

Displacement Effect in Multicomponent Chromatography

The study of interference effects is of fundamental importance in understanding multicomponent chromatography. In this work, a displacement effect is examined and shown to be able to explain the dominating interference effects in three major modes of chromatography—frontal, elution, and displacement—involving competitive isotherms. It is concluded that the concentration profile of a component usually becomes sharper due to the displacement effect from another component, while the concentration front of the displacer is usually diffused. Five factors that escalate the displacement effect in multicomponent elution were investigated. A binary elution with a competing modifier in the mobile phase was also discussed. This study was carried out using computer simulations based on a general nonlinear multicomponent rate equation model that considers axial dispersion, external mass transfer, intraparticle diffusion, and Langmuir isotherms. The use of the general model helps the visualization of the multicomponent interactions in chromatography under mass transfer conditions.

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Introduction

Chromatography for analytical purposes usually involves small and dilute samples. Thus, interference effects among different species are often negligible. Preparative and large-scale chromatography often involve high feed concentrations and large sample volumes. In such cases, competition among different species can no longer be ignored, and the study of interference effects becomes important in the understanding and optimization of multicomponent chromatography.

In the past, systematic studies of interference effects were based mostly on the interference theory by Helfferich and Klein (1970) and a mathematically parallel treatise by Rhee et al. (1970) and Rhee and Amundson (1982). The former was developed primarily for ion exchange involving isotherms with constant separation factors, with extension to Langmuir isotherms, and the latter was for adsorption and displacement processes with Langmuir isotherms. Both assume direct local equilibrium between the liquid phase and the stationary phase, and neglect mass transfer effects, which can be quite important in preparative and large-scale chromatography. It should be pointed out that in their monograph, Helfferich and Klein

(1970) also devoted a chapter to the discussion of extensions of their theory to more general cases. Lee et al. (1989) studied the mass transfer effects in multicomponent ion-exchange elution chromatography and concluded that the interference theory was able to predict the general location (or retention time) of the elution peaks, but failed to describe details of the concentration profiles when the mass transfer effects were large.

In this work, a general nonlinear multicomponent rate equation model was used to simulate various chromatographic processes. The effects of axial dispersion, external film mass transfer resistance, intraparticle diffusion, and nonlinear multicomponent isotherms were included in the model. The model is able to describe and anticipate some important phenomena, such as roll-up, in all the three major modes of chromatography, frontal, displacement, and elution under mass transfer conditions. The use of the general rate equation model involving various mass transfer mechanisms gives a more accurate account and thus helps the visualization of the dynamics of the chromatographic processes.

Tiselius (1940) was the first to use the phrase "displacement effect" to describe the competition for binding sites in multicomponent elution. It will be shown in this work that the displacement effect is, in fact, the dominating factor in multicomponent interference interactions that are directly attributed to the competition for binding sites among different components, and

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this effect exists in all the three major operational modes. Many observed multicomponent interactions due to competitive adsorption can be satisfactorily explained by using this simple concept. Although a few systems exist with synergistic (cooperative) isotherms (Helfferich and Klein, 1970) where the presence of other solutes enhances adsorption, the competitive isotherms are the most common type in practical operation (Wankat, 1986). The competitive Langmuir isotherm was chosen in this work. The conclusions in most cases can be readily extended to multicomponent systems with other types of competitive isotherms.

Model

Consider a chromatographic column that is filled with porous solid adsorbents with uniform spherical shape and size, and suppose the process is isothermal with no concentration gradient in the radial direction of the column, and all the diffusional and mass transfer parameters are constants. Assuming that there exists a local equilibrium for each component between the pore surface and the stagnant liquid phase in the macropores in the particle phase, the following dimensionless governing equations for component i in the bulk fluid and particle phases can be obtained by means of differential mass balances.

$$-\frac{1}{Pe_{Li}} \cdot \frac{\partial^2 c_{bi}}{\partial z^2} + \frac{\partial c_{bi}}{\partial z} + \frac{\partial c_{bi}}{\partial \tau} + \xi_i(c_{bi} - c_{pi,r=1}) = 0 \quad (1)$$

$$\frac{\partial}{\partial \tau} [(1 - \epsilon_p)c_{pi}^s + \epsilon_p c_{pi,l}] - \eta_i \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_{pi}}{\partial r} \right) \right] = 0 \quad (2)$$

Initial conditions

$$\tau = 0, \quad c_{bi} = c_{bi}(0, z) \quad (3)$$

$$c_{pi} = c_{pi}(0, r, z) \quad (4)$$

Boundary conditions

$$z = 0, \quad \partial c_{bi} / \partial z = Pe_{Li} (c_{bi} - C_{fi}(\tau) / C_{0i}) \quad (5)$$

For frontal adsorption, $C_{fi}(\tau) / C_{0i} = 1$

$$\text{For elution, } C_{fi}(\tau) / C_{0i} = \begin{cases} 1 & 0 \leq \tau \leq \tau_{imp} \\ 0 & \text{else} \end{cases}$$

After the sample has been introduced (in the form of frontal adsorption):

$$\text{if component } i \text{ is displaced, } C_{fi}(\tau) / C_{0i} = 0$$

$$\text{if component } i \text{ is a displacer, } C_{fi}(\tau) / C_{0i} = 1$$

$$z = 1, \quad \frac{\partial c_{bi}}{\partial z} = 0 \quad (6)$$

$$r = 0, \quad \frac{\partial c_{pi}}{\partial r} = 0 \quad (7)$$

$$r = 1, \quad \frac{\partial c_{pi}}{\partial r} = Bi_i (c_{bi} - c_{pi,r=1}) \quad (8)$$

Numerical Solution

This general nonlinear multicomponent rate equation model was solved using an efficient and robust numerical procedure by Gu et al., (1990). Finite-element and orthogonal collocation methods were used to discretize the bulk fluid phase and particle phase partial differential equations, respectively. The resulting ordinary differential equation system was then solved by using Gear's stiff method.

All the computer simulations were carried out on a SUN 4/280 computer. Parameter values used for simulations are listed in Table 1 or are mentioned in the discussion.

Results and Discussion

For comparison and simplicity, we ignore the component mixing effect on some physical properties, such as diffusion and mass transfer coefficients. The multicomponent Langmuir isotherm is expressed as follows.

$$C_{pi}^s = \frac{a_i C_{pi}}{1 + \sum_{j=1}^{Ns} b_j C_{pj}}$$

$$\text{i.e., } C_{pi}^s = \frac{a_i c_{pi}}{1 + \sum_{j=1}^{Ns} (b_j C_{0j}) c_{pj}} \quad (\text{dimensionless}) \quad (9)$$

in which a_i can also be expressed as $b_i C_i^\infty$. In this work, the adsorption saturation capacity ($C_i^\infty = a_i / b_i$) was set the same for different species in a multicomponent system. Note that $b_j C_{0j}$ may be treated as a dimensionless group for each component j .

Displacement operation

The displacement effect is most noticeable and is also relatively well known in displacement chromatography. In Figure 1 the solid lines show a simulated chromatogram (effluent history) of a stepwise displacement process in which component 2 (displacer) is introduced to a column presaturated with component 1 by a step change. A roll-up peak appears in the concentration profile of component 1, which is a clear indication of the displacement effect. The concentration profile of component 1 is sharpened compared with the dashed line, which represents the corresponding desorption operation when only an inert mobile phase is used to wash out component 1 from the column. In other words, the use of the displacer reduces the tailing and thus concentrates component 1. This is also evident in Figure 2, which shows a simulated chromatogram of a three-component displacement train in which components 1 and 2 are introduced to the column by frontal adsorption lasting $\tau_{imp} = 4.0$ before component 3 (displacer) is pumped into the column. In this volume overload case, component 2 has two peaks, of which the roll-up peak is due to the displacement effect from the displacer, component 3. Such a concentrating effect was proven by experiments carried out by Helfferich (1962). In Figure 2 there is also a roll-up peak for component 1 that is the result of the displacement effect from component 2. The first, smaller component 2 peak should not be mistaken as a displacement band for a separate component.

Competition can be viewed as a mutual interaction. The displaced component, while being displaced, in return also

Table 1. Parameter Values Used for Simulation*

Fig. No.	Species	Physical Parameters					Numerical Parameters	
		Pe_{Li}	η_i	Bi_i	a_i	$b_i \times C_{0i}$	Ne	N
1	1	300	10	3	3	6×0.1	10	2
	2	300	15	4	2	4×0.4		
2	1	200	10	2	2	2×0.2	11	1
	2	200	10	2	30	30×0.2		
	3	200	10	2	80	80×0.24		
3	1	100	1	2	1	2×0.1	5	2
	2	100	1	2	10	20×0.1		
4	1	300	30	1	1	10×1	16	1
	2	400	40	2	4	40×0.1		
	3	500	90	0.9	9	90×0.1		
5	1	300	40	1	0.4	0.8×0.1	10	1
	2	350	50	0.9	4	8×0.1		
9	1	300	40	1	0.4	0.8×0.1	10	1
	2	350	50	0.9	4	8×0.1		
	3	350	50	0.9	10	20×0.1		
10	1	300	80	2	10	5×0.2	14	1
	2	400	90	1.2	24	12×0.2		
	3	350	95	1	3	1.5×0.8		

*In all cases, $\epsilon_b = 0.4$ and $\epsilon_p = 0.5$. For elution cases, $\tau_{imp} = 0.1$, or otherwise as mentioned. The error tolerance of the ODE solver is $\text{tol} = 10^{-5}$. Double precision is used in the Fortran code.

exerts some influence on the displacer. Figure 1 illustrated that the concentration front of the displacer is diffused by component 1 in the displacement process. The concentration profile of component 2 is actually its breakthrough curve under the interference from component 1. As compared with the breakthrough curve of pure component 2, the dash-dot line in Figure 1, the concentration front of component 2 becomes diffused due to component 1.

The concentrating effect and roll-up phenomenon in displacement chromatography with negligible mass transfer effects were predicted by the ideal theories, including the interference theory (Tiselius, 1943; Glueckauf, 1949; Helfferich and Klein, 1970; Rhee and Amundson, 1982; Ruthven, 1984; Frenz and Horvath, 1985; Anita and Horvath, 1989). The general model presented in this work describes the roll-up phenomenon under mass transfer conditions.

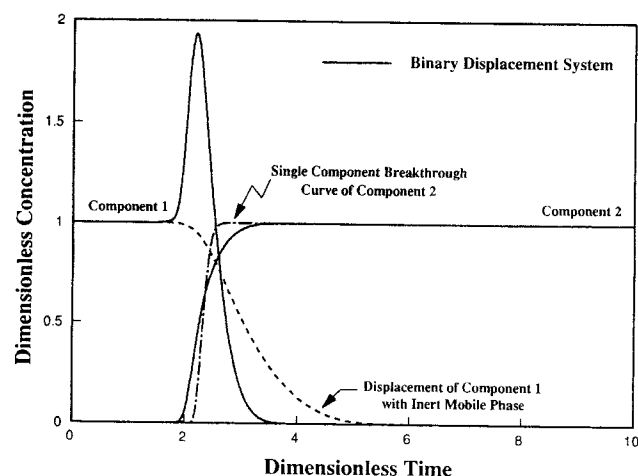


Figure 1. Two-component displacement system.

Frontal adsorption

Figure 3 shows a simulated chromatogram of a binary frontal adsorption process in which component 1 has a weaker affinity than component 2. The concentration profile of component 1 reaches a maximum that is larger than its feed concentration before leveling off. This roll-up phenomenon is the result of the displacement effect. The concentration front of component 1, which has a weaker affinity, migrates faster than the concentration front of component 2 inside the column. Component 1 takes advantage of the relative absence of component 2 and initially occupies a disproportionate share of binding sites. When the concentration front of component 2 catches up, it displaces some portions of component 1 such that the concentration of component 1 may exceed its feed value, causing the roll-up. The column finally reaches adsorption equilibrium when each compo-

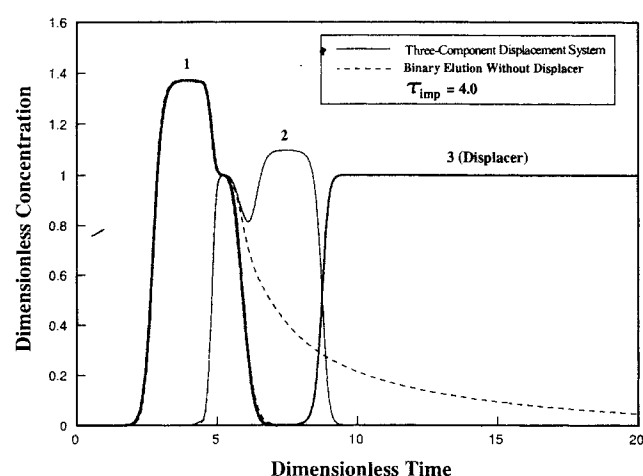


Figure 2. Three-component displacement system.

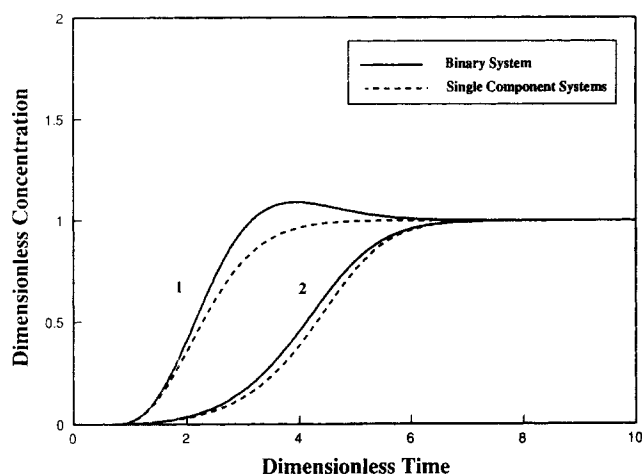


Figure 3. Binary frontal adsorption with a roll-up peak.

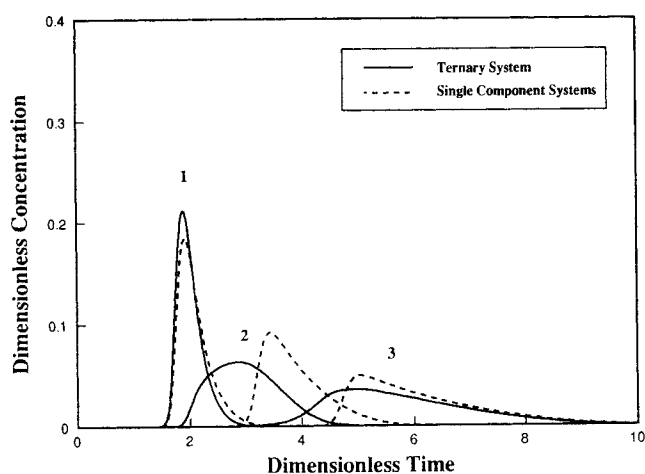


Figure 4. Ternary elution

nent occupies its share of binding sites according to the governing multicomponent isotherms. Experimental observations and simulations for this kind of roll-up in frontal adsorption with mass transfer effects have been reported by many researchers (Thomas and Lombardi, 1971; Rhee and Amundson, 1974; Hsieh et al., 1977; Liapis and Rippin, 1978; Liapis and Litchfield, 1980; Santacesaria et al., 1982; Kapoor and Yang, 1987).

A comparison of the breakthrough curves of the binary system and their corresponding pure-component breakthrough curves in Figure 3 indicates that earlier breakthrough results for each component in the binary system. This reflects the lower hold-up capacity of each component in the column compared to the corresponding pure-component case.

Elution

Multicomponent elution with an inert mobile phase results in a shortened retention time for each component, Figure 4. The retention times here are based on the first moments rather than the positions of the peak maxima. The peak height of component 1, which has a weaker affinity than component 2, is increased, indicating that less band spreading occurs as compared with the corresponding single-component case. Its front is diffused and tailing is reduced for the component 2 peak. Conversely, the peak height of component 3 is significantly decreased and its front is severely diffused.

These observations again can be explained by a displacement effect. When the three components are migrating inside the column with different speeds depending primarily on their

adsorption affinities, they separate from each other. Since component 2 has a higher affinity than component 1, it travels behind, and displaces and concentrates component 1, thus reducing the tailing of the component 1 peak. This results in a slightly shorter retention time, a larger peak height, and less band spreading for component 1. The displacement effect for such a case was also mentioned by other researchers (Tiselius, 1940; Antia and Horvath, 1989).

Mutual displacement causes the portion of component 2 that is in the mixing zone with component 1 to migrate faster than for the pure-component case inside the column, while the unmixed portion of component 2 migrates with the same speed as the pure-component case. This causes the diffusion of the front of the component 2 peak. In comparison, the displacement effect of component 3 on component 2 reduces the tailing of the component 2 peak. In return, component 2 diffuses the front of the component 3 peak. Since component 3 elutes last, the tail of its peak hardly changes as compared to its pure-component case. The effect of surrounding components is further illustrated by component 2, Figure 4, where the diffusion effect of component 1 reduces the peak height of component 2, while the displacement effect of component 3 tends to do the opposite. Therefore, the net effect of these two influences will determine the relative peak height of component 2.

The influences of the displacement effect on nonlinear multicomponent elution with an inert mobile phase are summarized in Table 2, with the understanding that the effects listed in the table may not always be noticeable, depending on the severity of the displacement effect. The severity of the displacement effect

Table 2. Summary of Nonlinear Multicomponent Elution (Compared with Pure-component Elutions)

Peak Position in Chromatogram	Retention Time, First Moment	Peak Height	Front Flank	Tailing
First peak	decreases	increases	sharpens	decreases
Middle peak(s)	decreases	increases or decreases	diffuses	decreases
Last peak	decreases	decreases	diffuses	*

*The tail end-point does not change much while the tail may become flatter, see Figures 4 and 6.

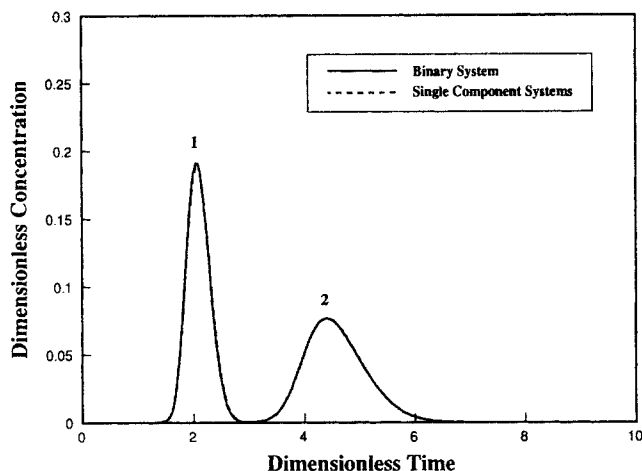


Figure 5. Binary elution showing slight displacement effect.

depends on the level of competition among all the components and the nonlinearity of the system. In multicomponent elution the following five factors have impacts on the displacement effect.

1. *Effect of the Adsorption Equilibrium Constants, b_i .* As the values of b_i increase, the nonlinearity of the isotherm and the competition for binding sites also increase. This escalates the displacement effect. If the values of b_i in a binary elution system are similar, the contact time between the two components is maximized as they migrate through the column. This increases the displacement effects. Figures 5 and 6 have the same conditions, except that in Figure 6 the affinity of component 1 is larger, thus closer to that of component 2; see Table 1. Compared with Figure 5, the displacement effect in Figure 6 is more pronounced.

2. *Low Adsorption Saturation Capacity, C_i^∞ .* Lower saturation capacity means fewer binding sites, and often increased competition for binding sites, especially in a system with large b_i values. In Figure 4, a system with small saturation capacity, C_i^∞ , was used in order to show a case with pronounced displacement effects. Figure 7 was obtained from Figure 4 by a fourfold

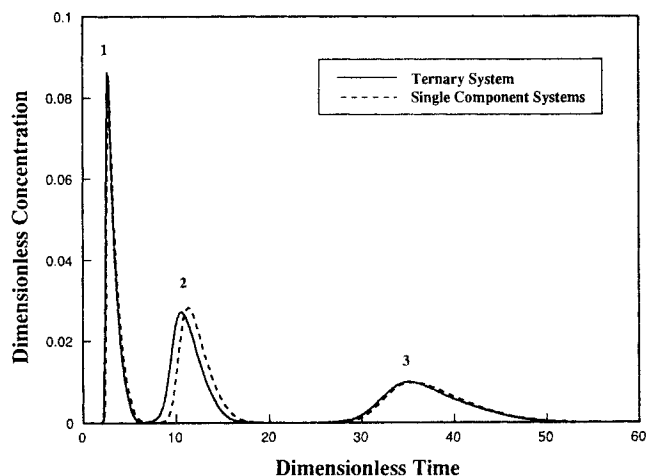


Figure 7. Ternary elution with increased adsorption capacity.

increase of the value of a_i for both components. The displacement effect is more pronounced in Figure 4 than in Figure 7.

3. *High Sample Feed Concentrations (Concentration Overload).* Increasing C_{0i} is equivalent to increasing b_i and reducing C_i^∞ proportionally, as is shown by the isotherm expression, Eq. 9. Thus, displacement effect escalates when increasing feed concentrations of the sample.

4. *Large Sample Size (Volume Overload).* When a larger sample size is used, the contact time between the components will increase, thus making the displacement effect more noticeable. Figures 5 and 8 have the same conditions except that in Figure 8, the sample size ($\tau_{imp} = 2.5$) is much larger than that in Figure 5 ($\tau_{imp} = 0.1$). The first half of Figure 8 actually represents the concentration profiles of the frontal adsorption curves, due to severe volume overload, with a roll-up peak.

The use of a large sample size in elution is not rare. In order to promote throughput, the column is often overloaded in terms of either sample size or sample concentration (Bauman et al., 1956; Giddings, 1965; Knox and Pyper, 1986; Eble et al., 1987; Ghodbane and Guiochon, 1988). Overload often increases the nonlinearity of the system, and thus the displacement effect.

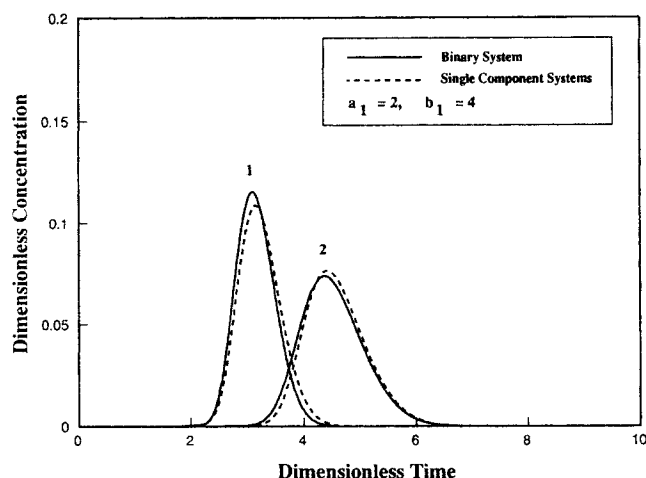


Figure 6. Binary elution with increased a_1 and b_1 values.

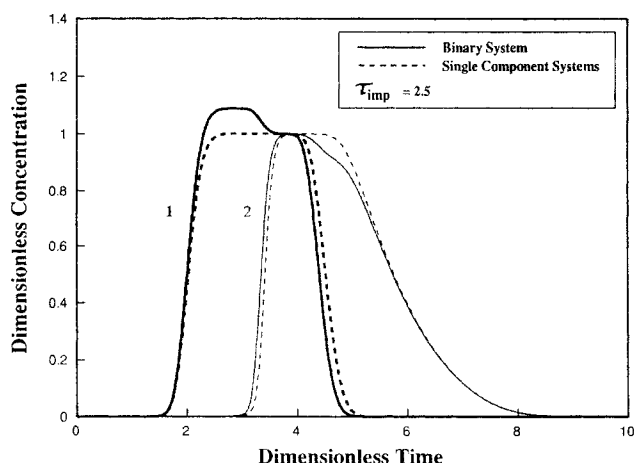


Figure 8. Binary elution with large sample size.

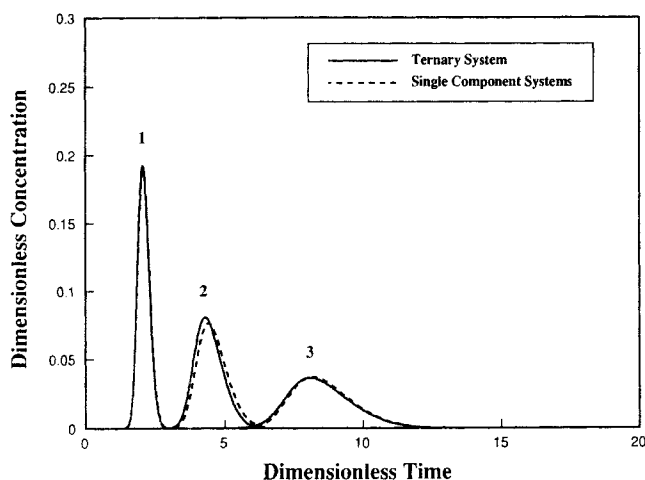


Figure 9. Effect of added component in sample.

5. *More Component(s)*. Adding more component(s) in the sample will increase the competition for binding sites among components. It also increases the nonlinearity of the isotherms, Eq. 9, thus escalating the displacement effect. The increased displacement effect in Figure 9 was obtained by adding one more component to the case presented in Figure 5.

When an additional component is present as a competing modifier in the mobile phase, the displacement effect becomes rather complicated. A competing modifier is sometimes added in the mobile phase to compete with sample components for binding sites in order to reduce their retention times (Snyder et al., 1988). The peaks corresponding to the concentration profile of the modifier in a chromatogram are often referred to as system peaks (Levin and Grushka, 1987). Figure 10 illustrates this concept, where component 3 is the modifier in the mobile phase. Cases similar to the solid lines in Figure 10 were reported by Golshan-Shirazi and Guiochon (1989a,b) based on a semi-ideal model, where the concentration of the modifier in the sample is the same as that in the mobile phase. The solid lines in Figure 10 show a positive system peak and two negative ones. Such system peaks are the result of the displacement effect of

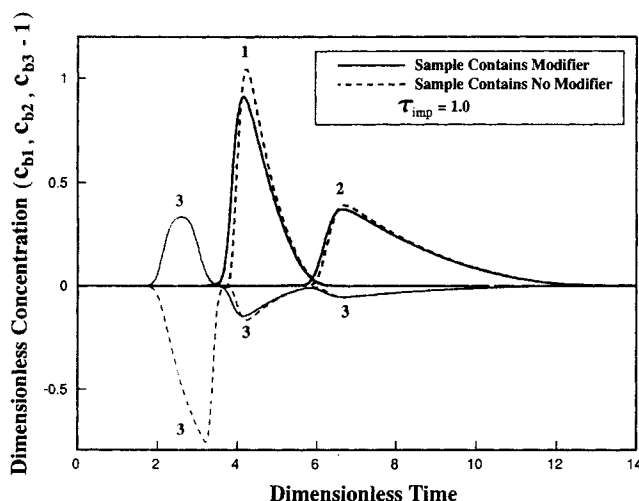


Figure 10. Binary elution with a competing modifier in mobile phase.

the sample solutes on the modifier, and are thus also referred to as displacement peaks (Solms et al., 1971). When the sample does not contain the modifier the deficit may cause a negative system peak at the front, as shown by the dashed lines in Figure 10.

Conclusions

For multicomponent chromatography involving competitive isotherms, the dominating interference effect can be attributed to the displacement effect, which occurs not only in the displacement mode but also in the other two major modes of chromatography, frontal and elution. Five factors that may escalate displacement effect in elution chromatography were investigated. In brief, these five factors either promote competition for binding sites among components or prolong such competition, or both. From a mathematical point of view, these factors can be interpreted as being able to either increase or prolong the nonlinearity of the isotherms. It has also been shown that roll-up exists not only in frontal adsorption and displacement, but also in elution. It is concluded that the displacement effect tends to reduce the tailing of the displaced species, while the concentration front of the displacer is diffused by the displaced species in all the three major modes of chromatography.

The use of a general nonlinear multicomponent rate equation model provides a systematic study of interference effects in multicomponent chromatography. The model accounts for various diffusional and mass transfer effects. The graphical representation of the results aids the visualization of multicomponent interactions, and thereby promotes a better understanding of the primary causes of the interference effects. The discussion presented in this work should be useful in the optimization of the chromatographic separation processes.

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Notation

- a_i, b_i = constants in Langmuir isotherm for component i
- Bi_i = Biot number of mass transfer for component i , $(k_i R_p / \epsilon_p D_{pi})$
- $c_{bi} = C_{bi} / C_{0i}$
- C_{bi} = bulk phase concentration of component i
- C_{fi} = feed concentration of component i
- C_{0i} = feed or sample concentration of component i used for nondimensionalization, $(\max \{C_{fi}(t)\})$
- $c_{pi} = C_{pi} / C_{0i}$
- C_{pi} = concentration of component i in fluid phase within particle
- $c_{pi}^s = C_{pi}^s / C_{0i}$
- C_{pi}^s = concentration of component i in solid phase within particle, based on unit volume of particle solid, excluding pores
- C_i^∞ = adsorption capacity (saturation limit) for component i
- D_{bi} = axial dispersion coefficient of component i
- D_{pi} = effective diffusivity of component i
- k_i = film mass transfer coefficient of component i
- L = column length
- N = number of interior collocation points
- Ne = number of quadratic elements
- Ns = number of components
- Pe_{Li} = Peclet number in bulk fluid phase for component i , (vL / D_{bi})
- R = radial coordinate for particle
- R_p = particle radius
- $r = R / R_p$
- t = time

v = interstitial velocity
 Z = axial coordinate variable
 $z = Z/L$

Greek letters

ϵ_b = bed void volume fraction
 ϵ_p = particle porosity
 η_i = dimensionless constant for component i , $(\epsilon_p D_{pi} L / R_p^2 v)$
 ξ_i = dimensionless constant for component i , $[3B_i \eta_i (1 - \epsilon_b) / \epsilon_b]$
 τ = dimensionless time, $[t / (L/v)]$
 τ_{imp} = dimensionless time duration for rectangular pulse of sample

Literature Cited

- Antia, F. D., and C. Horvath, "Operational Modes of Chromatographic Separation Processes," *Ber. Bunsenges. Phys. Chem.*, **93**, 961 (1989).
- Bauman, W. C., R. M. Wheaton, and D. W. Simpson, "Ion Exclusion," *Ion Exchange Technology*, Nachod and Schubert, eds., Academic Press, New York (1956).
- Eble, J. E., R. L. Grob, P. E. Antle, and L. R. Snyder, "Simplified Description of HPLC Separation under Overload Conditions, Based on the Craig Distribution Model," *J. Chromatogr.*, **384**, 25 (1987).
- Frenz, J., and C. Horvath, "High-Performance Displacement Chromatography: Calculation and Experimental Verification of Zone Development," *AIChE J.*, **31**, 400 (1985).
- Ghodbane, S., and G. Guiochon, "Influence of the Relative Concentrations of Two Components of a Binary Mixture on Their Overloaded Elution Profiles," *J. Chromatogr.*, **400**, 9 (1988).
- Giddings, J. V., *Dynamics of Chromatography. I: Principles and Theory*, Dekker, New York, 75 (1965).
- Glueckauf, E., "Theory of Chromatography. VII: The General Theory of Two Solutes following Nonlinear Isotherms," *Discuss. Faraday Soc.*, **7**, 12 (1949).
- Golshan-Shirazi, S., and G. Guiochon, "Theoretical Study of System Peaks and Elution Profiles of High Concentration Bands of Binary Mixtures Eluted by a Binary Eluent Containing a Strongly Retained Additive," *Anal. Chem.*, **61**, 2373 (1989a).
- , "Experimental Study of System Peaks and Elution Profiles of High Concentration Bands of Binary Mixtures Eluted by a Binary Eluent Containing a Strongly Retained Additive," *Anal. Chem.*, **61**, 2380 (1989b).
- Gu, T., G. J. Tsai, and G. T. Tsao, "New Approach to a General Nonlinear Multicomponent Chromatography Model," *AIChE J.*, **36**, 784 (1990).
- Helfferich, F., "Ligand Exchange. II: Separation of Ligands Having Different Coordinative Values," *J. Am. Chem. Soc.*, **84**, 3242 (1962).
- Helfferich, F., and G. Klein, *Multicomponent Chromatography—Theory of Interference*, Dekker, New York, 32, 273 (1970).
- Hsieh, J. S. C., R. M. Turian, and C. Tien, "Multicomponent Liquid Phase Adsorption in Fixed Bed," *AIChE J.*, **23**, 263 (1977).
- Kapoor, A., and R. T. Yang, "Roll-up in Fixed-Bed, Multicomponent Adsorption under Pore-Diffusion Limitation," *AIChE J.*, **33**, 1215 (1987).
- Knox, J. H., and H. M. Pyper, "Framework for Maximizing Throughput in Preparative Chromatography," *J. Chromatogr.*, **363**, 1 (1986).
- Lee, C. K., Q. Yu, S. U. Kim, and N.-H. L. Wang, "Mass Transfer Effects in Isocratic Nonlinear Elution Chromatography," *J. Chromatogr.*, **484**, 25 (1989).
- Levin, S., and E. Grushka, "System Peaks in Liquid Chromatography: Their Relation to the Adsorption Isotherm," *Anal. Chem.*, **59**, 1157 (1987).
- Liapis, A. I., and R. J. Litchfield, "Ternary Adsorption in Columns," *Chem. Eng. Sci.*, **35**, 2366 (1980).
- Liapis, A. I., and D. W. T. Rippin, "The Simulation of Binary Adsorption in Activated Carbon Columns Using Estimates of Diffusional Resistance within the Carbon Particles Derived from Batch Experiments," *Chem. Eng. Sci.*, **33**, 593 (1978).
- Rhee, H.-K., and N. R. Amundson, "Shock Layer in Two-Solute Chromatography: Effect of Axial Dispersion and Mass Transfer," *Chem. Eng. Sci.*, **29**, 2049 (1974).
- , "Analysis of Multicomponent Separation by Displacement Development," *AIChE J.*, **28**, 423 (1982).
- Rhee, H.-K., R. Aris, and N. R. Amundson, "On the Theory of Multicomponent Chromatography," *Philos. Trans. R. Soc. (London) Ser. A*, **267**, 419 (1970).
- Ruthven, D. M., *Principles of Adsorption and Adsorption Processes*, Wiley, New York, 287 (1984).
- Santacesaria, E., M. Morbidelli, A. Servida, G. Storti, and S. Carra, "Separation of Xylenes on Y Zeolites. 2: Breakthrough Curves and Their Interpretation," *Ind. Eng. Chem. Process Des. Dev.*, **21**, 446 (1982).
- Snyder, L. R., J. L. Glejch, and J. J. Kirkland, *Practical HPLC Method Development*, Wiley, New York, 27 (1988).
- Solms, D. J., T. W. Smuts, and V. Pretorius, "Displacement Peaks in Liquid Elution Chromatography," *J. Chromatogr. Sci.*, **9**, 600 (1971).
- Tiselius, A., "A New Method for Adsorption Analysis of Solutions," *Ark. Kem., Mineral. Geol.*, **14B**, 1 (1940).
- , "Displacement Development in Adsorption Analysis," *Ark. Kem., Mineral. Geol.*, **16A**, 1 (1943).
- Thomas, W. J., and J. L. Lombardi, "Binary Adsorption of Benzene-Toluene Mixtures," *Trans. Inst. Chem. Eng.*, **49**, 240 (1971).
- Wankat, P. C., *Large-Scale Adsorption and Chromatography*, CRC Press, 1, 9–13 (1986).

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