

DEVELOPMENT OF A MATHEMATICAL ANALYSIS METHOD FOR THE MULTICOMPONENT SEPARATION BY DISPLACEMENT DEVELOPMENT

Kisay Lee

Department of Chemical Engineering, Myong-Ji University, Yongin, Kyongki-do 449-728, Korea

(Received 26 September 1995 • accepted 8 January 1996)

Abstract—A simple mathematical method for the analysis of multicomponent displacement development was developed. Calculations in this method utilizes the information residing in the isotactic condition which is established after the full development of solute propagation occurring in the chromatographic separation operated by the mode of displacement development. Transient shock wave velocities and concentration changes are determined based upon the equilibrium theory of chromatography and the basic rules required in constructing the (t,z)-diagram of solute propagation along the column. Calculations involve solving simple algebraic equations to predict the transient behaviors of propagating solutes inside the column, the elution profiles of final products, and the minimum column length required for the complete separation.

Key words: Chromatography, Displacement Development, Isotactic Condition, Shock Wave, Solute Propagation

INTRODUCTION

Displacement development or displacement chromatography (DPC) is an operation mode of chromatographic separation. In DPC, a packed column is first equilibrated with a weak carrier solvent in adsorption processes or with a weakly exchangeable ion in ion exchange processes. A slug of feed mixture is then introduced to the column, followed by a solution containing a so-called displacer which has a greater affinity to adsorbent than that of any other feed components. The front of the displacer solution travelling behind the feed mixture drives the feed components to rearrange themselves and form adjacent pure zones which move at the same velocity as the displacer front, and an isotactic condition is finally established. Since the displacer competes with the feed solutes for adsorption sites, the solutes are distributed during propagation in the order of decreasing affinity along the column distance and finally the solutes exit the column as adjacent pure bands. The displacer is then removed from the adsorbent and thus the column is regenerated for reuse. DPC allows loading of a large amount of feed compared to the conventional elution type chromatography. By the virtue of strong affinity of displacer to the adsorbent, tailing is greatly reduced and concentrated products can be obtained.

Theoretical analysis methods for the solute propagation in DPC have been proposed [DeVault, 1943; Claesson, 1949; Aris and Amundson, 1973; Wankat, 1990] since Tiselius [1943] reported that the band concentrations depend only on the displacer concentration used in DPC. Helfferich and Klein [1970], Helfferich and James [1970], and Rhee et al. [1970, 1982, 1986] developed mathematical analysis methods for the system of general multicomponent chromatographic separation by assuming constant separation factor, local equilibrium, and no axial dispersion. A special case of those theories can be applied to analyze the system of displacement development. Helfferich and Rhee invented the so-called *h*- and *u*-transformation functions, respectively, which convert simultaneous partial differential equations of multicomponent

material balance to the ordinary differential equations. These ordinary equations are solved to determine the transient behaviors as well as the steady-state development of solute propagation in terms of the shock wave and boundary velocities of propagating solutes. Although these methods have a good generality in multicomponent chromatographic separation and are mathematically well-elaborated, the underlying physical concepts are not so easy for laymen at works to understand, and the application procedures involve complicated numerical calculations.

In this study, a simple algebraic method is developed for the multicomponent DPC processes to determine transient behaviors of propagating solutes in the column, the minimum column length required for the complete separation of feed mixture, and the elution profiles of final products. This method is developed based upon the information in the isotactic states which is established after the full development of propagating solutes in DPC.

PREREQUISITE RULES

The following rules are applied for the construction of a complete (t,z)-diagram in the separation of feed mixture containing *N* different components. These rules are nothing but a summary of physical features which can be observed in the solute propagation of DPC [Claesson, 1943; Helfferich and Klein, 1970; Rhee and Amundson, 1982; Hong, 1988].

1. In DPC, only shock waves propagate along the column due to the driving action of displacer which has the greatest affinity to the adsorbent. No diffusive wave is formed. All the solute concentrations in mobile and stationary phases show jump changes, not gradual, at the boundary between two states with different solute composition. This is satisfied when displacer concentration is higher than a critical value.

2. If a slug of feed mixture containing *N* components is introduced to the column of initial state, *N* waves propagate from the origin (Fig. 1a).

3. If a displacer is introduced at time *t*, after the period of

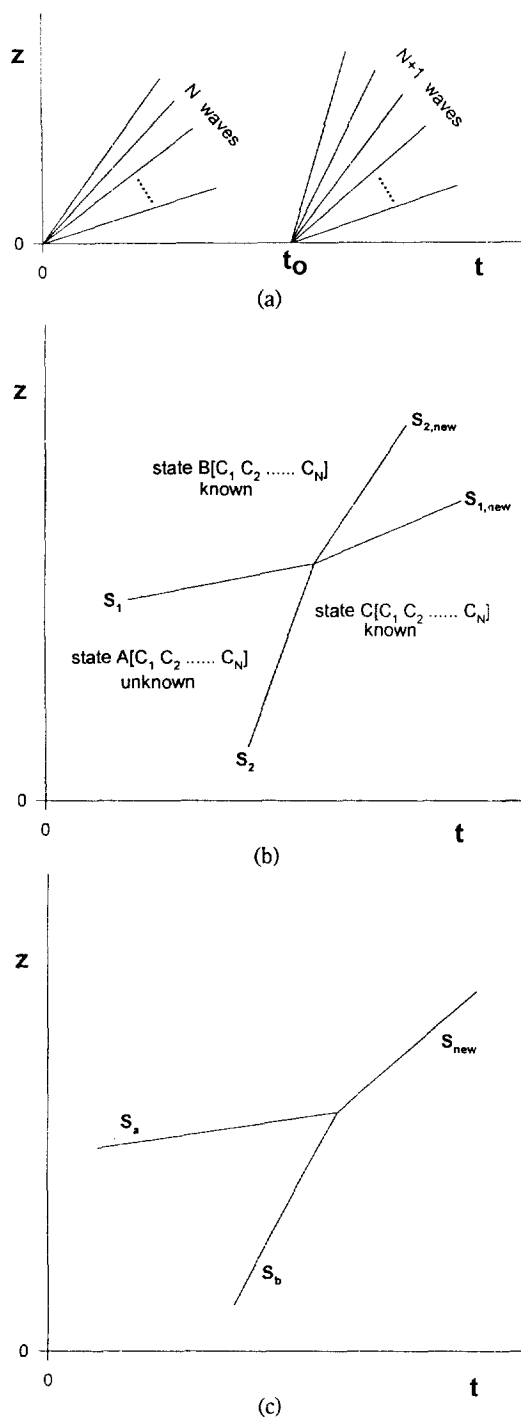


Fig. 1. Construction of solute propagation diagram in (t, z) -plane.

(a) Initial waves, (b) Wave interaction, (c) Wave merge.

feed injection, $N+1$ waves propagate from t_0 (Fig. 1a).

4. Two new waves are generated when two waves interact in the middle of propagation (Fig. 1b). The relationship between the slopes of shock wave in (t, z) -plane, or the solute velocities, are $S_1 < S_{1,new} < S_{2,new} < S_2$ if the two slopes of the original waves are $S_1 < S_2$.

5. After travelling a certain distance in the column, two waves merge to form a single wave of pure solute (Fig. 1c). Therefore $N+1$ parallel waves are propagated at the same speed, which

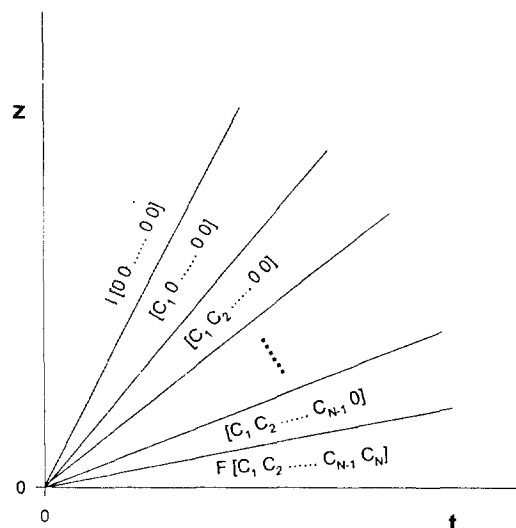


Fig. 2. N waves propagating from the column entrance after mixture loading.

represents the isotactic condition obtained as the final result of displacement development.

CALCULATION PROCEDURE

Feed and displacer concentrations are given as experimental conditions. If the feed mixture contains N different solutes, N waves propagating from the origin and $N+1$ constant states between the wave lines are formed. The involved components in each constant state can be identified by the frontal analysis [Claesson, 1949], which are shown in Fig. 2. The differential equation of material balance for solute i can be given as

$$\frac{\partial C_i}{\partial t} + \phi \frac{\partial q_i}{\partial t} + u \frac{\partial C_i}{\partial z} = 0 \quad (1)$$

where C_i is in mol per unit volume of fluid and q_i is in mol per unit volume of adsorbent. u is the interstitial velocity of the fluid and ϕ is the phase ratio $(1-\epsilon)/\epsilon$ where ϵ is the void fraction of the bed. The equilibrium relation between q_i and C_i can be given by the competitive Langmuir type isotherm:

$$q_i = \frac{a_i C_i}{1 + \sum_{j=0}^N b_j C_j} \quad (2)$$

In displacement development, a slug of feed mixture is fed from $t=0$ to $t=t_0$ and displacer feeding starts at $t=t_0$ (Fig. 1a). The slopes of shock wave line in (t, z) -plane are obtained by the method of characteristics [Aris and Amundson, 1973; Rhee et al., 1986] as:

$$S_i = \frac{\Delta z}{\Delta t} = \frac{u}{1 + \phi \frac{[q_i]}{[C_i]}} \quad \text{for all } i \quad (3)$$

where $[q_i]$ and $[C_i]$ represent the jump changes of solute i concentration in stationary and mobile phases, respectively, across the shock wave S_i . The slopes should be identical with respect to all components in two constant states across the shock wave line involved:

Table 1. Langmuir parameters and concentrations

C_F represents concentration in the feed mixture and C_D the displacer concentration.

$$\phi = (1 - \varepsilon)/\varepsilon = 1.5, \quad \varepsilon = 0.4$$

$$t_0 = 10 \text{ min}$$

$$C_D = 0.35 \text{ mol/L}$$

$$u = 10 \text{ cm/min}$$

Parameter	Solute			
	1	2	3	4 (displacer)
a	5	10	15	20
b	5	10	15	20
C_F	0.05	0.05	0.05	0
C_D	0	0	0	0.35

$$\frac{[q_1]}{[C_1]} = \frac{[q_2]}{[C_2]} = \dots = \frac{[q_N]}{[C_N]} \quad (4)$$

The solute concentration in fully developed pure band can be easily calculated with Eq. (4) by using a given displacer concentration.

A general procedure to determine concentrations and slopes will be described with Fig. 1b. Constant states are characterized by the set of component concentrations $[C_1, C_2, \dots, C_{N-1}, C_N]$. Suppose that the concentrations of all components in constant states B and C are known and that we shall determine N unknown concentrations in constant state A. Eq. (4) should be satisfied across the shock waves S_1 and S_2 , and thus the Eq. (4) becomes

$$\frac{q_{1A} - q_{1B}}{C_{1A} - C_{1B}} = \frac{q_{2A} - q_{2B}}{C_{2A} - C_{2B}} = \dots = \frac{q_{NA} - q_{NB}}{C_{NA} - C_{NB}} = \frac{[q]_{S1}}{[C]_{S1}} \quad (5)$$

$$\frac{q_{1A} - q_{1C}}{C_{1A} - C_{1C}} = \frac{q_{2A} - q_{2C}}{C_{2A} - C_{2C}} = \dots = \frac{q_{NA} - q_{NC}}{C_{NA} - C_{NC}} = \frac{[q]_{S2}}{[C]_{S2}} \quad (6)$$

where q_j and q_j represent the concentration of solute i in constant state J for the fluid phase and adsorbent phase, respectively. The determination of unknown concentrations is done by solving algebraic Eq. (5) or (6). The slopes of lines surrounding the constant state A are determined with Eq. (3) as:

$$S_1 = \frac{u}{1 + \phi \frac{[q]_{S1}}{[C]_{S1}}} \quad (7)$$

$$S_2 = \frac{u}{1 + \phi \frac{[q]_{S2}}{[C]_{S2}}} \quad (8)$$

ILLUSTRATION

We shall consider a displacement development of three solutes to illustrate the calculation procedure. Langmuir parameters and concentrations are given in Table 1. Given concentrations are F [0.05, 0.05, 0.05, 0] for feed and D [0, 0, 0, 0.35] for displacer. Fig. 3 shows the characteristic diagram constructed on the basis of the prerequisite rules. Three shock waves propagate at the origin and four shock waves propagate at $(t_0, 0)$.

It is convenient to determine first the product concentrations in isotactic region. The concentrations in pure bands P_1 , P_2 , and P_3 are determined from

$$\frac{q_1(C_{1P1})}{C_{1P1}} = \frac{q_2(C_{2P2})}{C_{2P2}} = \frac{q_3(C_{3P3})}{C_{3P3}} = \frac{q_4(C_{4D})}{C_{4D}} \quad (9)$$

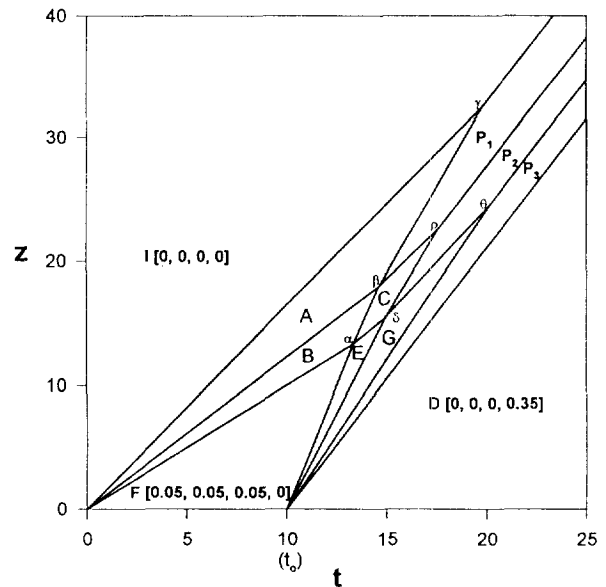


Fig. 3. Schematic propagation diagram for the separation of three solutes driven by displacer. I, F, D, A, B, C, E, G, P_1 , P_2 , and P_3 represent constant states. α , β , γ , δ , θ , and ρ represent intersection points.

$$\text{or } 5/(1 + 5C_{1P1}) = 10/(1 + 10C_{2P2}) = 15/(1 + 15C_{3P3}) = 2.5$$

with $C_{4D} = 0.35$. The concentrations of pure bands are determined as P_1 [0.2, 0, 0, 0], P_2 [0, 0.3, 0, 0], and P_3 [0, 0, 0.333, 0]. These values show that concentrated recovery is achieved compared with feed concentrations F [0.05, 0.05, 0.05, 0] initially loaded.

Since the concentrations of P_2 and P_3 are known, the concentrations of state G can be determined as explained with the Fig. 1b. The state G is composed of solutes 2 and 3 because the states P_2 and P_3 contain solute 2 and 3, respectively. Therefore the adsorbent phase concentration q for solutes 2 and 3 in the state G are the functions of C_{2G} and C_{3G} in the form of the Eq. (2). According to the Eq. (4), the ratio of jump concentration changes in adsorbent and fluid phases should be identical for the solutes 2 and 3 across the shock wave boundaries around the state G. Eq. (10) is obtained by applying the Eq. (4) across the shock wave between the states G and P_2 :

$$\frac{q_2(C_{2G}, C_{3G}) - q_2(C_{2P2})}{C_{2G} - C_{2P2}} = \frac{q_3(C_{2G}, C_{3G})}{C_{3G}} \quad (10)$$

$$\text{or } -3.75 + 12.5C_{2G} + 11.25C_{3G} = 0.$$

The ratio of jump concentration changes in adsorbent and fluid phases should be identical for the solutes 2 and 3 across the state G and P_3 . Thus Eq. (11) is obtained by applying the Eq. (4) across the shock wave between the states G and P_3 :

$$\frac{q_2(C_{2G}, C_{3G})}{C_{2G}} = \frac{q_3(C_{2G}, C_{3G}) - q_3(C_{3P3})}{C_{3G} - C_{3P3}} \quad (11)$$

$$\text{or } -2.5 + 8.3333C_{2G} + 7.5C_{3G} = 0.$$

Hence G [0, 0.1836, 0.1293, 0] is obtained by solving Eqs. (10) and (11) simultaneously.

In the same manner, the concentrations of state C can be determined from the compositions of P_1 and P_2 . From the C- P_1 bound-

ary:

$$\frac{q_1(C_{1C}, C_{2C}) - q_1(C_{1P1})}{C_{1C} - C_{1P1}} = \frac{q_2(C_{2C})}{C_{2C}} \quad (12)$$

$$\text{or } -1.5 + 7.5C_{1C} + 5C_{2C} = 0.$$

And from C-P₂ boundary:

$$\frac{q_1(C_{1C}, C_{2C})}{C_{1C}} = \frac{q_2(C_{1C}, C_{2C}) - q_2(C_{2P2})}{C_{2C} - C_{2P2}} \quad (13)$$

$$\text{or } -0.75 + 3.75C_{1C} + 2.5C_{2C} = 0.$$

By solving Eqs. (12) and (13), C [0.1163, 0.1255, 0, 0] is obtained.

The known concentrations of C [0.1163, 0.1255, 0, 0], G [0, 0.1836, 0.1293, 0], or F [0.05, 0.05, 0.05, 0] can be used to determine the concentrations of state E. Two equations for the E-G boundary and one equation for E-C boundary shall be used. For the shock wave across E and G,

$$\begin{aligned} \frac{q_1(C_{1E}, C_{2E}, C_{3E})}{C_{1E}} &= \frac{q_2(C_{1E}, C_{2E}, C_{3E}) - q_2(C_{2G}, C_{3G})}{C_{2E} - C_{2G}} \\ &\text{or} \\ &= \frac{q_3(C_{1E}, C_{2E}, C_{3E}) - q_3(C_{2G}, C_{3G})}{C_{3E} - C_{3G}} \end{aligned}$$

$$0.5335 - 1.9225C_{1E} + 1.1550C_{2E} - 5.7675C_{3E} = 0 \quad (14)$$

$$0.2404 - 2.0305C_{1E} - 4.0610C_{2E} + 3.9085C_{3E} = 0 \quad (15)$$

And across E and C,

$$\frac{q_1(C_{1E}, C_{2E}, C_{3E}) - q_1(C_{1C}, C_{2C})}{C_{1E} - C_{1C}} = \frac{q_3(C_{1E}, C_{2E}, C_{3E})}{C_{3E}} \quad (16)$$

$$\text{or } -1.5395 + 11.025C_{1E} + 2.05C_{2E} + 3.075C_{3E} = 0.$$

By solving Eqs. (14) through (16), the concentrations of state E are determined as E [0.1050, 0.0768, 0.0729, 0].

To determine the concentrations of state B, the predetermined concentrations of state F or C shall be used. There are surplus number of relations and we can choose any two of them freely. The concentrations of state B will be used subsequently to determine the composition of state A. First, F [0.05, 0.05, 0.05, 0] is used for B:

$$\begin{aligned} \frac{q_1(C_{1B}, C_{2B}) - q_1(C_{1F}, C_{2F}, C_{3F})}{C_{1B} - C_{1F}} &= \frac{q_2(C_{1B}, C_{2B}) - q_2(C_{1F}, C_{2F}, C_{3F})}{C_{2B} - C_{2F}} \\ &\text{or} \\ &= \frac{q_3(C_{1F}, C_{2F}, C_{3F})}{C_{3F}} \end{aligned}$$

$$1 + 5C_{1B} + 10C_{2B} = 5C_{1B}/(6C_{1B} - 0.2) \quad (17)$$

$$1 + 5C_{1B} + 10C_{2B} = 10C_{2B}/(6C_{2B} - 0.1) \quad (18)$$

and thus B [0.0554, 0.0817, 0, 0] is obtained. Subsequently from A-B boundary:

$$\frac{q_1(C_{1A}) - q_1(C_{1B}, C_{2B})}{C_{1A} - C_{1B}} = \frac{q_2(C_{1B}, C_{2B})}{C_{2B}} \quad (19)$$

$$\text{or } 5C_{1A}/(1 + 5C_{1A}) = 4.7755C_{1A} - 0.1323,$$

we obtain A [0.0952, 0, 0, 0].

RESULTS AND DISCUSSION

The concentrations calculated by the above procedure with the

Table 2. Concentrations (mol/L) of components consisting of constant states in the propagation diagram shown in Fig. 3

State	Solute			
	1	2	3	4 (displacer)
D	0.	0.	0.	0.35
P ₁	0.2	0.	0.	0.
P ₂	0.	0.3	0.	0.
P ₃	0.	0.	1/3	0.
G	0.	0.1836	0.1293	0.
C	0.1163	0.1255	0.	0.
E	0.1050	0.0768	0.0729	0.
A	0.0952	0.	0.	0.
B	0.0554	0.0817	0.	0.
F	0.05	0.05	0.05	0.

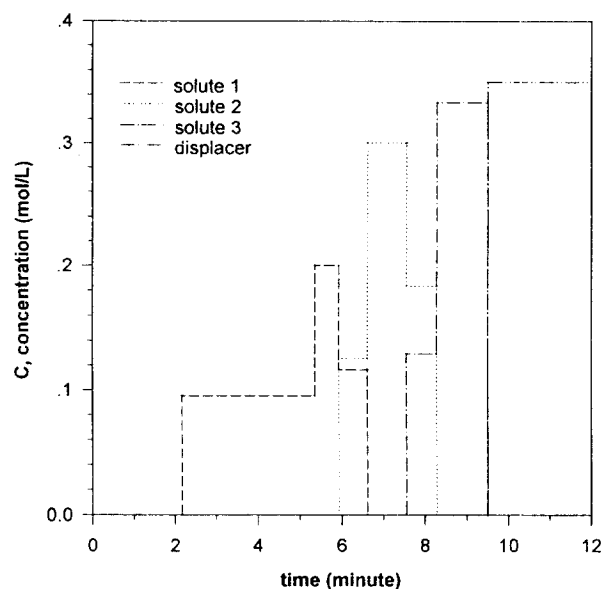
Table 3. Intersection points in the propagation diagram shown in Fig. 3

Point	t-value	z-value
α	13.33	13.33
β	14.61	17.89
γ	19.79	32.54
δ	15.00	15.49
ρ	17.57	22.61
θ	20.20	24.64

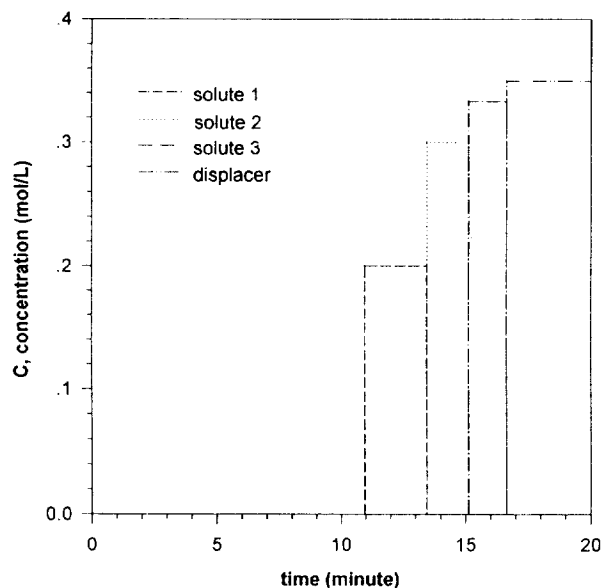
operation conditions in Table 1 are listed in Table 2. By using these concentrations and Eqs. (7) and (8), the slope of each shock wave and (t, z)-coordinate of any intersection point in Fig. 3 can be determined. The intersection points in (t, z)-plane are shown in Table 3; α [13.33, 13.33], β [14.61, 17.89], γ [19.79, 32.54], δ [15.00, 15.49], ρ [17.57, 22.61], and θ [20.20, 24.64]. The z value of point γ , 32.54 cm, is the minimum column length required to achieve the fully developed pure bands and the complete separation. The minimum time to obtain the complete separation with a column which has the minimum column length will be 20.20 min which is the t value of point θ .

Based upon the above results, the effect of column length on the final product profile was examined by comparing two different z values. The concentration histories are shown in Fig. 4 for two cases. The starting time of displacer feeding is taken as time zero in plots of Fig. 4. For z=20 cm (Fig. 4a), which is shorter than the minimum column length, the solutes are not completely separated by showing mixed regions of solutes 1, 2, and 3. Solute 3 appears as a pure band partially, but it is not a state of complete concentration. For z=35 cm (Fig. 4b), which is longer than the minimum column length, concentrated pure bands are eluted from the column in the order of increasing affinity. Although further time is elapsed with this column length, the shapes of pure band of the solutes 1, 2, and 3 will not change any more and they simply propagate side by side at the same speed.

In Fig. 5, concentration profiles are constructed at various stages in the time course of the development to visualize how the separation is realized. The time in each plot represents the one elapsed after the start of displacer feeding. At t=0 (Fig. 5a), the feed mixture has just been loaded to the column before the displacer injection. All the solutes 1, 2, and 3 stay near to the entrance by forming three-component region. Their composition is the same as that in the feed mixture. Then, a two-component



(a)

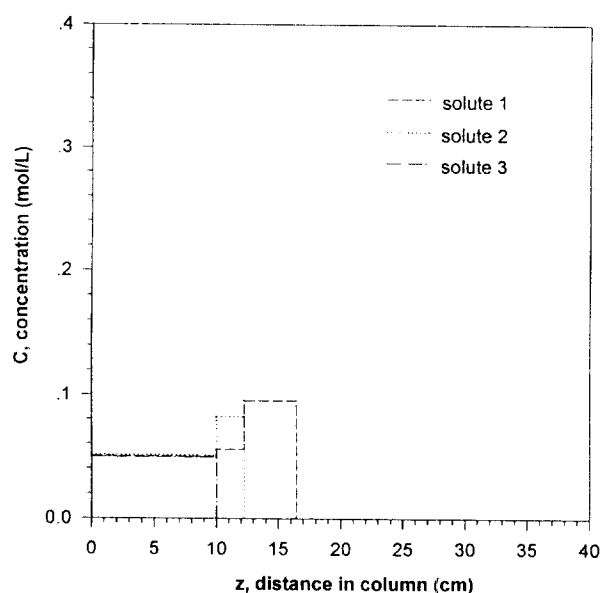


(b)

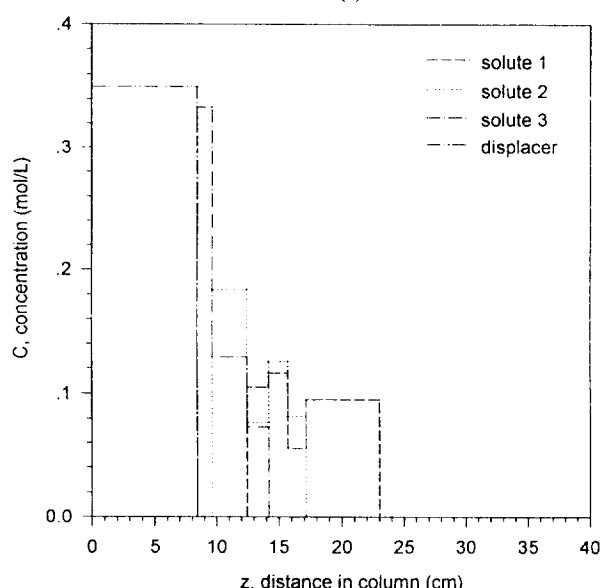
Fig. 4. Concentration histories for two columns with different length. (a) $z=20$ cm, (b) $z=35$ cm.

region with solutes 1 and 2 are appeared next to the three-component region. The solute 1 with the weakest affinity travels longer by showing a pure band. At $t=4$ minutes after the displacer feeding (Fig. 5b), the pure band of the solute 3 appears partially, but any of the solutes are not completely separated each other yet. Fig. 5c (at $t=7$ minutes) shows that further separations of the solute 1 from the solute 2 and the solute 2 from the solute 3 have been proceeded, respectively, although the separation is not completed. The pure bands of solutes 1 and 2 have appeared partially. At $t=11$ minutes (Fig. 5d), the completely pure bands of all the solutes are established and the isotactic propagation will be maintained if further time is elapsed.

CONCLUSIONS



(a)

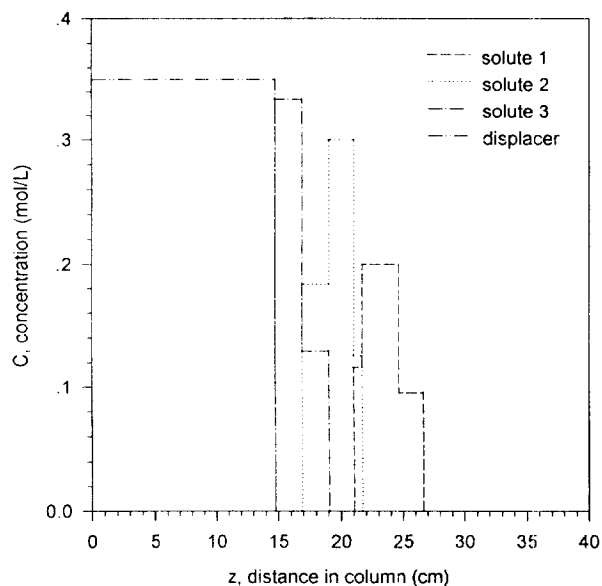


(b)

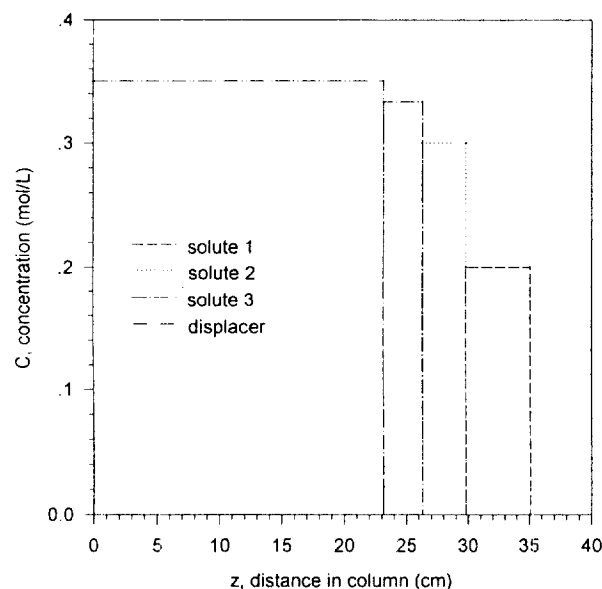
Fig. 5. Concentration profiles at various stages in the time course of development.

(a) $t=0$, (b) $t=4$ minutes, (c) $t=7$ minutes, (d) $t=11$ minutes

A simple analysis method for the ideal displacement development has been developed. This method is logically deductive in the sense that it utilizes the information in the isotactic state which is established after the full development of solute propagation in DPC. Transient shock wave velocities and concentration changes during the solute propagation are determined based upon the equilibrium theory of chromatography and the basic rules required in constructing the (t, z) -diagram. Calculation to find the compositions in all constant states occurred during the solute propagation involves solving simple algebraic equations composed of isotactic relations and Langmuir type isotherms. The determined compositions are subsequently used in the calculation of



(c)



(d)

Fig. 5. Continued.

the slopes and intersection points of the shock waves. Based upon this information, a complete (t, z) -diagram of solute propagation is constructed and simulations are carried out to predict the product band profiles and the minimum column length required for the complete separation. Elution histories can be predicted for different column lengths. Transient solute behaviors occurred during the separation inside column can also be predicted by plotting the concentration profiles for a given column.

ACKNOWLEDGEMENTS

This study was financially supported by Myong-Ji University. The author also thanks to Professor Juan Hong at the University of California, Irvine, for the valuable discussion for this research.

NOMENCLATURE

- a : Langmuir isotherm parameter
- b : Langmuir isotherm parameter
- C_i : fluid phase concentration of solute i [mmol/mL]
- C_{ij} : fluid phase concentration of solute i in constant state J [mmol/mL]
- D : displacer
- F : feed
- I : initial bed condition
- P_i : state of pure band containing solute i only
- q_i : concentration of solute i in the adsorbent phase [mmol/cm³ of adsorbent]
- q_{ij} : concentration of solute i of constant state J in the adsorbent phase [mmol/cm³ of adsorbent]
- S : slope of propagating line [cm/min]
- t : time [min]
- t_e : time of displacer injection [min]
- u : interstitial velocity [cm/min]
- z : distance in flow direction [cm]

Greek Letters

- ε : void fraction of the bed
- γ : intersection point which z coordinate is the minimum column length
- ϕ : phase ratio, $(1-\varepsilon)/\varepsilon$

REFERENCES

- Aris, R. and Amundson, N. R., "Mathematical Methods in Chemical Engineering, Vol. 2, First-Order Partial Differential Equations with Applications", Prentice-Hall, Englewood Cliffs, NJ, 1973.
- Claesson, S., "Theory of Frontal Analysis and Displacement Development", *Discuss. Faraday Soc.*, **7**, 34 (1949).
- DeVault, D., "The Theory of Chromatography", *J. Am. Chem. Soc.*, **65**, 532 (1943).
- Helfferich, F. and James, D. B., "An Equilibrium Theory for Rare-earth Separation by Displacement Development", *J. Chromatogr.*, **46**, 1 (1970).
- Helfferich, F. and Klein, G., "Multicomponent Chromatography: Theory of Interference", Marcel Dekker, New York, NY, pp. 52-105, 1970.
- Hong, J., "Optimal Operation Conditions for Displacement Chromatography", Paper Presented at AIChE Annual Meeting, Washington D.C., November, 1988.
- Rhee, H. K., Aris, R. and Amundson, N. A., "First-Order Partial Differential Equations, Vol. 2, Theory and Applications of Hyperbolic Systems of Quasilinear Equations", Prentice-Hall, Englewood Cliffs, NJ, pp. 338-359, 1986.
- Rhee, H. K., Aris, R. and Amundson, N. R., "On the Theory of Multicomponent Chromatography", *Phil. Trans. Roy. Soc. London*, **A267**, 419 (1970).
- Rhee, H. K. and Amundson, N. R., "Analysis of Multicomponent Separation by Displacement Development", *AIChE J.*, **28**, 423 (1982).
- Tiselius, A., "Displacement Development in Adsorption Analysis", *Arkiv for Kemi, Mineral. Geol.*, **16A**, No. 18, 1 (1943).
- Wankat, P. C., "Rate-Controlled Separations", Elsevier Science Publ., New York, NY, pp. 239-251, 1990.