)^2 + 4\gamma_1\right)^{1/2}\right)\right\} - 1\right)$$
$$\times \exp\left(\frac{L'}{2}\left\{\frac{u_0}{E} - \left(\left(\frac{u_0}{E}\right)^2 + 4\lambda\right)^{1/2}\right\}\right) \quad (6)$$

where

$$\gamma = \left(-\frac{\varepsilon_p c_0}{E} + \frac{3(1-\varepsilon_p)}{r_p E}k_f\left\{\frac{\gamma_2 \sinh(\sqrt{\gamma_4}\,r_p)}{r_p}\right.\right.$$
$$\left.\left. + \frac{\gamma_5}{\gamma_4}\right\}\right)/\gamma_1 \quad (7)$$

$$\gamma_1 = \left(-\frac{\varepsilon\, s}{E} + \frac{3(1-\varepsilon)}{r_p E}k_f\left\{ 1 - \frac{\gamma_3 \sinh(\sqrt{\gamma_4}\,r_p)}{r_p}\right\}\right) \quad (8)$$

$$\gamma_2 = -\gamma_5 k_f/\gamma_4\,(D_e\{\sqrt{\gamma_4}\,r_p\cosh(\sqrt{\gamma_4}\,r_p)$$
$$- \sinh(\sqrt{\gamma_4}\,r_p)\}/r_p^2 + k_f\sinh(\sqrt{\gamma_4}\,r_p)/r_p) \quad (9)$$

$$\gamma_3 = \frac{-\gamma_4}{\gamma_5 \gamma_2} \quad (10)$$

$$\gamma_4 = \frac{1}{D_e}(\varepsilon_p s + A_p k_g)$$
$$- \frac{A_p k_g^2 \cosh\left(\sqrt{\dfrac{S}{D_1}}\delta\right)}{D_e K\{\sqrt{D_1}s\sinh\left(\sqrt{\dfrac{S}{D_1}}\delta\right) + k_g \cosh\left(\sqrt{\dfrac{S}{D_1}}\delta\right)/K\}} \quad (11)$$

$$\gamma_5 = \frac{A_p k_g}{D_e K}\left\{ \frac{Kc_0}{s}\right.$$
$$- \frac{\dfrac{k_g c_0}{s}\cosh\left(\sqrt{\dfrac{S}{D_1}}\delta\right)}{\sqrt{D_1}s\sinh\left(\sqrt{\dfrac{S}{D_1}}\delta\right) + k_g\cosh\left(\sqrt{\dfrac{S}{D_1}}\delta\right)/K}\right\}$$
$$+ \frac{c_0}{D_e}. \quad (12)$$

The resulting Laplace transformed equations [Eqs. (1) and (6)] should be converted into the real time domain. For an approximation technique, the equations are inverted numerically with the curve fitting procedure by Dang and Gibilaro [21]. The kinetic constant and other parameters used in the simulations are listed in Table 1 [18]. The axial dispersion coefficient, E, and effective diffusivity, D_e, were estimated by analysis of frequency domain. The molecular diffusivity in an eluant of N_2 was calculated from the Chen and Othmer equation and the diffusion coefficient in SLP, D_M, was calculated from the Wilke-Chang equation using the molar volume by Tyn and Calus method for a SLP of dinonylphthalate. The dependence of interparticle mass transfer coefficient, k_f, on superficial velocity of eluant and particle size can be expressed by the semiempirical correlation [22]. For the intraparticle mass transfer coefficient, k_g, the correlation formula proposed by Ergun was used with the assumption that it was not affected by the superficial velocity of eluant [23].

RESULTS AND DISCUSSION

When a mixture of DEE, DMM, and DCM is continuously injected, the concentration profiles in a partition section are shown in Figure 2. The curves in the partition section were calculated by the numerical inversion of the Laplace transformed equation (17). In this case, the switching time is determined as 90 sec just before the elution of the DMM.

The effects of operating conditions on the number of theoretical plates in the partition section are listed in Table 2. Under the assumption of the large theoretical number of plates [24], it is calculated by the following, equation,

$$N = 8\pi\,(v/a)^2. \quad (13)$$

As the column temperature was increased, the total elution volume of the carrier gas necessary to exclude the component from the column was smaller, because the partition coefficient decreased exponentially with the temperature. In the partition section the column

Table 1. Partition coefficients and kinetic constants used in simulation work

1. Effect of mesh size and % liquid loading

Mesh size:

	60/80	45/60	20/30
r_p (m)	0.0000996	0.000136	0.000314

% liquid loading:

1 60/80 mesh, 45/60 mesh

	25	20	15
ϵ_p	0.62	0.66	0.69

2 20/30 mesh

	25	20	15
ϵ_p	0.50	0.54	0.57

% liquid loading:

	25	20	15
$\delta(\mu m)$	0.1270	0.0955	0.0650

3. Constants

A_p (m^2/m^3)	1300000.0
ϵ	0.41
D_e ($\times 10^{-9}$ m^2/sec)	1.00 (DEE) 1.19 (DMM) 2.00 (DCM)

2. Effect of column temperature

(DEE) temperature	D_1	K	D_M
°C	10^{-10} m^2/sec		10^{-5} m^2/sec
25	0.471	184.2	0.88
30	0.561	152.1	0.90
35	0.650	126.3	0.93
40	0.793	105.6	0.96
45	1.090	88.7	0.99

(DMM) temperature	D_1	K	D_M
°C	10^{-10} m^2/sec		10^{-5} m^2/sec
25	0.520	263.4	0.94
30	0.648	217.4	0.97
35	0.790	180.5	1.00
40	0.876	150.8	1.03
45	1.115	126.7	1.06

(DCM) temperature	D_1	K	D_M
°C	10^{-10} m^2/sec		10^{-5} m^2/sec
25	0.595	437.1	1.02
30	0.750	359.2	1.05
35	0.901	297.1	1.08
40	1.020	247.2	1.12
45	1.275	206.8	1.15

temperature have directly affected on the switching time, that is, higher column temperature resulted in shorter switching time. The table also shows that the column efficiency expressed as the number of theoretical plates was considerably affected by the change in liquid loading. Elution time of the component was shorter at lower liquid loading, but more feed mixtures can not be separated due to the limited quantity of SLP. However, higher liquid loading increased the separation time and especially with high temperature in the system. This is often detrimental to the capacity of a column, since relative retention volumes between two components diminish with higher temperatures. Therefore, optimum liquid loading might exist in a practical operation. As a large sample is usually injected in the scaled-up chromatographic system, a column packing with high liquid loadings was generally used. Finer particles size made the slope of the leading edge in the concentration profile of the partition section sharper due to increased column efficiency. However, in a gas chromatographic column, larger pressure drop caused by these smaller particle sizes was not desirable, because the best column efficiency is obtained at low inlet-to-outlet ratio of the pressure throughout the column. The majority of practical gas chromatographic system are performed generally at the outlet of atmospheric pressure, so that the inlet pressure is adjusted somewhat to operate at the optimum flow rate in the chromatographic column.

The concentration profiles of the three components in a desorption section are shown in Figure 3. The curves in the desorption section were calculated by the numerical inversion of the Laplace transformed equation (29). Effect of desorbent velocity on the total elution time with the additional column in the de-
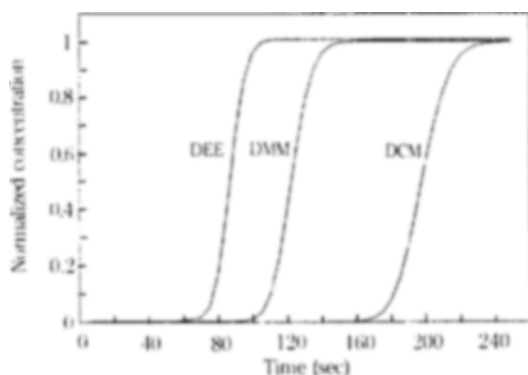
Fig. 2. Theoretical concentration profiles in partition section.

(L = 1.0 m, u_0 = 0.15 m/sec, 35°C, 25% liquid loading, 45/60 mesh)

Fig. 3. Theoretical concentration profiles in desorption section.

(L = 1.0 m, L' = 2.0 m, u_0 = 0.15 m/sec, 35°C, 25% liquid loading, 45/60 mesh)

sorption section is shown in Figure 4. The desorbent velocity needs to be adjusted for the remained component to be completely eluted from the desorption section within a switching time to achieve continuous operation. In a certain condition of the partition section, the switching time can be determined as the duration from the start-up of injection to just before the elution of DMM.

The resolution is used to investigate the optimum operating conditions, and it is defined by

$$R_{1,2} = 2 (b_2 - b_1) / (a_2 - a_1). \qquad (14)$$

With increase in the desorption section of the additional column length, two resolutions of neighboring components were improved gradually (Figure 5). In analytical chromatography, generally, the shape of a resolution is sharp, whereas in preparative system, the top of a peak is flattened caused by larger volume of feed mixture [25].

Effect of column temperature in the desorption section on the resolution is shown in Figure 6. The components were eluted out faster with higher temperature. In this system, the column temperature was to be kept uniformly in the two sections. Because the higher temperature decreases the total elution time, the resolution may be worse due to the fast elution of the two components. For 20% liquid loading, the optimum column temperature is about 41°C, which was slightly over the boiling points of the components, DEE and DCM. The chromatographic separation is reportedly operated around the boiling points of the components to be separated [26].

Increase in the weight percentage of a liquid loading in stationary phase (% liquid loading) improved
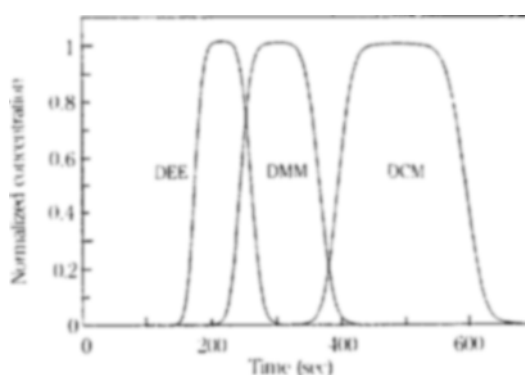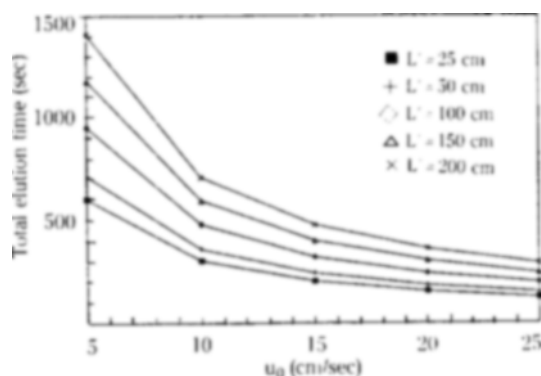

Fig. 4. Effect of desorbent velocity with additional column length on total elution time in desorption section.

(L = 1.0m, 35°C, 20% liquid loading, 45/60 mesh)

the resolution (Figure 7), but it also increased the total elution time. And the smaller particle size improved the resolution (Figure 8).

Separation of the three components in the desorption section was decisively affected by increase in the additional column length more than particle size and % liquid loading. By adjusting the desorbent velocity, the remained components in the desorption section should be separated within a switching time to perform the operation of the system continuously. Therefore, too small particle size and too large loading of SLP should be avoided to meet the condition of the switching time.

From the experimental results of the binary components (DEE and DCM), the efficient separation method was that the DEE was obtained purely in parti-

Table 2. Number of theoretical plates in partition section

u_0 m/sec $\times 10^{-2}$	column temperature °C	% liquid loading	particle size	N		
				DEE	DMM	DCM
2.0	35.0	20.0	45/60	859	1103	1580
3.0	35.0	20.0	45/60	334	665	845
4.0	35.0	20.0	45/60	316	509	971
5.0	35.0	20.0	45/60	377	465	540
10.0	35.0	20.0	45/60	377	323	341
15.0	35.0	20.0	45/60	124	204	358
20.0	35.0	20.0	45/60	179	72	166
25.0	35.0	20.0	45/60	97	50	84
15.0	25.0	15.0	45/60	183	149	270
15.0	25.0	25.0	45/60	96	131	141
15.0	30.0	15.0	45/60	123	169	238
15.0	30.0	25.0	45/60	64	105	173
15.0	35.0	15.0	45/60	109	111	131
15.0	35.0	25.0	45/60	54	112	139
15.0	40.0	15.0	45/60	75	58	183
15.0	40.0	25.0	45/60	55	91	135
15.0	45.0	15.0	45/60	83	109	188
15.0	45.0	25.0	45/60	70	72	115
15.0	25.0	20.0	20/30	19	21	42
15.0	25.0	20.0	45/60	157	173	202
15.0	25.0	20.0	60/80	353	170	291
15.0	30.0	20.0	20/30	21	27	42
15.0	30.0	20.0	45/60	88	86	205
15.0	30.0	20.0	60/80	230	145	312
15.0	35.0	20.0	20/30	26	25	44
15.0	35.0	20.0	45/60	143	93	138
15.0	35.0	20.0	60/80	173	181	305
15.0	40.0	20.0	20/30	18	24	48
15.0	40.0	20.0	45/60	57	102	197
15.0	40.0	20.0	60/80	57	108	195
15.0	45.0	20.0	20/30	9	25	35
15.0	45.0	20.0	45/60	45	77	112
15.0	45.0	20.0	60/80	86	111	185

tion section, a mixture of DEE and DCM was separated in desorption section by increase in column length, and the whole process should be finished within a designated time [17]. Uniqueness of the system was that several columns were added in series in the desorption section to separate the non-eluted components effectively, compared to other continuous chromatographic systems. The theoretical concentra-

tion profiles assumed by uniform film thickness and linear partition equilibrium were in good agreements with the experimental data of the binary components for this chromatographic system.

In the model equations, the assumption were that the equilibrium isotherm was linear and no interaction between the two components existed. When the feed concentration is increased, the phenomena in the
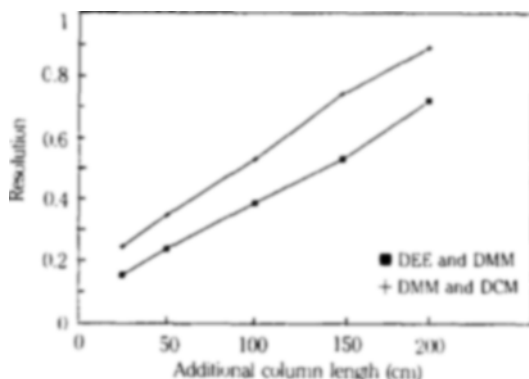
Fig. 5. **Effect of additional column length on resolution in desorption section.**
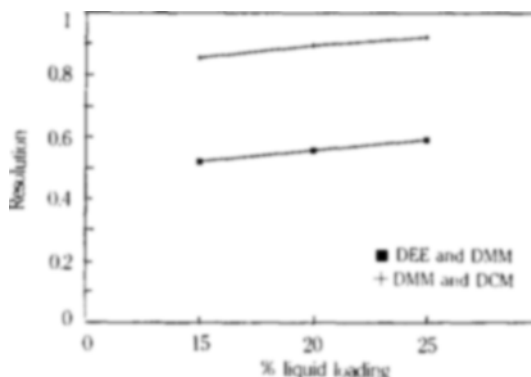(L = 1.0 m, u₀ = 0.15 m/sec, 35°C, 20% liquid loading, 45/60 mesh)

Fig. 7. **Effect of % liquid loading on resolution in desorption section.**
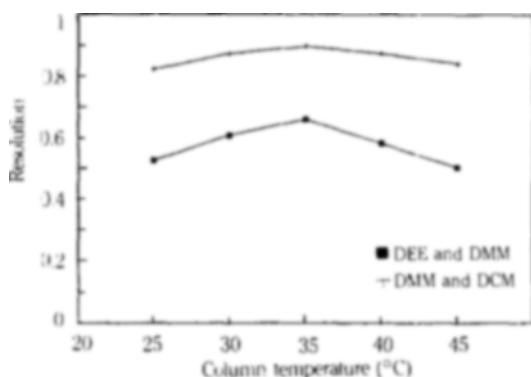(L = 1.0 m, L' = 2.0 m, u₀ = 0.15 m/sec, 35°C, 45/60 mesh)

Fig. 6. **Effect of column temperature on resolution in desorption section.**
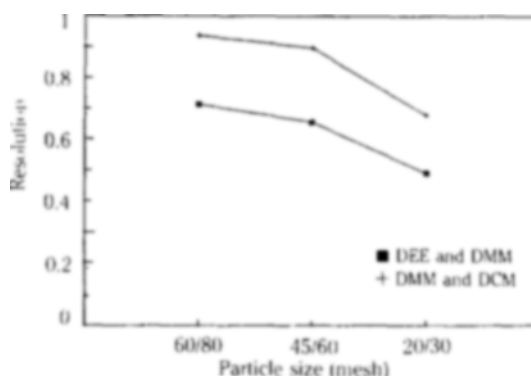(L = 1.0 m, L' = 2.0 m, u₀ = 0.15 m/sec, 20% liquid loading, 45/60 mesh)

Fig. 8. **Effect of particle size on resolution in desorption section.**
(L = 1.0 m, L' = 2.0 m, u₀ = 0.15 m/sec, 35°C, 20% liquid loading)

column become more complex, and the information about the nonlinear isotherm is needed for better prediction. Moreover, the assumption that the velocity of carrier gas and desorbent remained constant throughout a column is not thought to be reasonable, because higher pressure drop by a smaller particle size and a longer column length caused the variation of the gas velocity, and the solute concentration changes along the length of the column by absorption is necessarily by change in the velocity. Although it was assumed in Eq (18) that the components were partitioned in the desorption section with the feed concentration, c_0, the more-absorbed components were not exactly for the case, because during the previous switching time, the component was not withdrawn from the partition section. However, the simple model of the uniform

film thickness concept might be used as a suitable estimation of optimum operating conditions for the combined continuous and preparative chromatographic system.

CONCLUSIONS

Mathematical models have been adopted to simulate the performance of the combined continuous and preparative chromatographic system. The model equations were the transient material balances with the assumption of uniform film thickness of SLP in porous solid support and linearity of the equilibrium isotherm, and these could be successfully used to investigate the resolution of the three components, DEE, DMM and DCM with operating conditions.

Among the various conditions, the additional column length in the desorption section had greatly influenced to the resolution. Continuous operations can be achieved if feed materials are separated with the longer additional column length and higher desorbent velocity in the desorption section within a switching time.

NOMENCLATURE

a   : peak width cut by the two tangents in unit of volume [m^3]

A_p : surface area of porous particle per unit volume [m^2/m^3]

b   : retention volume from injection to peak maximum [m^3]

c   : concentration of solute in the mobile phase [mol/m^3]

c_0 : inlet concentration of solute [mol/m^3]

C(s) : Laplace transform of c(t)

D_e : diffusion coefficient in the pore spacing [m^2/sec]

D_1 : diffusion coefficient in the SLP [m^2/sec]

D_M : molecular diffusion coefficient [m^2/sec]

E   : axial dispersion coefficient [m^2/sec]

k_f : interparticle mass transfer coefficient [m/sec]

k_g : intraparticle mass transfer coefficient with respect to SLP-film [m/sec]

K   : partition coefficient

L   : column length in the partition section or the desorption section [m]

L   : additional column length in the desorption section [m]

N   : number of theoretical plates

r_p : radius of porous particle [m]

R_{ij} : resolution between components, i and j

s   : variable of Laplace transform

t   : time [sec]

t_0 : time of feed-injection [sec]

T   : column temperature [K]

u   : interstitial velocity of carrier gas or desorbent [m/sec]

u_0 : superficial velocity of carrier gas or desorbent [m/sec]

v   : retention volume corresponding to point of infliction [m^3]

z   : axial distance [m]

Greek Letters

ν, ν_1, ν_2, ν_3, ν_4, ν_5: values defined by Eq. (7) to Eq. (12)

δ : film thickness of SLP [μm]

ϵ : void fraction of chromatographic column

ϵ_p : porosity with the presence of SLP

λ, λ_1, λ_2, λ_3:values defined by Eq. (2) to Eq. (5)

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