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Theoretical study of the effect of a difference in column saturation capacities for the two components of a binary mixture on their elution band profiles and separation in non-linear chromatography

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ABSTRACT

The elution profiles of large samples of binary mixtures are determined using the classical competitive Langmuir isotherm equations, with different values of the column saturation capacities for the two components. It is shown that the elution profile of an incompletely separated binary band system depends on the ratio of the two loading factors rather than on the relative concentrations of the feed. The ratio of the two column loading capacities is as important as the relative composition in determining the two band profiles. Thus, if the column saturation capacity is lower for the first-eluted component than for the second, the displacement effect will appear to be smaller than would be predicted on the basis of the feed composition. Conversely, the tag-along effect will appear to be more important. The reverse is true if the column saturation capacity is larger for the first-eluted component than for the second.

INTRODUCTION

In previous publications[1–5], we considered in detail the influence of the relative retentions of the two components of a binary mixture and of various experimental conditions (*e.g.*, sample size, relative concentrations of the feed, mobile phase velocity, column efficiency) on the separation of high concentration bands in preparative chromatography. These theoretical studies were performed using competitive Langmuir isotherms to account for the interactions between the two bands during their progressive separation and assuming that the column saturation capacities for the two components are equal.

Recently, experimental data have been presented suggesting that the competition between the two components of a binary mixture results in band profiles that depend considerably on the relative column saturation capacity[6]. The theory of the

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ideal model of chromatography[7] show that the relative intensities of the displacement and the tag-along effects in this model depend on the ratio of the loading factors of the two components, not on the relative composition of the feed[8]. We show here that the semi-ideal model supports the same results. We also demonstrate that conclusions regarding the validity of the Langmuir competitive isotherm model cannot be derived merely from the qualitative consideration of the pattern of interfering bands for a series of mixtures with different relative compositions.

THEORY

Competitive equilibrium isotherms

The use of Langmuir isotherms to account for experimental data in phase equilibria is extremely convenient. Langmuir isotherms are most often in excellent agreement with the results of measurements made for the adsorption equilibrium of pure compounds in normal- or reversed-phase chromatographic systems[9–11]. In the few cases where significant, systematic disagreement has been reported, a bi-Langmuir isotherm was found to be satisfactory[12,13]. In the case of competitive equilibria, however, the situation is more complex.

First, the theoretical basis of the Langmuir isotherms has been established in the case of gas or vapor adsorption, where there is no matrix adsorption. The fraction of the surface that is not covered by the adsorbate is really free, *i.e.*, bare. Even in gas chromatography there is not much adsorption of the carrier gas. The extension to the case of liquid–solid equilibria is not straightforward because, even with a pure solute, there is competition between the solute and the solvent for adsorption[14].

In the case of competitive adsorption of two components, the Langmuir binary isotherm model is thermodynamically correct only if the molecules of the two components occupy the same surface area on the adsorbent surface (*i.e.*, have the same "footprint") and the column saturation capacity is the same for both compounds[15]. Otherwise, the Gibbs–Duhem relationship is not satisfied. This condition is generally not fulfilled, although in many practical cases we are interested in the separation of closely related compounds and the ratio of their column saturation capacities will not be very different from unity. Unrelated compounds which interfere in a given chromatographic system can usually be separated easily in a different system.

In spite of these theoretical reservations, it turns out that in many practical cases the Langmuir isotherm model gives an acceptable fit of the experimental data. The quality of this fit can be deceptive, however. When isotherms are determined using the classical frontal analysis method for a binary mixture[16] or the "simple wave" method[17], the data obtained at constant feed composition and variable feed sample size are well accounted for by the Langmuir competitive model, although the variation with the feed composition of the coefficients obtained by a least-squares fit of the data to the Langmuir model does not agree well with the prediction of this model[11,17]. In most practical cases, it seems that the Langmuir model is no more than a satisfactory or fair first-order approximation to the real competitive isotherms, especially when the column saturation capacities of the two components are different.

The considerable practical advantage of the competitive Langmuir isotherms, which explains the great popularity of this model, is that the numerical values of all the coefficients are those for the pure compound isotherms. Only the experimental determination of the single-component isotherms is required, which is considerably simpler than that of the competitive isotherms. As the Langmuir competitive isotherm is an acceptable approximation which is easy to estimate, its use as an empirical model is justified in general investigations such as the present one.

Computer calculations

The calculations reported and discussed here are based on the same principles as for our previous results using the semi-ideal model of chromatography[1–5,18]. We use the system of two partial differential equations stating the mass balance of the two components of a binary mixture, with the assumption of an ideal model (*i.e.*, the column efficiency is infinite). This system, completed with a set of isotherm equations, is solved numerically, and the values of the time and space increments are adjusted to account for the finite column efficiency, a licit calculation procedure[19–21]. In the cases where a comparison has been possible, experimental studies show excellent agreement between the profiles simulated for a pure compound and those recorded experimentally[22,23]. In the case of a binary mixture, excellent agreement is obtained when the exact competitive isotherm is used[17].

In all the following, the calculations were performed for a column having 5000 theoretical plates. The injection profile is assumed to be rectangular. The ratio of the concentrations of the two components in the feed was varied from 1:8 to 8:1. The isotherms are competitive Langmuir equations [*i.e.*, $Q_i = a_i C_i/(1 + b_1 C_1 + b_2 C_2)$].

For the sake of simplicity in the symbols, we define as RX the ratio of the values of X for the two components of the binary mixture studied (*i.e.*, $RX = X_2/X_1$). Thus:

$$RC_0 = C_2^0/C_1^0 \tag{1a}$$

$$RQ_s = Q_{s,2}/Q_{s,1} \tag{1b}$$

$$RL_f = L_{f,2}/L_{f,1} = RC_0/RQ_s \tag{1c}$$

where $L_{f,1}$ and $L_{f,2}$ are the individual loading factors of the first- and second-eluted components of the mixture, respectively, C_1^0 and C_2^0 are the concentrations of the first and second components in the feed, respectively, and $Q_{s,1}$ and $Q_{s,2}$ are the column saturation capacities for the lesser and more strongly retained components, respectively. The loading factor is the ratio of the sample size to the column saturation capacity. The column saturation capacity of a component i is equal to the ratio of its individual equilibrium isotherm parameters, a_i and b_i multiplied by the volume of the stationary phase.

In order to study the effect of a difference between the column saturation capacities for a given relative feed composition, RC_0, we vary the saturation capacity of either component with respect to that of the other component, which is kept constant in any given series of calculations. The saturation capacity ratio, RQ_s, is varied between 0.5 and 2, which covers the most useful range of values. This is achieved by changing the parameter b in the isotherm equation of one component, while a_1, a_2 and the b coefficient of the other component remain constant in all the calculations. Thus, the isotherm slopes at infinite dilution for the two solutes and their ratio, the relative retention, are not modified in the process.

Obviously, when RQ_s is smaller than 1, the saturation capacity of the second component is smaller than that of the first and the pure compound isotherms intersect. It has been shown, however, that this intersection has no direct physical meaning[11,24]. The planes $(Q_1, C_1, 0)$ and $(Q_2, 0, C_2)$ have nothing in common, except the vertical axis, and the coordinates of the intersection of the isotherms depend on the unit chosen for the concentrations. The real question is rather what the intersection curve of the two surfaces, $Q_1 = f_1(C_1, C_2)$ and $Q_2 = f_2(C_1, C_2)$ is and whether it is contained in the vertical plane of the equation $a_1C_1 = a_2C_2$, as predicted by the Langmuir model of competitive adsorption[11,24]. A more detailed investigation of this problem and its practical consequences is in progress and will be reported later[24].

The influence of the ratio of the column saturation capacities of the two compounds on the degree of band interference can be studied by computer simulation, as described previously[19], but theoretical considerations based on the properties of the analytical solution of the ideal model[8] help in the understanding of the results. The program used for the calculation of band profiles was written in Pascal and run on the VAX-8900 of the University of Tennessee Computer Center. The calculation of a complete set of profiles lasts *ca.* 5 min.

Properties of the displacement effect

The intensity of the displacement effect can be measured by the ratio of the concentrations of the first component in the front side and in the rear side of the second shock, $C_{1,A'}$ and $C_{1,M}$, respectively[7,8]. Using the ideal model, we have shown recently[8] that the ratio of these two concentrations is given by

$$C_{1,A'}/C_{1,M} = 1 + RL_f \tag{2a}$$

Hence

$$C_{1,A'}/C_{1,M} = 1 + RC_0/RQ_s \tag{2b}$$

Therefore, it is only when the column saturation capacities of the two components are equal that the intensity of the displacement effect depends simply on the relative feed composition, increasing with increasing relative concentration of the second component in the feed. On the other hand, at constant value of the relative feed composition, the loading factor ratio and the intensity of the displacement effect decrease with increasing value of the column saturation capacity ratio, RQ_s. Hence, the intensity of the displacement effect increases with decreasing column saturation capacity for the second component and/or with increasing column saturation capacity for the first.

The solution of the ideal model of chromatography in the case of a binary mixture with Langmuir competitive isotherms[7] permits a quantitative description of the displacement effect. It has been shown that the retention time of the second shock, $t_{f,2}$, is given by an equation which can be rewritten as follows, assuming the width of the injection pulse to be small, and the root r_1 of eqn. 22 in ref. 7 to be equal to $1/RC_0$, as shown in ref. 8:

$$t_{f,2} = t_0\left[1 + k'_{0,2}\cdot\frac{RL_f + 1}{RL_f + 1/\alpha}(1 - \sqrt{L'_f})^2\right] \tag{3}$$

where t_0 is the column dead time, $k'_{0,2}$ is the retention factor of the second component (at infinite dilution), α ($= a_2/a_1$) is the relative retention and L'_f is the adjusted loading factor, given by the equation[7]

$$L'_f = \left(1 + \frac{RQ_s}{\alpha RC_0}\right)\frac{n_2}{Q_{s,2}(1 - \varepsilon)SL} \tag{4a}$$

or

$$L'_f = L_{f,2}\left(1 + \frac{1}{\alpha RL_f}\right) = L_{f,2} + \frac{L_{f,1}}{\alpha} \tag{4b}$$

where n_2 is the amount of second component injected and $(1 - \varepsilon)SL$ accounts for the volume of packing in the column. Replacing L'_f in eqn. 3 by its value in eqn. 4 shows that the retention time of the second shock depends on the column dead time, the ratio of the two loading factors, the loading factor for the second component and the coefficients a_1 and a_2 of the equilibrium isotherms. According to eqns. 3 and 4, the retention time of the second shock depends strongly on $(1 - \sqrt{L'_f})^2$. L'_f in turn depends on both RQ_s and $Q_{s,2}$, so the discussion of the influence of the column saturation capacity on the resolution between the two bands must consider separately the influence of $Q_{s,1}$ and $Q_{s,2}$.

There are two simple ways to decrease RQ_s. We can either decrease $Q_{s,2}$ at constant $Q_{s,1}$ or increase $Q_{s,1}$ at constant $Q_{s,2}$. In the latter case, when we increase $Q_{s,1}$, $L_{f,1}$ and hence L'_f decrease (eqn. 4b). The retention time of the second front increases (eqn. 3) and the resolution between the two bands improves, while the intensity of the displacement effects increases. In the former case, when we decrease $Q_{s,2}$, $L_{f,2}$ and hence L'_f increase (eqn. 4b). The retention time of the second front decreases (eqn. 3) and the resolution between the two bands deteriorates, although the intensity of the displacement effect increases.

In summary, the intensity of the displacement effect always increases with decreasing ratio of the column saturation capacities, but the separation (and hence the production rate and/or the recovery yield) can either improve or deteriorate. The separation will improve with increasing column saturation capacity for either the first or the second component.

For a given chromatographic system and for mixtures of the same compounds, but with different compositions, the intensity of the displacement effect depends on the relative composition. It can be shown that in the mixed zone, where the two components coexist, their concentration profiles are simply related to RQ_s. Eqns. 43 and 44 in ref. 7 can be rewritten as

$$C_1 = \frac{FQ_{s,1}}{k'_{0,1}(1 + RL_f)}\left(\sqrt{\frac{1 + RL_f}{1 + \alpha RL_f} \cdot \frac{k'_{0,1}t_0}{t - t_0}} - 1\right) \tag{5}$$

where F [$= (1 - \varepsilon)/\varepsilon$] is the phase ratio and ε the packing porosity and

$$C_2 = \frac{FQ_{s,2}}{k'_{0,2}(1 + 1/RL_f)}\left(\sqrt{\frac{1 + RL_f}{RL_f + 1/\alpha} \cdot \frac{k'_{0,2}t_0}{t - t_0}} - 1\right) \tag{6}$$

The practical importance of the mixed zone depends largely on the ratio C_2/C_1. The larger the latter is, the smaller is the relative magnitude of this zone and the higher are the recovery yields. This ratio depends essentially on RL_f:

$$\frac{C_2}{C_1} = \frac{RC_0}{\alpha} \cdot f(RL_f) \tag{7}$$

where $f(RL_f)$ represents the ratio of the two terms in parentheses at the end of eqns. 5 and 6, respectively. As α is close to unity in most practical cases, the ratio $f(RL_f)$ varies only slowly with RL_f. Note that if $\alpha = 1$, there is no separation and C_2/C_1 becomes equal to RC_0.

Properties of the tag-along effect

The tag-along effect is a consequence of the influence of the local concentration of the first component on the velocity associated with a concentration of the second component[7,8]. Further, the velocity associated with a given concentration of the second component when pure is lower than the limit of the velocity associated with the same concentration of the second component, but in the presence of the first component, when the concentration of this first component tends towards zero. Thus, a plateau appears on the rear of the second component profile when the concentration of the first component becomes zero[7].

The width, Δt, of the plateau is given by the following equation[8]:

$$\Delta t = \frac{1 + RL_f}{(\alpha RL_f + 1)^2}(k'_{0,2} - k'_{0,1})t_0 \tag{8}$$

where $k'_{0,1}$ and $k'_{0,2}$ are the column capacity factors of the first and the second components, respectively, at infinite dilution. The intensity of the tag-along effect depends on the loading factor ratio and on the difference between the retention factors of the two components at infinite dilution. In the calculations reported here, the retention factors of the two components at infinite dilution are kept constant so the intensity of the tag-along effect depends only on RL_f.

RESULTS AND DISCUSSION

Both the displacement and the tag-along effects have been observed, the former in preparative liquid chromatography when the column is overloaded for a high production rate[6,25,26] and the latter in detailed investigations of individual band profiles[27]. An experimental study of the influence of the ratio of column saturation capacities for the two components has been presented[6]. Based on the theoretical conclusions reported above, we discuss the results of numerical calculations made using the semi-ideal model of chromatography[1,18–21].

Study of the displacement effect

With Langmuir equilibrium isotherms the velocity associated with a certain concentration of a compound[28] increases with increasing concentration of this compound. Hence the front of each elution band must be a shock in the ideal model and a shock layer in practice, because of the smoothing effect of a finite mass transfer kinetics.

The displacement effect is due to the fact that the concentration of each compound in the stationary phase is a function of the mobile phase concentrations of all the other components. The appearance of the second shock (a positive jump in the concentration of the second component) at the rear of the first component band causes a negative shock in the concentration of the first-eluted solute[7]. Alternately, we know that, with a convex isotherm, the velocity associated with a certain concentration of the first component increases with increasing concentration of the second component. Only high concentrations of the first component can move faster than the concentration of the first component which moves with the front of the second component[7].

As shown in the Theory section, the intensity of the displacement effect depends on the ratio of the column saturation capacities. Increasing RQ_s can be done either by decreasing $Q_{s,1}$ (as done in Fig. 1a and b) or by increasing $Q_{s,2}$ (*i.e.*, decreasing b_2, as done in Fig. 2a–e).

Influence on the displacement effect of a change in the column saturation capacity of the first component

In this case, we increase RQ_s by decreasing $Q_{s,1}$. Then L_f' increases, as $L_{f,1}$

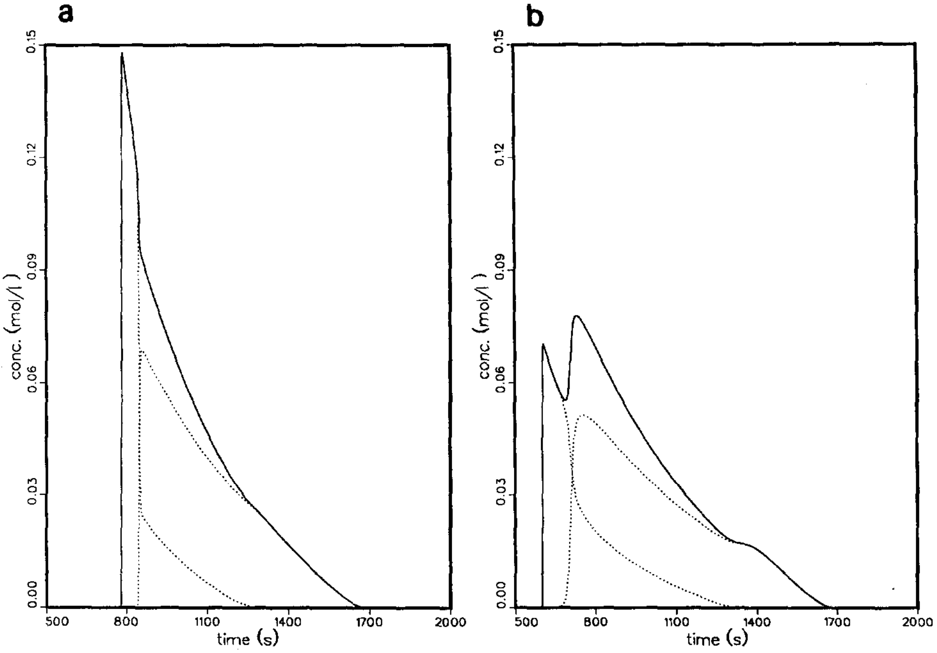

Fig. 1. Influence of the loading factor ratio on the intensity of the displacement effect and the separation between bands. Effect of the column saturation capacity for the first component. Chromatograms calculated for a binary mixture of constant composition (RC_0 = 2.0, 1:2 mixture) for columns of different saturation capacity for the first component. Langmuir competitive isotherms (a_1 = 24, a_2 = 28.8, b_1 = 4.8, α = 1.20, $Q_{s,2}$ = 5.0). Constant sample size: 0.40 mmol of second component ($L_{f,2}$ = 9.7%) and 0.20 mmol of first component. (a) RQ_s = 0.5, RL_f = 4.0, $L_{f,1}$ = 2.4%; (b) RQ_s = 2.0, RL_f = 1.0, $L_{f,1}$ = 9.7%.

increases and $L_{f,2}$ remains constant. RL_f also decreases and the intensity of the displacement effect weakens. The retention time of the second shock decreases (eqn. 3) and the separation deteriorates. C_1 decreases more slowly with increasing time at lower values of $Q_{s,1}$. The change in the individual elution profiles is illustrated in Fig. 1a and b.

In this series of calculations, the feed composition (C_1°/C_2°) is kept constant and equal to 1/2. The sample size is kept constant and the loading factor for the second component remains equal to 9.7%. From Fig. 1a to Fig. 1b RQ_s increases from 0.5 to 2 and RL_f decreases from 4.0 to 1.0. As predicted by theory, the displacement effect decreases and the separation becomes worse, as demonstrated by the longer, more important tail of the first component band behind the second shock.

For real columns, the reduction in the recovery yield and production rate due to the lesser degree of separation of the bands is enhanced by the consequences of a less strong displacement effect. The front of the second component band and the rear shock layer of the first component band are less steep (compare Fig. 1a and b). Hence kinetic effects reinforce the negative consequences of thermodynamic effects.

Influence on the displacement effect of a change in the column saturation capacity of the second component

In this case, we increase RQ_s by increasing $Q_{s,2}$, at constant sample size. L_f' decreases since $L_{f,2}$ decreases and $L_{f,1}$ is constant (eqn. 4b) and the retention time of the second component front increases (eqn. 3). The intensity of the displacement effect decreases. C_2 increases slowly with increasing $Q_{s,2}$ (eqn. 6). The change in the two individual profiles is illustrated in Fig. 2a–e. In this series of calculations, the relative feed composition (C_1°/C_2°) is kept constant and equal to 1/8. The sample size is also kept constant and the loading factor for the first component remains equal to 0.725%. From Fig. 2a to Fig. 2e RQ_s increases from 0.5 to 2 and RL_f decreases from 16.0 to 4.0.

When RQ_s increases at constant RC_0, RL_f decreases (eqn. 1c) and the decrease in both solute concentrations along the profile in the mixed zone is faster, while the mixed zone becomes narrower. As the sample size and the elution time of the second component tail are constant, the throughput remains constant in Fig. 2a–e. As $Q_{s,2}$ is increased, however, $L_{f,2}$ and hence L_f' decrease (see eqn. 4) and the degree of band overlap decreases, and the production rates and recovery yields of both components increase with increasing column saturation capacity for the second component from Fig. 2a (RQ_s = 0.5) to Fig. 2e (RQ_s = 2), although the intensity of the displacement effect decreases. This result is easily explained by the decreasing degree of column overloading when the sample size is kept constant while the column saturation capacity for the second component is increased.

From Fig. 2a to Fig. 2e, while RQ_s increases at constant RC_0, the steep front of the second component band recedes (the retention time increases from 820 to 1180 s). In the same time, the end of the first component tail moves only from 1220 to 1260 s, but the retention time of the first front increases from 790 to 1080 s. The velocity of the concentration shocks and/or shock layers decreases with decreasing value of the loading factor ratio (16.0 for Fig. 2a, 8.0 for Fig. 2c, 4.0 for Fig. 2e), but the effect is more important for the second component (the column saturation capacity of which is increasing) than for the first one (the column saturation capacity of which remains constant). The second shock, moving in the rear of the first band and displacing it,

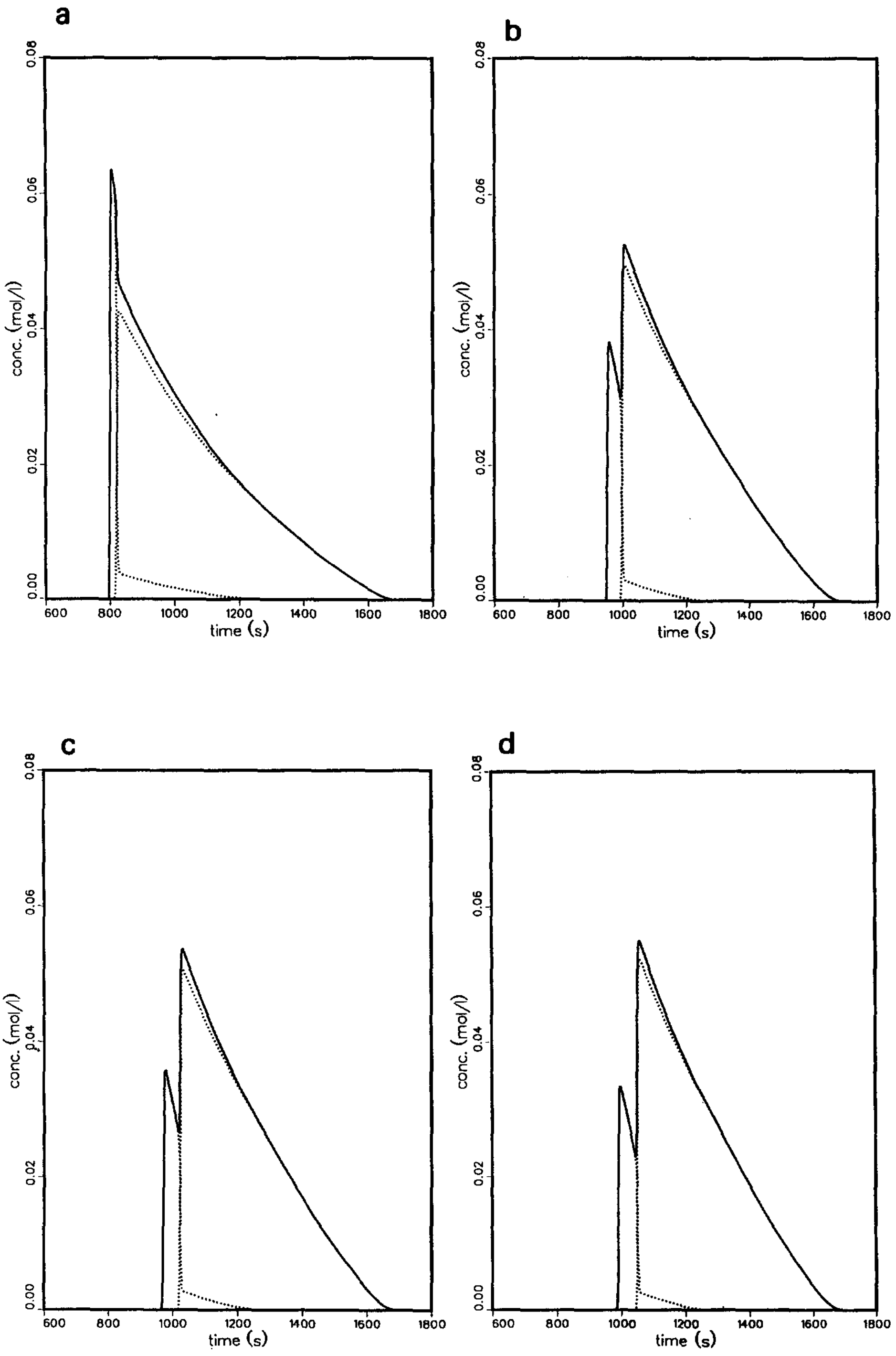

Fig. 2

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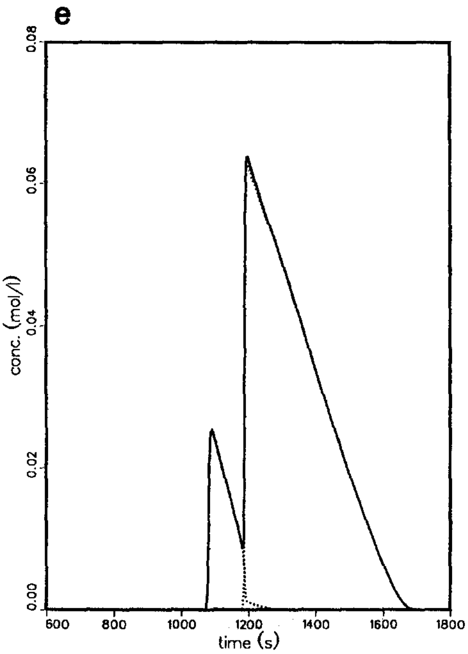

Fig. 2. Influence of the loading factor ratio on the intensity of the displacement effect and the separation between bands. Effect of the column saturation capacity for the second component. Chromatograms calculated for a binary mixture of constant composition ($RC_0 = 8.0$, 1:8 mixture) for columns of different saturation capacity for the second component. Langmuir competitive isotherms ($a_1 = 24$; $a_2 = 28.8$, $b_1 = 4.8$, $\alpha = 1.20$, $Q_{s,1} = 5.0$). Constant sample size: 0.030 mmol of the first component ($L_{f,1} = 0.725\%$) and 0.24 mmol of the second component. (a) $RQ_s = 0.50$, $RL_f = 16.0$, $L_{f,2} = 11.6\%$; (b) $RQ_s = 0.91$, $RL_f = 8.80$, $L_{f,2} = 6.4\%$; (c) $RQ_s = 1.0$, $RL_f = 8.0$, $L_{f,2} = 5.8\%$; (d) $RQ_s = 1.11$, $RL_f = 7.21$, $L_{f,2} = 5.23\%$; (e) $RQ_s = 2.0$, $RL_f = 4.0$, $L_{f,2} = 2.9\%$.

becomes farther and farther from the first shock. The degree of band overlap decreases. As the second shock moves more slowly and the mixed zone narrows, the concentration of the more retained solute at the front of the second shock becomes higher. These effects can be observed in Fig. 2a–e.

Displacement effect at constant column saturation capacity

At constant RQ_s, the intensity of the displacement effect increases with increasing relative concentration of the second component, *i.e.*, with increasing RC_0, as shown by comparing Figs. 2e, 3a and 3b. In these figures, the degree of band overlap increases with decreasing RC_0, from 8 (Fig. 2e) to 4 (Fig. 3a) and 2 (Fig. 3b), the displacement effect decreases and the tag-along effect (see next section) increases.

All these results illustrate the importance of the ratio of the loading factor for the two components and demonstrate the effect of this ratio on the intensity of the displacement effect.

Study of the tag-along effect

When RL_f becomes small compared with $1/\alpha$ (and thus with 1), the width of the plateau increases and tends towards $(k'_{0,2} - k'_{0,1})\, t_0$ (see eqn. 8). At low values of RL_f,

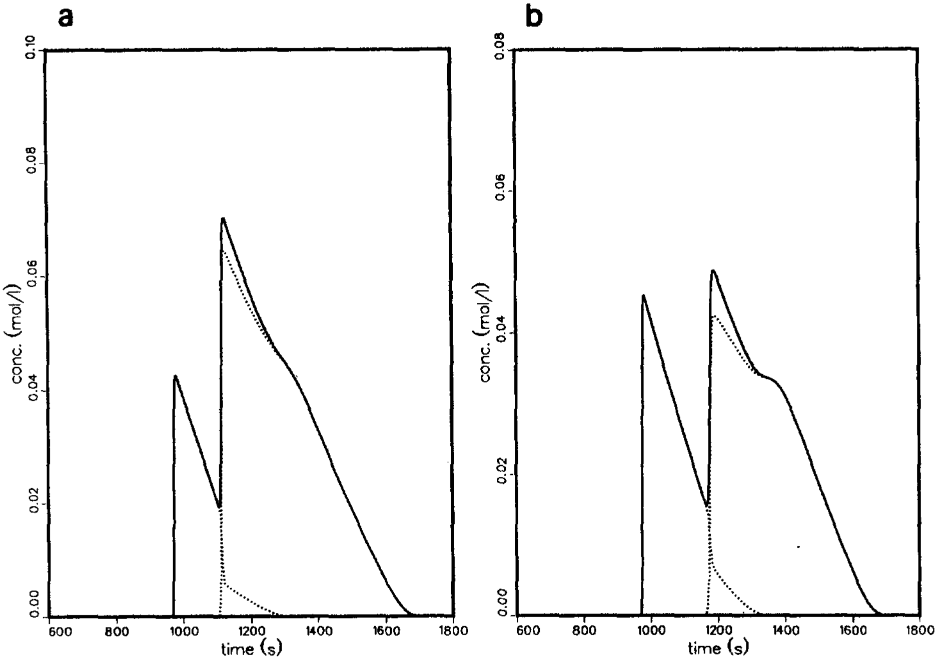

Fig. 3. Influence of the loading factor ratio on the intensity of the displacement effect. Effect of the relative concentration of the feed. Chromatograms calculated for columns of constant saturation capacities (RQ_s = 2.0, Q_1 = 5.0, Q_2 = 10) and with a binary mixture of variable composition. Same Langmuir competitive isotherms as for Fig. 1. See Fig. 1a, $RC_0 = 8$, $RL_f = 4$. (a) $RC_0 = 4.0$ (1:4 mixture), $RL_f = 2.0$ ($L_{f,1}$ = 1.81%), sample amount: 0.452 mmol, $L_{f,2}$ = 3.62%. (b) $RC_0 = 2.0$ (1:2 mixture), $RL_f = 1.0$ ($L_{f,1}$ = 2.42% = $L_{f,2}$), sample amount 0.361 mmol.

it is proportional to $[1 + (1 - 2/\alpha)RL_f](k'_{0,2} - k'_{0,1})t_0$. Under these conditions, the displacement effect is negligible.

When RL_f becomes very large the tag-along effect vanishes. The length of the plateau is proportional to $1/RL_f$ at large values of the loading factor ratio (see eqn. 8). In Fig. 2e, RL_f is equal to 4 and the tag-along effect is already insignificant. In contrast, in Fig. 4a–c RL_f increases from 0.5 to 2. All these figures exhibit a strong tag-along effect with a feed relative concentration of 1. The width of the plateau decreases progressively with increasing loading factor ratio, while the displacement effect increases.

At a fixed value of RQ_s, the loading factor ratio is proportional to the relative composition of the feed (see eqn. 1c) and the intensity of the tag-along effect increases with decreasing relative concentration of the second component[1]. This effect is illustrated in Fig. 5a–c, where the relative concentration of the second component decreases from 1/2 to 1/8 and the loading factor ratio decreases from 0.25 to 0.0625, for a constant ratio RQ_s equal to 2.0. If we compare Figs. 4a and 5a–c, we see that the length of the plateau increases progressively, as expected, and tends towards a limit which is nearly achieved in Fig. 5c.

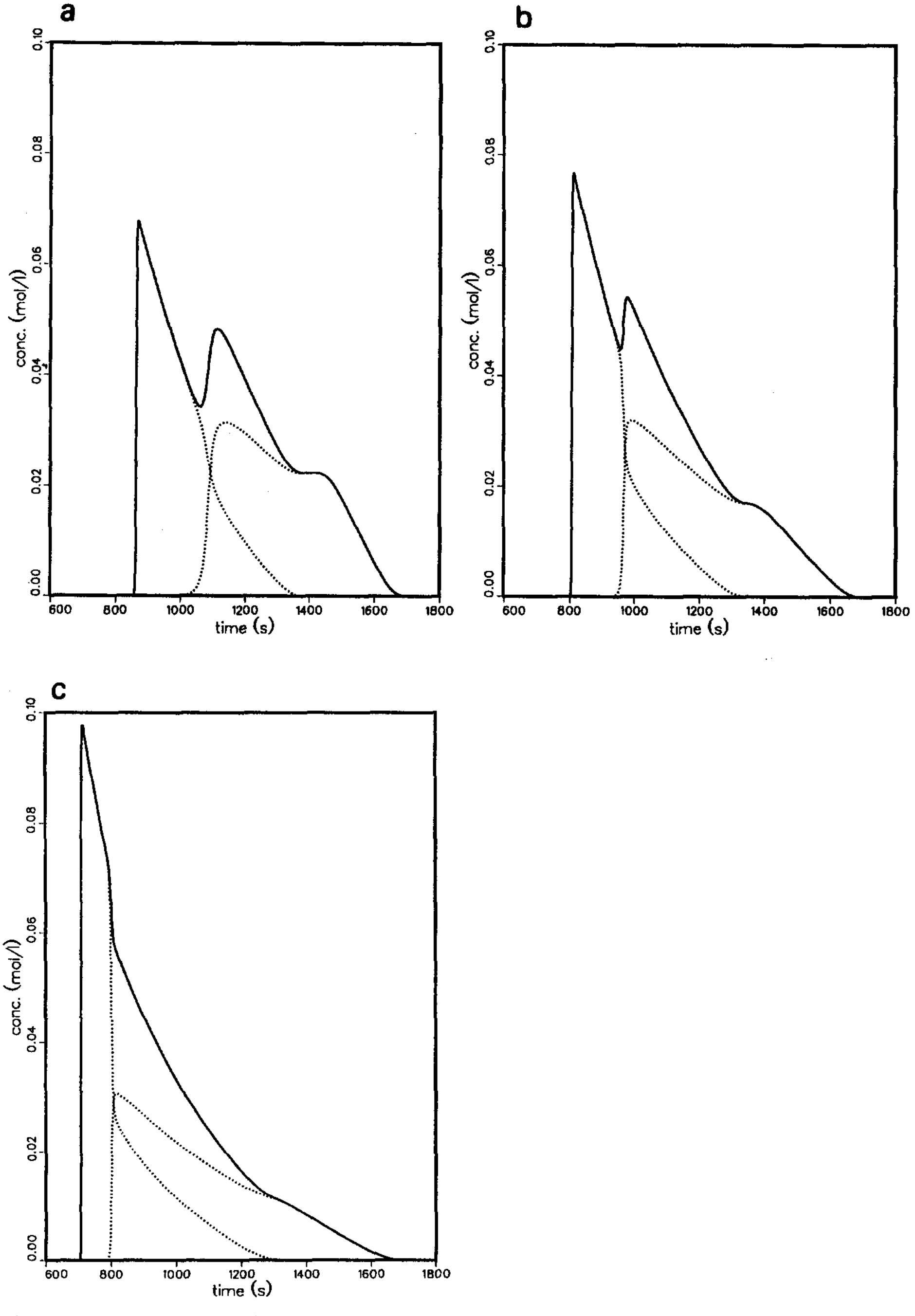

Fig. 4. Influence of the loading factor ratio on the intensity of the tag-along effect. Effect of the column saturation capacity for the second component. Chromatograms calculated for a binary mixture of constant composition (RC_0 = 1.0, 1:1 mixture) for columns of different saturation capacities for the second component. Same Langmuir competitive isotherms as for Fig. 1. Constant sample size: 0.483 mmol ($L_{f,1}$ = 4.83%). (a) RQ_s = 2.0, RL_f = 0.50, $L_{f,2}$ = 2.42%; (b) RQ_s = 1.0, RL_f = 1.0, $L_{f,2}$ = 4.83%; (c) RQ_s = 0.50, RL_f = 2.0, $L_{f,2}$ = 9.66%.

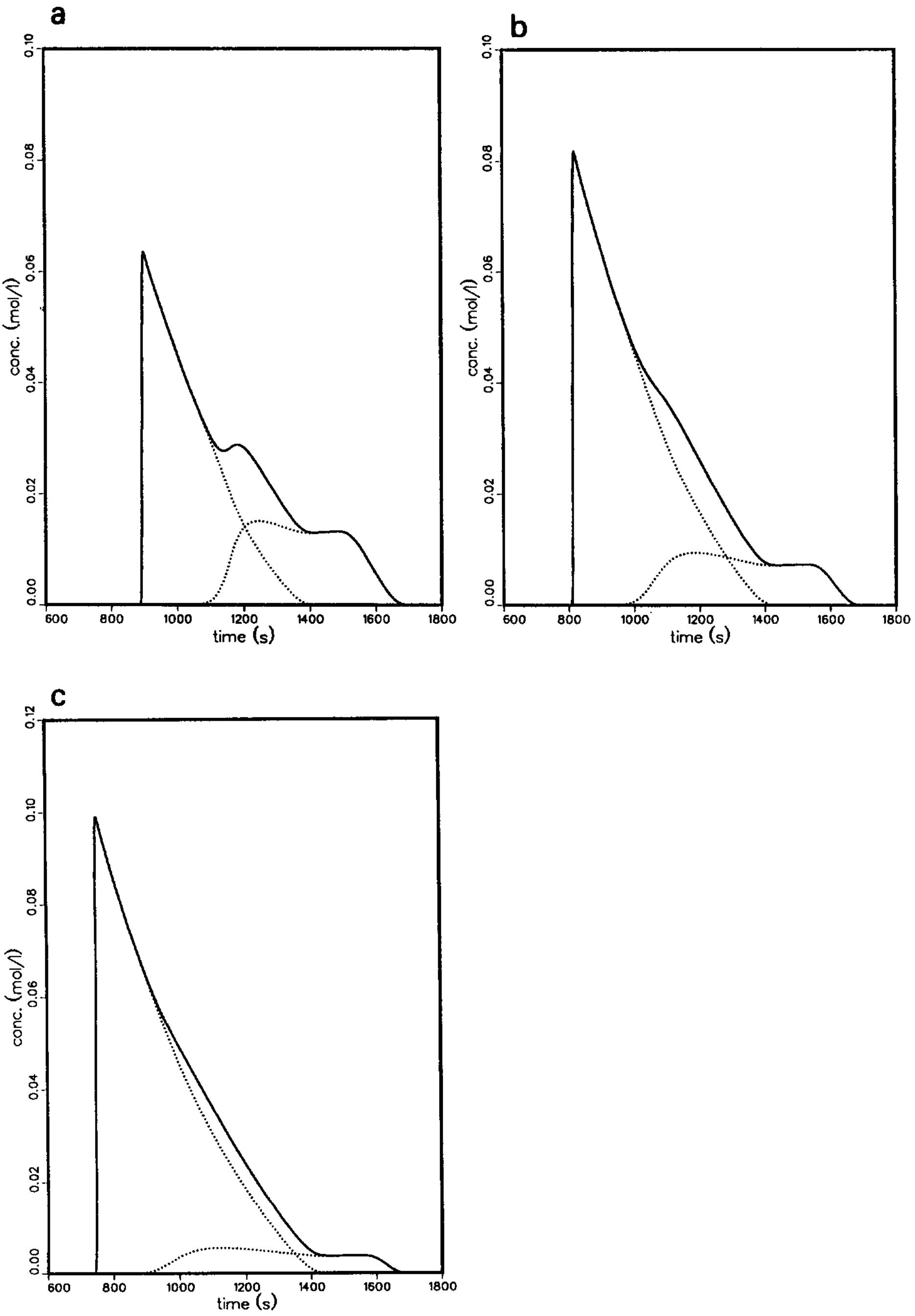

Fig. 5. Influence of the loading factor ratio on the intensity of the tag-along effect. Effect of the relative concentration of the feed. Chromatograms calculated for columns of constant saturation capacities (RQ_s = 2.0, Q_1 = 5.0, Q_2 = 10) and with a binary mixture of variable composition. Same Langmuir competitive isotherms as for Fig. 1. See Fig. 4a, RC_0 = 1, RL_f = 0.50. (a) RC_0 = 0.50 (2:1 mixture), RL_f = 0.25 ($L_{f,1}$ = 4.83%), sample amount 0.362 mmole, $L_{f,2}$ = 1.21%; (b) RC_0 = 0.25 (4:1 mixture), RL_f = 0.125 ($L_{f,1}$ = 7.25%), sample amount 0.453 mmol, $L_{f,2}$ = 0.91%; (c) RC_0 = 0.125 (8:1 mixture), RL_f = 0.0625 ($L_{f,1}$ = 9.67%), sample amount 0.544 mmol, $L_{f,2}$ = 0.60%.

CONCLUSION

The intensities of the displacement and the tag-along effects have been shown to be controlled by the loading factor ratio of the two components in the case of a binary mixture separation, not merely by the relative concentrations of the two components of the feed. The intensities of these two effects vary in opposite directions when the loading factor ratio is changed at constant total column loading. When the saturation capacity of the first-eluted component is lower than that of the more retained component, the intensity of the displacement effect is depressed whereas the intensity of the tag-along effect is increased, compared with the case where the column has the same saturation capacity for the two components. The inverse case produces the opposite variations: the intensity of the tag-along effect is less important and that of the displacement effect is enhanced if the column saturation capacity is lower for the second component than for the first.

The existence of a difference between the column saturation capacities of the two components to be separated has to be considered in any optimization procedure. Of special importance is a judicious choice of the stationary phase, which must take into account not only the relative retentions of the two components at low concentration, but also the dependence of the column saturation capacities for the two compounds and their ratio on the experimental conditions[29]. The influence of this ratio on the production rate at fixed purity may be important. It depends in a large part on the composition of the feed.

Finally, when the ratio of the column saturation capacities, RQ_s, is less than unity, the two single-component equilibrium isotherms plotted in the same graph intersect. As long as the mobile phase concentrations used are lower than those corresponding to this intersection point, the chromatograms obtained are those described here. Displacement chromatography can be achieved with a suitable displacer and no special problem arises from this "isotherm intersection". When concentrations higher than those corresponding to the intersection point are involved in an experiment, some theoretical and practical difficulties may arise. A detailed discussion of this interesting but complex problem will be reported soon[24]. The conclusions of the IAS model derived from single component Langmuir isotherms and those of the conventional binary competitive Langmuir isotherms are somewhat different. They will be compared.

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