Prediction of Binary, Overloaded Elution Profiles Using the Simple Wave Effect

The separation of binary mixtures in overloaded elution chromatography has been investigated experimentally and theoretically using the Rouchon-Golshan-Shirazi implementation of the semiideal model (equilibrium-dispersive model). A competitive Langmuir isotherm with parameters determined from single-component data gives good prediction of the experimental data. Improved predictions, however, can be obtained by directly measuring the binary isotherm using the method of the hodograph transform.

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Introduction

The calculation of the individual elution band profiles in preparative chromatography has attracted much interest in recent years (Goldshan-Shirazi et al., 1989; Golshan-Shirazi and Guiochon, 1990; Guiochon and Ghodbane, 1988; Howard et al., 1988; Katti and Guiochon, 1989; Phillips et al., 1988; Saunders et al., 1989; Yu and Wang, 1986; Yu and Wang, 1989). Success in this area and in investigating the effect of changes in the experimental conditions on these profiles is a necessary step toward the development of methods for optimizing the experimental parameters for maximum production rate or, in an industrial setting, for minimizing total production costs.

Two approaches have been described for the calculations of these profiles, using a kinetic model (Golshan-Shirazi et al., 1989; Howard et al., 1988; Phillips et al., 1988; Saunders et al., 1989; Yu and Wang, 1986; Yu and Wang, 1989) or the semiequilibrium model (Golshan-Shirazi and Guiochon, 1990; Guiochon and Ghodbane, 1988; Katti and Guiochon, 1989). While the former approach is more general and, in principle, more rigorous, it is by far more complicated. It requires that the mass transfer resistances between the mobile and the stationary phases be identified and accounted for properly in the kinetic equations. The estimation of the rate constants is more difficult than the determination of thermodynamic properties. On the contrary, the equilibrium-diffusive model assumes that, at any given time and position, the concentrations of all the components in the stationary and the mobile phase are related by the equilibrium isotherm. The model accounts for the effect of the axial dispersion and the finite rate of mass transfer by the use of an apparent dispersion coefficient in the mass balance equation. The value of this coefficient is related to the number of theoretical plates in the column (Golshan-Shirazi and Guiochon, 1990; Haarhoff and Van der Linde, 1966; Giddings, 1965). This approach assumes that the diffusion coefficient does not depend on the solute concentration. Although reasonable for small molecules, this assumption may break down for biopolymers (Bird et al., 1960). In this work we use the semiequilibrium model and apply it to the separation of phenyl-ethanol and phenyl-propanol, a problem typical of the separation of short chain homologs in the pharmaceutical industry.

Both the semiequilibrium model and the linear driving force kinetic model require the use of equilibrium isotherms. Conventional methods of determining competitive isotherms are long and tedious, and require significant amounts of material, which is impractical for the expensive products coming from the pharmaceutical and biotechnology industry. Besides the classical static methods which are clearly unacceptable, two chromatographic methods are available: frontal analysis (Jacobsen et al., 1987) and pulse chromatographic techniques (Helfferich and Peterson, 1963; Stalkup and Kobayashi, 1963; Ruff et al., 1986).

Frontal analysis is the classical method of determining single-component equilibrium isotherms (James and Phillips, 1954; Schay and Szekely, 1954). It has been extended to binary mixture by Jacobson et al. (1987). As for single-component isotherms, successive frontal steps of solutions of increasing concentration, but constant relative composition, are introduced, and the composition of the intermediate plateau formed

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is determined by on-line chromatographic analysis. This method provides sections of the isotherm surface; they are in vertical planes going through the origin at various angles corresponding to the relative composition of the solution used. This method gives satisfactory results (Huang and Guiochon, 1989), but it is time-consuming and requires rather large amounts of material as each concentration step injected gives only one point.

Tracer pulse techniques have been used for the study of gas-phase equilibria (Helfferich and Peterson, 1963). They are impractical in liquid chromatography, since a labeled sample of the compounds studied must be synthesized and a selective detector must be available. For complex compounds the synthesis would be costly. Current regulations make work with radio-labeled compounds most unattractive. Detection of molecules labeled with stable isotopes may be made by LC/MS, but this instrument is complex, expensive, and rarely available. The retention time of a small pulse injected on a concentration plateau permits the determination of the first differential of the isotherm (Stalkup and Kobayashi, 1963; Ruff et al., 1986). Like frontal analysis, both pulse methods, however, require the use of large volumes of solutions. Finally, they generate important wastes which must be handled properly.

We describe here a method of determining competitive equilibrium isotherms, which requires a much smaller amount of material than the other methods since only the injection of a few wide rectangular pulses of concentrated solutions is needed. The pulse width is selected so that the concentration plateau is not completely eroded at the column exit, providing a constant state for the elution profiles. The front and rear breakthrough curves are simple waves. A series of narrow fractions are collected on both sides of the band and analyzed for the two components of the mixture. A hodograph plot of the elution curve, i.e., a plot of C_1 vs. C_2 at a given time results in a line going through the constant state (the point of coordinates $C_{0,1}$, $C_{0,2}$). The experiment is repeated with rectangular pulses of different concentration and relative composition. The simple wave theory predicts the relationship between the equations of these lines and the parameters of the isotherm model chosen. Thus, by curve fitting, isotherm parameters are derived.

The advantages of the method over the classical frontal analysis with binary mixtures (Jacobson et al., 1987) is the improved accuracy, the shorter time required to acquire the experimental data, and the much smaller amounts of chemicals needed. The main inconvenience is that the isotherm points are not obtained directly, but rather the experimental data must be fitted on an isotherm. Thus, an isotherm model is necessary.

This paper compares experimental, overloaded elution profiles and those predicted on the basis of competitive Langmuir isotherms, the coefficients of which have been determined in two different ways. First, we had measured single-component isotherms, shown that experimental data agree with the single-component Langmuir model, and used the best values of the coefficients in binary Langmuir isotherms. Second, we used the set of parameters, which best account for the hodograph plot of the experimental data obtained by the Simple Wave Method. In both cases, the band profiles were calculated with the Rouchon–Golshan-Shirazi implementation of the semiideal model (Rouchon et al., 1987; Guiochon et al., 1988).

Table 1. Coefficients of the Langmuir Isotherms

$$b_1 = \frac{1-\alpha}{\alpha A_+} - \frac{b_2}{\alpha \xi_+}$$

$$b_2 = (1-\alpha)\cdot\left(\frac{1/A_+ - 1/A_-}{1/\xi_+ - 1/\xi_-}\right)$$

Theory

The simple wave theory and the general results regarding the properties of the *hodograph transformation* are derived within the framework of the ideal model, which assumes a column of infinite efficiency. We briefly recall these general results, show how they can be applied for the case of real columns, having finite efficiency, and how the isotherm parameters are determined.

Ideal model

In an ideal column, the two phases are in equilibrium and there is no dispersion (Aris and Amundson, 1973). The mass balance equation for component i ($i = 1, 2$) is written:

$$\frac{\partial C_i}{\partial t} + F\frac{\partial q_i}{\partial t} + u\frac{\partial C_i}{\partial z} = 0 \tag{1}$$

The concentrations in the two phases are related by the equilibrium isotherm:

$$q_i = f_i(C_1, C_2) \tag{2}$$

The functions, f_1 and f_2, relate the stationary-phase concentration of the two components as a function of their mobile-phase concentrations. They account for the competitive behavior of the phase equilibria. In liquid-solid chromatography, the classical binary Langmuir equation (Schwab, 1928) is the simplest competitive isotherm:

$$q_i = \frac{a_i C_i}{1 + b_1 C_1 + b_2 C_2} \tag{3}$$

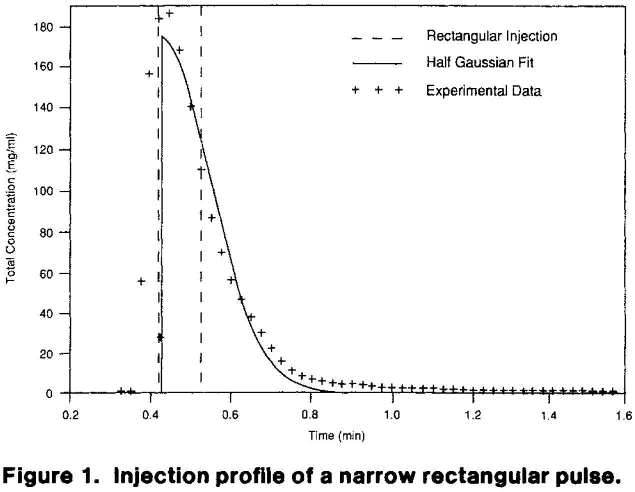

Figure 1. Injection profile of a narrow rectangular pulse.
Experimental profile obtained with a UV detector (symbols), equivalent rectangular profile (dashed line), and fitted curve used to represent the injection profile in calculations (solid line).

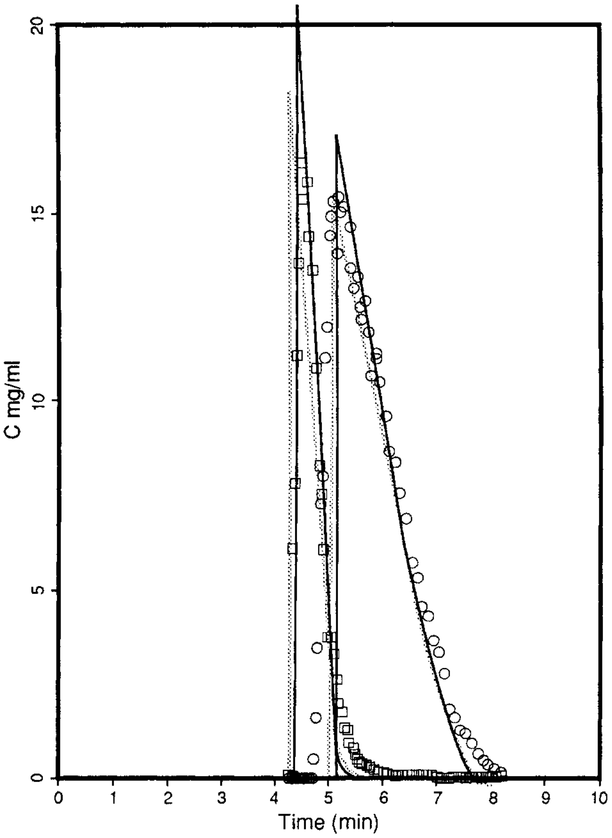

Figure 2. Experimental elution vs. individual profiles.

Elution profiles for a narrow pulse injection of 2-phenyl-ethanol (□) and 3-phenyl-propanol (○) and the individual profiles calculated assuming Langmuir competitive isotherms with numerical parameters derived from the single component isotherms measured by frontal analysis (·····) and the results of the Simple Wave Method (———). Sample relative composition: 1/3.

The elution profiles corresponding to the injection of a wide rectangular pulse are the solution of the system of the two partial differential equations 1 (with $i = 1$ and 2), with the following boundary and initial conditions:

$$\begin{aligned} C_1(t, z = 0) &= \phi_1(t) \\ C_2(t, z = 0) &= \phi_2(t) \\ C_1(t = 0, z) &= 0 \\ C_1(t = 0, z) &= 0 \end{aligned} \tag{4}$$

The two functions $\phi_i(t)$ are the injection profiles. Ideally, they are rectangular pulses, several minutes wide; but in practice, they are more complex, and exhibit exponential rise and decay. The ratio $\phi_1(t)/\phi_2(t)$ is constant during the injection.

Hodograph transformation

The hodograph transform exchanges the role of the functions, C_1 and C_2, and the role of the independent variables, z and t. Since the concentrations, C_1 and C_2, are functions of z and t, the location and time where the concentrations, C_1 and C_2, are found are functions of these concentrations. This exchange is possible

Table 2. Overloaded-Elution Experimental Data

Feed Comp.	Total Sample Size (mg)	PE* (mg)	PP** (mg)	PE* L_f(%)	PP** L_f(%)
1/3	28	7	21	5	15
1/1	20	10	10	7	7
3/1	40	30	10	21	7
10/1	30	28	1.7	21	2.3

*PE-2-phenyl ethanol
**PP-3-phenyl propanol
Loop volume, 0.1 mL; average column saturation capacity, 145 mg
The loading factor (L_f, ratio of sample amount to amount corresponding to saturation of the column surface) is based on single-component isotherm data.

whenever the Jacobian:

$$j = \frac{\partial(C_1, C_2)}{\partial(z, t)} = J^{-1} \tag{5}$$

has a finite value different from zero. It has been shown that if the Jacobian matrix does not have the system rank, i.e., 2 for a binary mixture, the hodograph transform of the solution of the system of equations 1 from the (z, t) space into the (C_1, C_2) space is singular (Aris and Amundson, 1973; Helfferich, 1986; Jeffrey, 1976; Shapiro, 1953; Whitham, 1974). If the rank of the Jacobian matrix becomes 1, the points of a whole region of the (z, t) space are mapped to a line of the (C_1, C_2) space. If the rank of the Jacobian matrix becomes zero, these points are mapped to

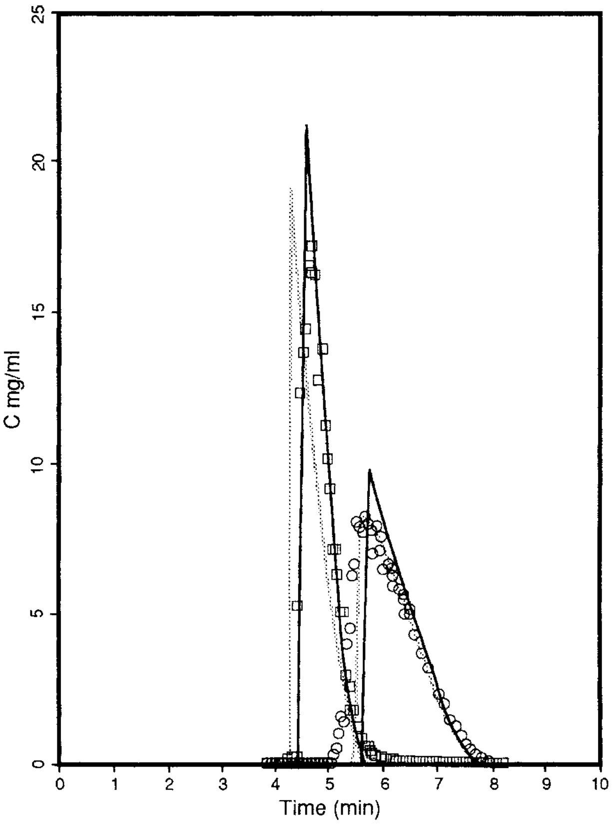

Figure 3. Same as Figure 2, except sample relative composition: 1/1.

a single point of the (C_1, C_2) space. The theory of partial differential equations shows that whenever there is a constant state, the characteristics of the (z, t) space are mapped into a single point and two straight lines in the (C_1, C_2) space. Then, the solutions are called simple wave solutions.

In chromatography, a constant state is achieved when a wide rectangular pulse is injected and its width is such that the plateau has not completely eroded during elution. On the plateau, the concentrations of the two components are constant and their partial derivatives are zero. The rank of the Jacobian is zero and the hodograph transform of the plateau is the point having coordinates ($C_{1,0}$, $C_{2,0}$). The simple wave theorem says that the hodograph transform of the elution profile is made of two lines (Lin et al., 1990). The following sections discuss this result as well as the correspondence between the elution profiles and its hodograph transform.

When the first component begins to elute, the corresponding point of the transform rises on the C_1 axis and remains on this axis as long as the concentration of the second component is zero. The concentration of the first component reaches a plateau and remains constant until the second component begins to elute (displacement effect) (Lin et al., 1990; Golshan-Shirazi and Guiochon, 1989). Then, while the concentration of the second component increases, the concentration of the first component decreases. The corresponding part of the hodograph transform is a curve which decreases monotonically with increasing second-component concentrations. Eventually, the plateau is reached and the first line (i.e., the transform of the band front) ends at the point ($C_{1,0}$, $C_{2,0}$). The reverse process takes place on the band tail, but now both concentrations decrease simultaneously, until the elution of the first band ends. The corresponding part of the hodograph transform is a second curve, starting at the constant state and intersecting the C_2 axis at the point corresponding to the end of the first band. Finally, the second-component concentration decreases to zero and the end of the hodograph transform is a segment of the second axis.

In general, the two curves obtained in the (C_1, C_2) space, referred later as the hodograph plot, are not straight lines. The equations of these lines are directly related to the equations of the competitive isotherms of the two components, so the experimental determination of the hodograph plot permits the derivation of these parameters. In the case of a Langmuir competitive isotherm (Eq. 3), however, the two curves of the hodograph transform are two straight lines (Lin et al., 1990). If (ξ_+, ξ_-) and (A_+, A_-), respectively, are the positive and negative slopes of these straight lines and their intercepts, the coefficients, b_1 and b_2, of the Langmuir isotherms are given by the equations in Table 1. The coefficients a_i, can be derived from the retention times of the two components at infinite dilution or from the single-component isotherms.

Experimental Studies

Equipment

A Waters (Milford, MA) high-pressure liquid chromatograph was used, which includes two Model 510 pumps controlled by a system interface module (SIM) connected to the serial port of a NEC APCIV (Boxborough, MA) by the

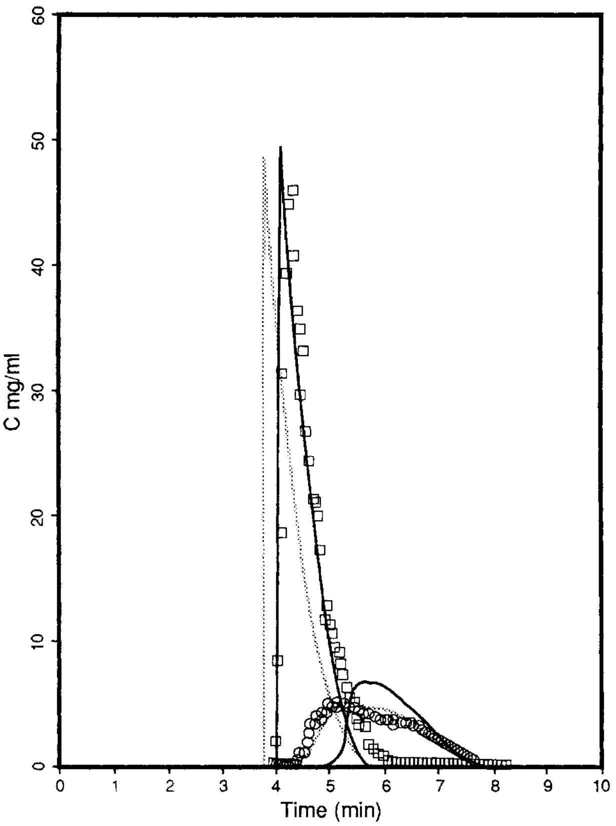

Figure 4. Same as Figure 2, except sample relative composition: 3/1.

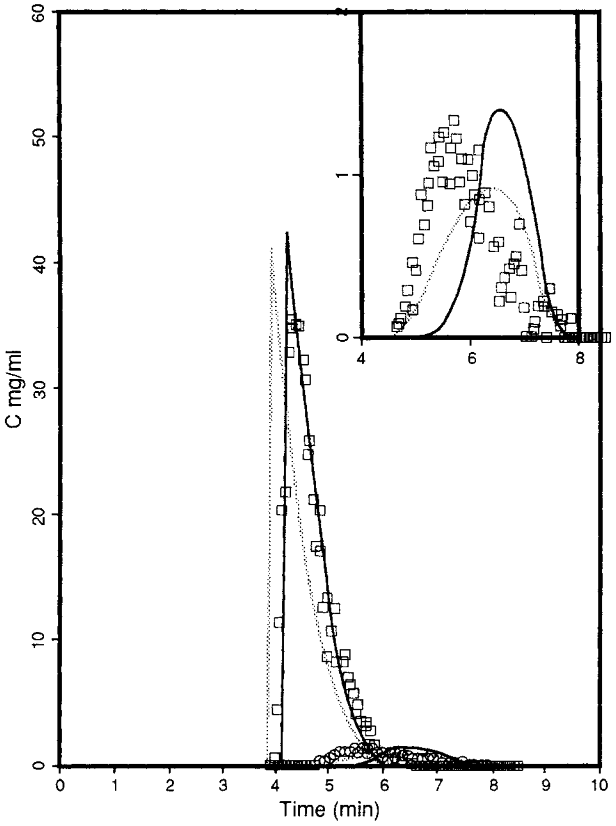

Figure 5. Same as Figure 2, except sample relative composition: 10/1.

Maxima 860 Dynamic Solutions (Ventura, CA) software. A Valco (Houston, TX) six-port electrically-activated valve, a Model 757 Kratos (Applied Biosystems, Ramsey, MJ), and a Gilson Model (Middleton, WI) 232-401 automatic sample processor were employed and connected to the SIM box for automatic data acquisition (Katti and Guiochon, 1989; Katti, 1990).

For the large-volume injection experiments, the six-port valve plumbing was arranged so that the chromatograph above pumped the eluent while an auxiliary Gilson Model 201 pump, connected to a SSI pulse dampener (State College, PA) followed by a flow-through pressure gauge, pumped the sample solution prepared (binary mixture dissolved in the mobile phase). By switching from the load to the inject position, the sample was pumped through the column. By returning the valve to the load position, the rectangular injection was completed and the mobile phase could elute the sample from the column. To minimize pressure surges when the valve is actuated, the sample stream from the Gilson pump is wasted through a pressure restrictor when the valve is in the load position while the stream of the mobile phase from the Waters pump is sent to waste through another pressure restrictor when the valve is in the inject position (Katti, 1990).

For the elution experiments, the six-port valve was arranged in standard format with a 100 μL loop. The fractions were analyzed by connecting the outlet of the Model 510 pumps directly to the Gilson automatic sample processor employed in automatic injection mode. A YMC (Morris Plains, NJ) fast analysis column was connected to the Rheodyne (Cotati, CA) sampling valve on the sample processor using a 20 μL loop. Partial loop injection using 10 μL aliquots taken from each sample vial was used for the analysis of the fractions.

Materials and products

The 4.5 mm x 25 cm column used for the elution of the wide rectangular pulses of binary mixtures and for the overloaded elution of narrow pulses was packed in our laboratory with 10 μm ODS silica from Vydac (Hesperia, CA). For the analysis of the fractions, a 4.6 mm x 5 cm YMC (Morris Plains, NJ) columns was employed.

The solvents used to prepare the mobile phase were water and methanol from Burdick and Jackson (Muskegon, MI). The 2-phenyl-ethanol and 3-phenyl-propanol are from Aldrich (Milwaukee, WI). The chemicals were used as received, without further purification.

Experimental procedure

The detector response at 272 nm was measured for several consecutive injections for both the overloaded elution and the large volume experiments involving the injection of wide rectangular pulses. After checking for reproducibility of the response curve, fractions were collected over the entire elution profile and reanalyzed for the composition of each component (Katti and Guiochon, 1989). In this analysis, the detector signal was monitored at 254 nm, a calibration curve was derived from the

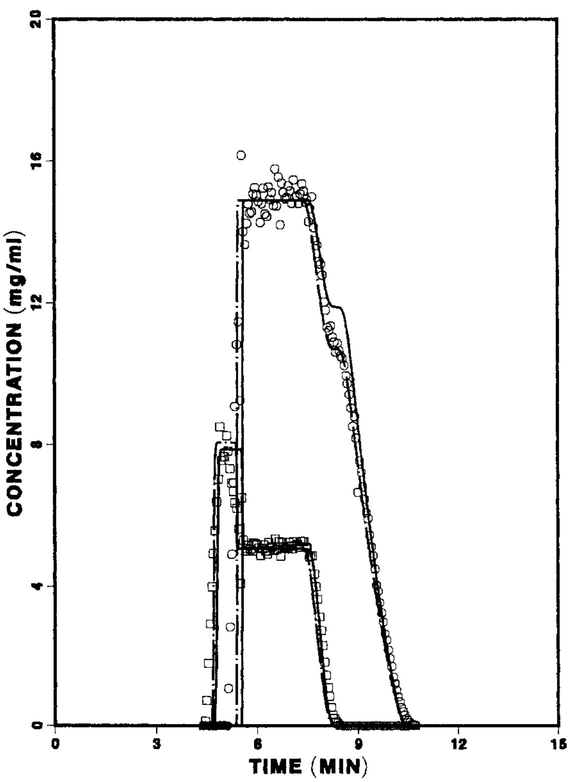

Figure 6a. Competitive equilibrium isotherms determined by simple wave method.

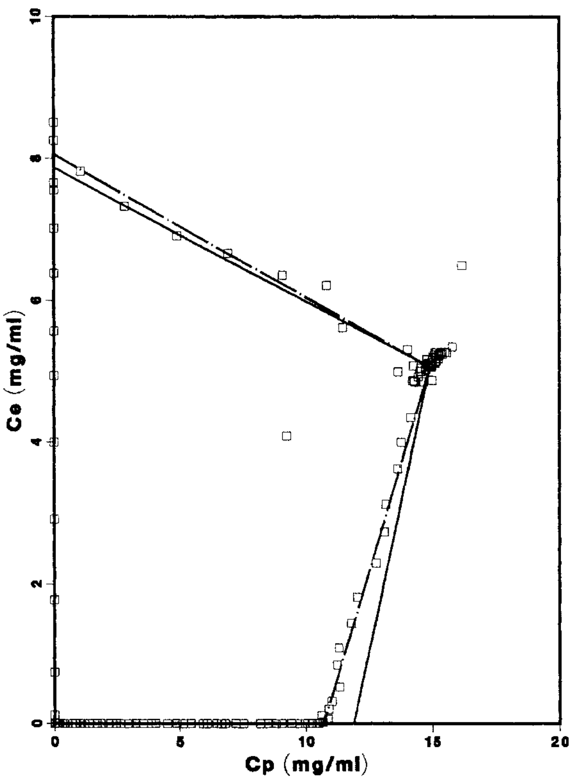

Figure 6b. Hodograph transform of the data in Figure 6a.

Experimental elution profiles for a wide rectangular injection of 2-phenyl-ethanol (□) and 3-phenyl-propanol (○). Profiles calculated assuming competitive Langmuir isotherms with numerical parameters derived from the single-component isotherms measured by frontal analysis (———) or derived from the simple wave method (——·——). Sample relative composition: 1/3.

chromatograms of known samples, and the quantitative analysis of each chromatogram was made using the Maxima software.

Results and Discussion

Figure 1 shows the injection profile for the narrow pulse typically used in overloaded elution, i.e., in preparative chromatography (symbols). It was obtained by connecting the standard subunits of a chromatograph in the nonconventional order pump, column, sampling valve, detector. This permits the pump to deliver the same mobile-phase flow rate through the column as under normal conditions and the detector to give the injection profile. This profile can be compared to the superimposed ideal rectangular profile (dashed line) corresponding to the loop volume (0.1 mL). The actual injection profile exhibits a 0.42 min offset, due to the extra column volume of the system and a significant dilution in the injector. As previously described by Golay and Atwood (1979), the profile shows a sharp rise followed by a tailing rear and can be approximated by a half-Gaussian curve. The band spreading due to the Poiseuille radial flow velocity profile has not yet achieved steady state conditions. Figure 1 shows a comparison between the experimental profile (symbols) and this fitted half-Gaussian curve (solid line). The steep front is approximated by a vetical line. The diffuse rear part of the profile tails somewhat longer than as modeled. The approximated profile in Figure 1 has been used in all the simulations described in the present work.

Figures 2 to 5 show the experimental profiles of the two-component bands obtained upon injection of mixtures of different composition (symbols). The four chromatograms were obtained under the same experimental conditions, with different feed compositions reported in Table 2. The individual elution band profiles have been determined by the analysis of fractions collected at a rate of one fraction every three seconds. The symbols in each figure represent the result of these analysis. Prior results have demonstrated that the fraction collection device introduces very little volume, hence no significant delay nor band broadening (Katti and Guiochon, 1990). The solid lines in these figures are: the band profiles calculated for each component using the finite difference algorithm previously developed in our laboratory (Rouchon et al., 1987; Guiochon et al., 1988; Czok and Guiochon, 1990); the injection profile modeled as described in the previous paragraph (see Figure 1); and competitive Langmuir isotherms, with the numerical values of the coefficients determined by measuring the single-component isotherms by frontal analysis (James and Phillips, 1954; Schay and Szekely, 1954).

In general, there is a substantial agreement between the two sets of data. Especially, the front of the first component is eluted exactly when predicted. The calculated profile of the rear part of the first component band is also in close agreement with the experimental data. On the contrary, the second component front is eluted much earlier than predicted with the simple competitive Langmuir isotherm. The rear part of the second component band profile is in a close agreement with the experimental data for the 1/1 (Figure 2) and the 1/3 (Figure 3) mixtures. The agreement is fair for the 3/1 mixture (Figure 4) and poor for the 10/1 mixture (Figure 5) where the second component is dilute (ca. 6% v/v). The agreement between the experimental and the calculated profiles in Figures 2 and 4 is somewhat better than in the similar figures in a previous publication (Katti, 1990; Katti and Guiochon, 1990), because in this work we have taken into account the effect of the actual injection profile (Figure 1).

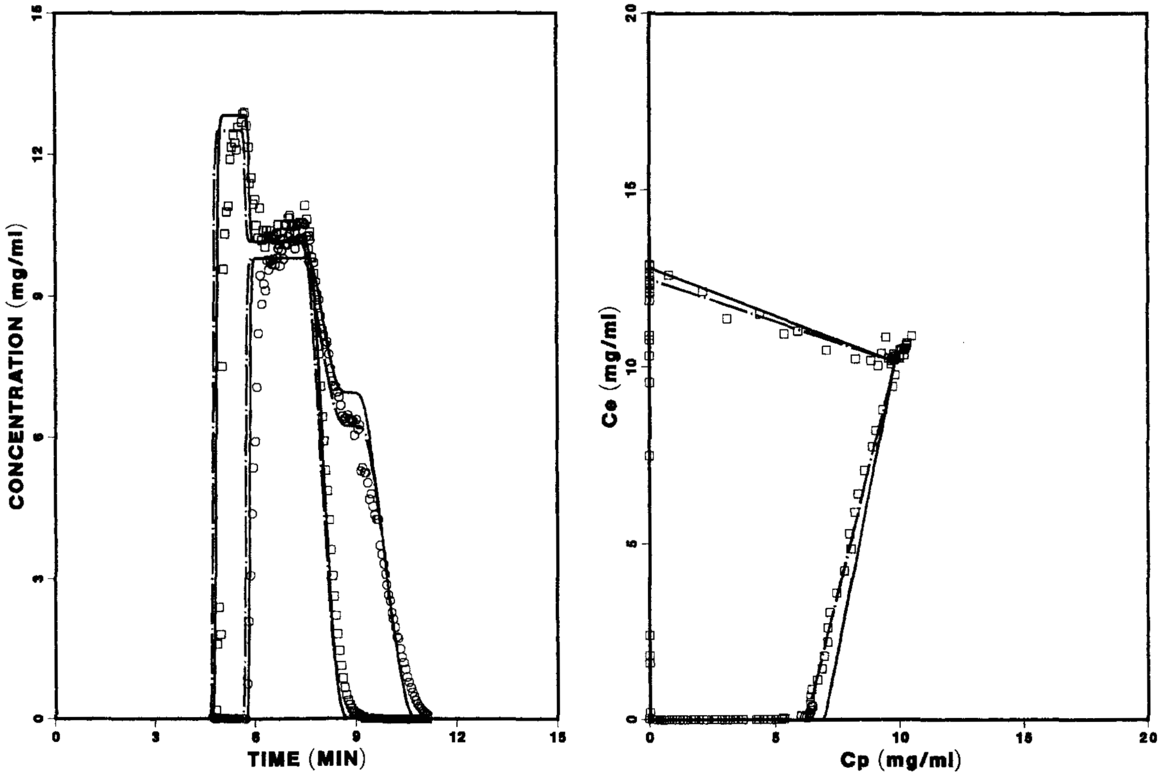

Figure 7. Same as Figure 6, except sample relative composition: 1/1.

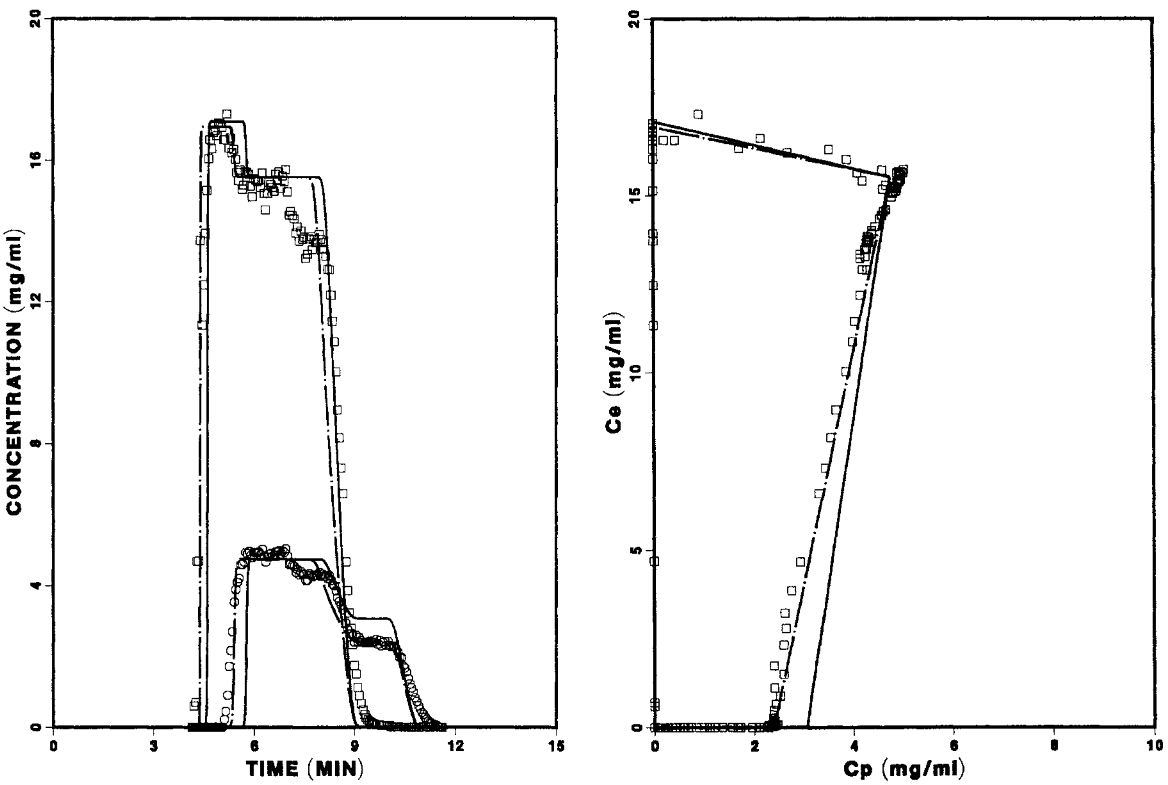

Figure 8. Same as Figure 6, except sample relative composition: 3/1.

We interpret these results as meaning that the competitive binary isotherm is only approximately accounted for by the simple Langmuir equations. The use of a more accurate isotherm model would be necessary to account correctly for the experimental results. The individual elution profiles are quite sensitive to minor changes in the values of the isotherm parameters (Lin et al., 1990).

To determine the competitive isotherms from binary mixture data, we have used the simple wave method and the hodograph transform of the elution data. A wide rectangular pulse of feed is injected and the individual component profiles are determined by analysis of fractions collected. The total amount of sample injected remained constant and we varied the concentration of the two components in the binary mixture. The composition of the four samples studied are listed in Table 2. Figures 6a, 7a and 8a show the individual elution profiles determined from the HPLC analysis of the fractions (symbols) and the individual elution profiles of the wide pulses predicted with the semiideal model (Guiochon et al., 1988) using single-component isotherm parameters in a competitive Langmuir model.

Figures 6b, 7b and 8b show the hodograph plots, the straight lines derived from the single-component Langmuir isotherm coefficients (solid lines) and the best straight lines going through the constant state (dash-dotted lines) and fitting the experimental data (symbols). These last lines are determined by a least square fit of the relevant data points. For the descending line, these points include all those of the band front, for which C_2 is different from 0 and both C_1 and C_2 are less than 0.95 times the coordinates of the constant state. For the ascending line, these points are those of the band rear for which C_1 and C_2 are both less than 0.95 the coordinates of the constant state and C_1 is different from 0. These lines should go through the point corresponding to the constant state, which has the composition of the feed as coordinates. If they do not but the coordinates of their intersection do not differ from (C_1^0, C_2^0) by more than a few percents, the results are still considered acceptable.

As in the case of Figures 2 to 5, there is a systematic deviation between the experimental data and the profiles calculated with the competitive Langmuir isotherm and the coefficients determined from the single-component Langmuir isotherms (cf symbols and solid lines in Figures 6a to 8a and 6b to 8b). This demonstrates that the competitive Langmuir isotherm equation does not account accurately for the competitive behavior of the two components. On the other hand, the experimental points are well represented by the least-square fit straight lines, on the wide rectangular pulse elution profiles (dash-dotted lines in Figures 6a to 8a) and on the hodograph transforms (Figures 6b to 8b). Especially, the position and profile of the shoulder on the rear of the elution band are much better accounted for. The larger scatter of the data on the descending line of the hodograph than that on the ascending one is related to the great steepness of the band front and the few data points available. The determination of A_- and ξ_- is not as accurate as that of A_+ and ξ_+.

The values of the isotherm coefficients calculated from the slope and intercept of the straight lines on Figures 6b, 7b and 8b using the equations in Table 1 are given in Table 3. The numerical values of these coefficients differ from those obtained from the single-component determination by frontal analysis. The coefficients calculated for the different injections differ slightly. We note that the column saturation capacity for 2-phenyl ethanol is markedly depressed, by approximately 40%, while the column saturation capacity for 3-phenyl propanol is

Table 3. Large-Volume Injection Parameters and Results

	1/1	3/1	1/3	Avg.	Single-Comp. Langmuir
b Coefficients					
b_E, mL/mg	0.0211	0.0266	0.0224	0.025	0.0148
b_P, mL/mg	0.0256	0.0297	0.0295	0.027	0.0255
b_E, $mM-1$	2.58	3.25	2.73	3.04	1.81
b_P, $mM-1$	3.48	4.05	4.04	3.69	3.48
a Coefficients					
a_E	1.92	1.92	1.92	1.92	1.92
a_P	3.55	3.55	3.55	3.55	3.55
Column saturation capacity					
$Q_{s,E}$, mg	98	78	93	83	140
$Q_{s,P}$ mg	150	129	130	142	150
Parameters					
HETP	0.0167	0.0085	0.0085		
u_z, cm/s	0.069	0.069	0.069		
u_0, cm/s	0.135	0.139	0.139		
Injection time, min	3.5	5.0	3.6		
$C_{0,E}$, mg/mL	10.3	15.11	5.15		
$C_{0,P}$, mg/mL	10.1	5.06	15.1		

Column length, 25 cm; porosity, 0.74

decreased by only about 5%. This is in agreement with the observation made above that the displacement effect of the first component by the second one appears to be stronger than predicted by the single-component parameters.

Finally, we have recalculated the individual elution profiles, using the same procedure as described above, using again competitive Langmuir isotherms, but with the average values of the coefficients determined from the hodograph plots (Table 3). The results are presented in Figures 2 to 5 (dotted lines). Compared to the solid line chromatograms in these figures, the agreement is somewhat less good for the steep front of the first component, but much better for the rest of the profiles, the rear of the first band profiles, and the entire profile of the second component. The agreement between experimental and calculated profiles is especially satisfactory for the second component in the 3/1 and 10/1 mixtures in Figures 4 and 5 (dotted lines), while it was poor for the solid lines in these figures.

The three experiments reported in Figures 6 to 8, where wide rectangular pulse injection are performed and the front and rear parts of the elution profiles are accurately determined by analysis of collected fractions, give three sections of the isotherm surfaces, $q_i = f(C_1, C_2)$, by the vertical planes of horizontal slopes C_1/C_2 equal to 1/3, 1, and 3, respectively (i.e., at C_1/C_2 constant and equal to 0.33, 1, and 3, respectively). Summarizing the results of these three sections by the average coefficients of competitive Langmuir isotherms is a rather crude way of representing these surfaces. The improvement over previous results derived from the single-component isotherms is significant, however. Still better results could probably be obtained if more experiments were carried out and their results fitted on a more complex isotherm equation, i.e., the ratio of two second-order polynomials (Lin et al., 1989). Considerably more data would be required, however, and it is dubious whether, in general, the additional improvement in the accuracy of the prediction of band profiles would be worth the cost and trouble in view of experimental errors.

Different numerical values are obtained for the best values of the coefficients of a competitive Langmuir isotherm, depending on whether the experimental data used to determine them are single-component or competitive adsorption data. This fact shows that the competitive Langmuir isotherm is not satisfactory. The two calculation procedures stretch the model in different ways. When using single-component isotherms, the fit is very good for the first component band and only fair for the second one. The converse is true when the coefficients are derived from competitive isotherm data. In principle, all the information regarding the isotherm is contained in the hodograph transforms (Figures 6b to 8b). More sophisticated isotherms (LeVan and Vermeulen, 1981; Lin et al., 1989; Moreau et al., 1990) can be used to fit the data. This requires the acquisition of either more accurate data than those reported here or more data—for example, studying the influence on the hodograph lines of changes made in one of the constant state concentrations at constant value of the other one (Lin et al., 1990).

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Notation

A_+, A_- = intercepts of straight lines in the Hodograph plot
a_1, a_2 = numerical coefficients of the competitive Langmuir isotherm equation
b_1, b_2 = numerical coefficients of the competitive Langmuir isotherm equation
$C_{1,0}, C_{2,0}$ = concentrations of two components in the rectangular pulse injection
C_1, C_2 = mobile-phase concentrations of two components, functions of time and length
F = phase ratio of the column packing $[F = (1 - \epsilon)/\epsilon]$
$f_i(C_1, C_2)$ = isotherm of component i
q_1, q_2 = stationary-phase concentrations of two components, functions of time and length
t = time
u = mobile-phase velocity
z = distance along the column

Greek letters

α = relative retention of two components under linear conditions (equal to the ratio a_2/a_1 of their Langmuir isotherm coefficients)
ϵ = internal porosity of the column packing
$\Phi_i(t)$ = injection profile for component i
ξ_+, ξ_- = slopes of straight lines in the hodograph plot

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