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Profiles of large-size system peaks and vacancy bands in liquid chromatography
I. Analytical solution of the ideal model

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Abstract

Often in chromatography, a compound which participates in the retention mechanism is added to the mobile phase. This permits control of the retention factors of the analytes and allows their indirect detection. Injection of large volumes of solutions having a composition different from that of the mobile phase causes perturbation of the equilibrium between the two phases of the chromatographic system, and may result in large positive or negative system peaks when the additive signal is monitored. If the equilibrium behavior is accounted for by competitive Langmuir isotherms, the positive bands, which contain an excess of the additive, are Langmuirian-shaped as in the classical elution case, while the large vacancy bands have an anti-Langmuirian profile. An explicit analytical solution is derived within the framework of the ideal model for the profiles of large-size pulses and vacancies. This solution permits the easy calculation of the retention times of the different parts of the bands, i.e., of its shocks and diffuse boundaries. This solution provides also a more profound explanation of the formation of the large system peaks than available so far and of their distinctive properties as compared to those of large-size bands in classical elution.

Keywords: System peaks; Vacancy bands; Preparative chromatography; Band profiles

1. Introduction

System peaks arise in chromatography whenever an injection is made in a system where the mobile phase is a solution containing one or several additives which can equilibrate between the mobile and the stationary phase, and which can be involved in the retention mechanism [1]. This is the case, for example, when small amounts of an alcohol are added to methylene chloride in normal-phase chromatography, or when a buffered solution of an organic acid or base whose structure includes a large hydrophobic group is used in ion-pair chromatography. Because the concentrations of these additives are relatively large, their equilibrium behavior is not linear. Accordingly, competition takes place between the additives and the sample components; this causes several effects which would not arise in linear chromatography. First and foremost, competition is responsible for the decrease in the retention factors of the analytes compared to their values in the pure weak solvent, and this is usually why the additive is

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being used[1]. However, a number of side effects take place in the same time, whose recognition depends on whether the detector responds or not to changes of the additive concentrations.

Because of the competitive nature of almost all isotherms at high concentrations, the injection of the sample causes the local equilibrium concentrations of the additives in the stationary phase to decrease. Once the sample components are gone, the initial equilibrium is restored. Thus, co-injection of a certain amount of additives is performed simultaneously with sample injection onto the column. It is followed by adsorption (i.e., by a negative injection) of the same amount of additives. The amount of the additives involved in this perturbation is a function of the sample composition. These phenomena lead to a set of concentration signals which may be relatively complex but are now well understood in analytical chromatography. In this case the samples are small, and hence the perturbation can be treated as linear, using first-order expansions [2].

Discovered experimentally by Fornstedt and Porath [4] and from a theoretical viewpoint by Helfferich and Klein [5], system peaks in analytical chromatography have been discussed abundantly in the literature. Applications have been detailed by Schill and co-workers [6–8], Crommen et al. [9,10] and Bidlingmeyer et al. [11,12]. Major theoretical contributions have been made by Schill and co-workers [13,14], Knox and Kaliszan [15], and Levin and Grushka [16,17]. A thorough theoretical analysis has been published by Golshan–Shirazi and Guiochon [2].

The results of this perturbative approach can be conveniently summarized as follows. In addition to the expected peaks of the sample components, peaks of the additives are observed. If the sample contains p components, there will be, for each additive, $p + 1$ additive peaks. Each additive peak is eluted at a time which is characteristic of the additive. The retention factor of this peak is proportional to the slope of the additive isotherm at the additive concentration in the mobile phase. The other p additive peaks co-elute with the p peaks of the sample components. Their size is proportional to the amount of the corresponding component in the sample. These peaks are usually ignored because in most applications the additive is selected for giving no detector response. However, in indirect detection [7–12], the phenomenon is used to quantitate those analytes which give no detector signal by using an appropriate additive with a large detector response factor.

Although the behavior of system peaks is well understood now in analytical chromatography, it is not in the preparative area. The injection of large-size samples results in major perturbations of the additive concentrations, and causes the profiles of the feed component bands to be more complex than when a pure mobile phase is used. When the sample size is progressively increased, the band profiles turn from a nearly Gaussian shape to one which is Langmuirian at moderate additive concentrations, and it is not exceptional to see anti-Langmuirian-shaped bands at high additive concentrations [18–23]. The latter transition is through Golshanian profiles which have humps or horns, and may exhibit front and rear shock layers, with an intermediate diffuse boundary which sometimes has the shape of a dome [23]. These profiles were first reported by Kirkland [24] and by Punčochářová et al. [25]. They have been studied theoretically and experimentally by Golshan–Shirazi and Guiochon [18–21] and more recently by Fornstedt and Guiochon [22,23].

The latter authors have shown that Golshanian band shapes arise when the following three conditions are met [22]: (i) the additive is more strongly retained than the component in the pure weak solvent; (ii) the concentration of the additive is high enough for the additive system peak to be eluted before the component peak; and (iii) the separation factor of the additive peak and the component peak is low, and the sample size large, so the two additive bands, the primary additive system peak and the component system peak interfere. In the course of their study, Fornstedt and Guiochon [22,23] determined the elution profiles of large-size sample and vacancy pulses of the additive. In their chromatograms (see Ref. [22], Fig. 2), they observed that samples containing an excess of additive (i.e., positive injections) give rise to bands that have a Langmuirian profile, while the vacancies (i.e., nega-

[1] Note that in reversed-phase chromatography this decrease arises essentially from the increased solubility of the analytes in the mobile phase; in this respect this technique is different from other chromatographic techniques [2,3].

tive injections) give rise to bands which are anti-Langmuirian. Furthermore, when the sample size is increased, the diffuse boundaries of the band profiles overlap in each of the two series of bands, as expected (see Ref. [22], Fig. 2), but they do not seem to originate from the same point.

This result is easy to explain within the framework of the ideal and the equilibrium-dispersive models [26]. It provides an excellent illustration of the usefulness of the ideal model and the shock theory [26]. Shock theory and its applications to the study of high-concentration band profiles in liquid chromatography have been discussed by Lin et al. [27]. The influence of a finite column efficiency results from a balance between the self-sharpening effects of the non-linear behavior of the isotherms and the dispersive effects due to the finite rate of the mass transfer kinetics in the column and to axial dispersion. This is easily explained by the shock layer theory [28,29] which has been recently shown to predict quite accurately the profiles of breakthrough curves [30], at least under favorable conditions [28–30].

The goal of the present paper is to present the solution of the system of equations of the ideal model in the case of an additive in equilibrium between the mobile and the stationary phases (initial condition) and for the injection of large samples with an excess or a deficiency of the additive (boundary condition). Besides its obvious theoretical interest, the solution of this problem has some practical importance. It is always possible to dilute an analytical-size sample in a large volume of solvent without changing significantly the peak profiles in linear chromatography, provided the total sample volume is below half the standard deviation of this peak (assumed to have a Gaussian profile). The solvent used for this dilution may have an additive concentration markedly different from that of the mobile phase, either higher or lower. It is thus possible to generate a major system peak and to use its elution profile as a gradient to compress the peaks of trace components and improve their detectability [31,32]. Optimization of this method would become easier if the influence of the parameters which control the additive profile is better understood. One example is the achievement of the maximum possible compression effect. It has been shown that a thin shock layer thickness at the rear of the vacancy profile of the additive is essential for successful compression of co-eluting peaks of analytes [33].

2. Theory

The basic assumptions of the ideal model are that (i) the stationary and mobile phase are in constant state of equilibrium and (ii) there is no axial dispersion. Thus, the column is assumed to have an infinite efficiency. Although real columns have a finite efficiency, this efficiency is high in most cases, and the influence of the non-linear behavior of the isotherm becomes the controlling factor of band profiles at moderate or high concentrations.

2.1. System of equations of the ideal model

The mass balance of the additive is given by

$$\frac{\partial C}{\partial t} + F\frac{\partial q}{\partial t} + u\frac{\partial C}{\partial z} = 0 \tag{1}$$

where C and q are the mobile- and stationary-phase concentrations of the additive, respectively, t is the time, z is the column position, F is the phase ratio ($F = (1 - \epsilon)/\epsilon$, where ϵ is the total column porosity), and u is the mobile phase velocity. C and q are related by the isotherm equation

$$q = f(C) \tag{2a}$$

For further calculations in this work, we use the Langmuir isotherm

$$q = \frac{aC}{1 + bC} \tag{2b}$$

The initial condition is

$$C(z, t = 0) = C_0 \tag{3}$$

where C_0 is the additive concentration in the mobile phase. Since the ideal model assumes that there is no axial dispersion, the boundary condition is

$$C(z = 0, t) = C_a \quad 0 < t < t_p \tag{4a}$$

$$C(z = 0, t) = C_0 \quad t_p < t \tag{4b}$$

where C_a is the additive concentration in the injected sample, and t_p is the injection duration. Thus, the

sample is supposed to be a rectangular plug of width t_p and height C_a.

2.2. Shock theory

Eq. 1 can be rewritten [24,26] as

$$\frac{\partial C}{\partial t} + \frac{u}{1 + F\frac{dq}{dC}}\frac{\partial C}{\partial z} = 0 \tag{5}$$

This equation shows that a velocity is associated to each concentration. This velocity, u_z, is given by

$$u_z = \frac{u}{1 + F\frac{dq}{dC}} \tag{6}$$

As pointed out by Helfferich and Peterson [34], however, matter does not move in the column at the velocity u_z. Concentrations, i.e., signals or information, move at this velocity. Matter, or molecules, move at the velocity U_s, or shock velocity. It can be shown [26,28] that Eq. 1 can propagate concentration discontinuities, or shocks, and that the velocity of these shocks is given by

$$U_s = \frac{u}{1 + F\frac{\Delta q}{\Delta C}} \tag{7}$$

where Δq and ΔC are the differences between the stationary- and mobile-phase concentrations immediately after and before the shock, respectively. In the case of the propagation of molecules, Δq and ΔC are the differences between the local concentration and the reference concentration (in this case, 0). While dq/dC is the slope of the isotherm at the additive concentration, C_0, $\Delta q/\Delta C$ is the slope of the corresponding chord. Thus, U_s is always lower than u_z for a convex upwards isotherm.

In the case of a Langmuir isotherm, Eqs. 6 and 7 become respectively

$$u_z = \frac{u}{1 + \frac{k_0'}{(1 + bC)^2}} \tag{8a}$$

$$U_s = \frac{u}{1 + \frac{k_0'}{1 + bC}} \tag{8b}$$

with $Fa = k_0'$, the retention factor at infinite dilution. The velocity associated with a concentration increases with increasing concentration (Eq. 8a). Thus, since high concentrations cannot actually pass lower ones, concentrations pile up in the front of the band, and a discontinuity or concentration shock is formed and propagates. Behind this shock, the velocity associated with a concentration decreases with decreasing concentration, the concentrations spread, and a diffuse boundary appears [26].

A rectangular injection has two shocks, one in front, one at the back. The rear shock is unstable and collapses, giving rise to a diffuse rear boundary, as just explained. Each concentration moves at the velocity given by Eq. 8a, and the retention time of a concentration C on this diffuse boundary is

$$t_R(C) = t_p + \frac{L}{u_z} = t_p + t_0\left(1 + F\frac{dq}{dC}\right)$$

$$= t_p + t_0\left(1 + \frac{k_0'}{(1 + bC)^2}\right)$$

$$0 \le C \le C_a \tag{9}$$

The front shock of the rectangular injection is stable and propagates at the velocity given by Eq. 8b. However, this shock erodes progressively and its height does not remain constant. If we consider the tip of the shock, it belongs to both the shock and the diffuse boundary. Its velocity as a shock is given by Eq. 8b. Its velocity as a point on the diffuse boundary is given by Eq. 8a. Obviously, for the same value of C, $u_z > U_s$, hence the point will disappear. So, Eq. 8b cannot be integrated simply to derive the retention time of the shock. This time is easily derived, however, by observing that the band area must remain constant during its migration [35]. Since its profile is known, a simple integration gives the retention time of the band maximum. In the case of a Langmuir isotherm, we obtain

$$t_R(M) = t_p + t_0\left[1 + k_0'(1 - \sqrt{L_f})^2\right] \tag{10}$$

where $t_0 = L/u$ is the hold-up time, and L_f the loading factor, or ratio of the sample size and the column saturation capacity [$L_f = nb/(\epsilon SLk_0')$, where n is the sample size, a and b are coefficients of the Langmuir isotherm, L is the column length, and S is the column cross-section area].

2.3. Application to system peaks

The propagation of a finite concentration additive system peak involves both similarities and differences compared to the classical elution of the same band in a pure weak solvent. The similarities permit the straightforward extension of the solution of the ideal model to the calculation of the profile of an overloaded system peak. The only difference between the classical elution problem and the system-peak problem is in the initial condition. In the system-peak problem, the initial concentration of the component in the column is different from 0, while it is 0 in the elution problem. The boundary condition corresponds to the injection of a rectangular pulse of width t_p of a solution of weak solvent containing a concentration, C_a, of additive, either higher (pulse) or lower (vacancy) than the additive concentration, C_0, in the mobile phase before and after injection. These initial and boundary conditions are summarized in Eqs. 3, 4a and 4b.

This injection causes a large perturbation of the additive concentration. Depending on the sign of the perturbation, either the front or the rear shock of the rectangular injection is stable.

Profile of a pulse

If the perturbation is positive ($C_a > C_0$), the situation is very much like the one encountered in elution. The only difference is that now the elution of the pulse takes place on a plateau concentration of the component. The velocity associated with a concentration, given in Eq. 8a, increases with increasing concentration. Accordingly, the front shock of the injection pulse is stable. It propagates, while being eroded. The rear shock is unstable, because the concentration decreases on the band rear and the retention time of a concentration increases with decreasing concentration (Eq. 8a). The equation giving the rear diffuse profile of the band is the same as Eq. 9. Since the concentration definition is now changed, we rewrite it as

$$t_R(C) = t_p + t_0\left(1 + \frac{k_0'}{(1+bC)^2}\right)$$

$$C_0 \le C \le C_a \qquad (11a)$$

This profile ends when the concentration becomes equal to the additive concentration, C_0. Then the retention time of the last point of the profile is

$$t_R(C_0) = t_p + t_0\left(1 + \frac{k_0'}{(1+bC_0)^2}\right) \qquad (11b)$$

It is shorter than the retention time of the last point of an elution profile. If the injection band is wide enough, and a plateau at the injection concentration is still a part of the elution profile, the shock height remains constant, and the shock propagates at a constant velocity, U_s, given by Eq. 8b, with $\Delta C = C_a - C_0$. Hence

$$\Delta q = q(C_a) - q(C_0) = \frac{a\Delta C}{(1+bC_a)(1+bC_0)} \qquad (12a)$$

$$U_s = \frac{u}{1 + \dfrac{k_0'}{(1+bC_a)(1+bC_0)}} \qquad (12b)$$

$$t_R(M) = t_0\left(1 + \frac{k_0'}{(1+bC_a)(1+bC_0)}\right) \qquad (12c)$$

The retention time of the last point on the injection plateau, $t(C_a)$, is obtained by introducing C_a in Eq. 11a. If the injection pulse width, t_p, is too narrow, and the retention time given by Eq. 12c is longer than $t(C_a)$, the injection plateau has been completely eroded away, and the solution is that of a narrow injection band. In this latter case, the shock erodes during its migration along the column and its velocity does not remain constant. As in elution, the retention time of this shock is obtained by integrating the diffuse boundary from the shock retention time, $t_R(M)$ to the end of the profile at $t_R(C_0)$. We obtain

$$t_R(M) = t_p + t_0\left[1 + k_0'\left(\frac{1 - \sqrt{L_f'(1+bC_0)}}{1+bC_0}\right)^2\right] \qquad (13)$$

where L_f' is an apparent loading factor, or difference between the amount of additive actually injected in the sample pulse, and the amount existing in the same volume of mobile phase, at concentration C_0

$$L_f' = \frac{nb}{\epsilon SLk_0'} = \frac{t_p(C_a - C_0)b}{t_0 k_0'} \qquad (14)$$

Profile of a vacancy

This case is the opposite of the previous one, and it is impossible in elution. If the additive concentration is lower in the sample than in the mobile phase, the additive concentrations will be lower than C_0 during the entire elution of the perturbation, which will appear to be negative by respect to the baseline. Since the velocity associated with a concentration decreases with decreasing concentration, the front shock is now unstable, while all the concentrations will tend to pile up at the rear of the profile, and the rear shock is stable. Otherwise, the equation derived above remains valid, with a minor change due to the simple fact that the rear shock of the injection pulse enters the column at a time t_p later than the front shock. So, the retention time of a concentration C on the front diffuse boundary is

$$t_R(C) = t_0\left(1 + \frac{k_0'}{(1+bC)^2}\right) \quad C_a \le C \le C_0 \qquad (15a)$$

and the profile begins at the time

$$t_R(C_0) = t_0\left(1 + \frac{k_0'}{(1+bC_0)^2}\right) \qquad (15b)$$

The retention time of the rear shock of a wide injection band is given by

$$t_R(M) = t_p + t_0\left(1 + \frac{k_0'}{(1+bC_a)(1+bC_0)}\right) \qquad (16)$$

and the retention time of the maximum concentration of a narrow injection pulse is given by

$$t_R(M) = t_0\left[1 + k_0'\left(\frac{1+\sqrt{|L_f'|(1+bC_0)}}{1+bC_0}\right)^2\right] \qquad (17)$$

where L_f' is defined as in Eq. 14, and is now negative.

The combination of these equations defines entirely the elution profiles of the high-concentration bands of additive.

2.4. Calculations

All calculations of band profiles using the equations of the ideal model given above were carried out with a simple spreadsheet calculation program running on a personal computer. The numerical values of the parameters used in these calculations are as follows: flow-rate, 1.0 ml/min; column diameter, 0.46 cm; phase ratio, $F = 0.215$ (thus, $u = 0.12$ cm/s); sample volume, 0.25 ml (thus, $t_p = 15$ s); parameters of the Langmuir isotherm, $a = 30$, $b = 0.30$ mM^{-1} (thus, $q_s = 0.10$ M).

3. Results and discussion

As a reference, Fig. 1a and 1b show the elution profiles of a large size sample on a short column ($L = 0.5$ cm) and on a long column ($L = 10$ cm), respectively. In the former case (Fig. 1a), the plateau at the injection concentration has been eroded away only slightly. It has completely disappeared in Fig. 1b, where the height of the peak is nearly three times lower than in Fig. 1a. Note that the velocity of the point at the rear of the plateau in Fig. 1a is 1.55 times higher (Eq. 8a, $bC_0 = 0.3$) than the velocity of a zero concentration, which explains the rapid spreading of the band.

Fig. 2a and 2b illustrate the band profiles obtained at the end of the same two columns, for the same injection as in Fig. 1, but when the concentration of the additive in the mobile phase is constant and equal to 1.0 mM. Eqs. 11–14 were used to calculate these profiles. The shape of these profiles and those in the corresponding Fig. 1a and 1b are the same. The retention times of the profiles are shorter because, for the same deviations from the baseline, $C - C_0$, the actual concentrations, C, are higher (cf Fig. 1a and Figs. 2a, 1b and 2b). Therefore, the velocities associated with these concentrations are larger (Eq. 8a). Also, the Eqs. 8b and 12b for the velocities of the front shocks are different. The quantitative differences are minor, however, and will be discussed later.

The band profiles obtained upon injection of a vacancy of the additive are shown in Fig. 3a and 3b, for a vacancy size equal in absolute value and opposite in sign to the size of the pulse injected in Fig. 1 and Fig. 2, and on the same column, under the same experimental conditions as in Fig. 2. Eqs. 15–17 were used to calculate these profiles. The band corresponds to a negative perturbation of the steady additive concentration, and its profile appears

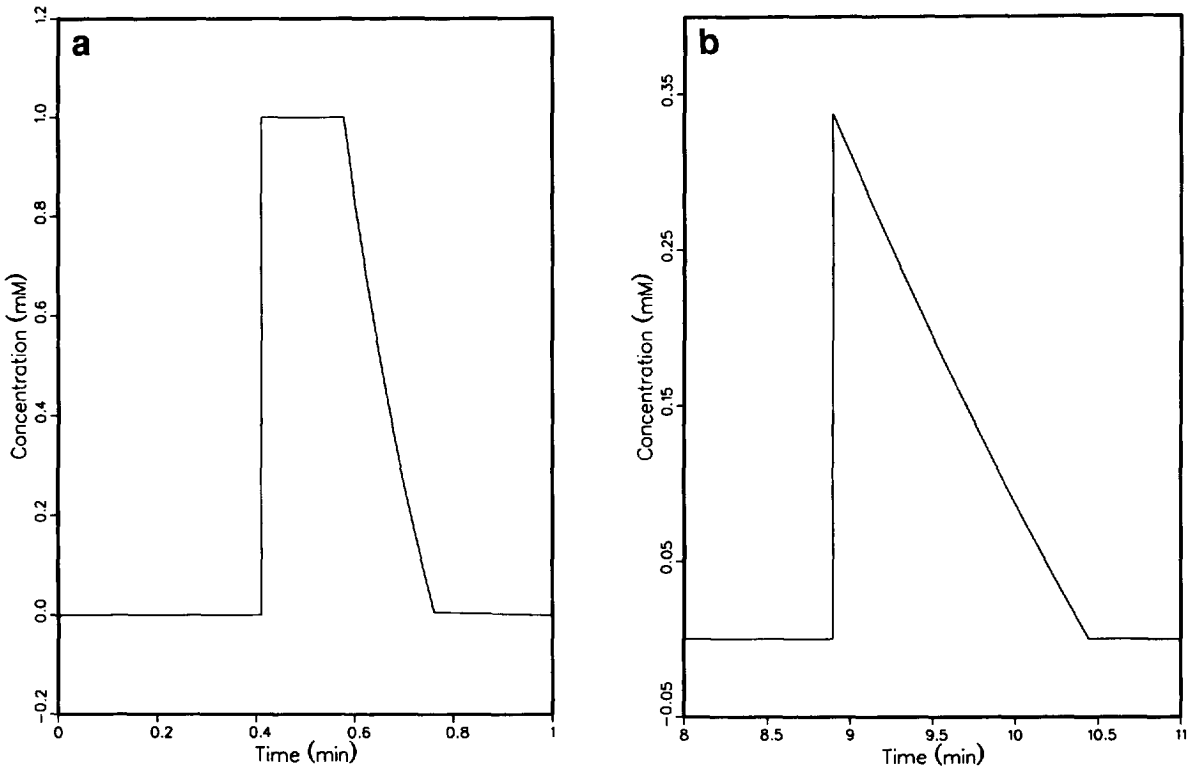

Fig. 1. Chromatograms calculated with the ideal model, for the elution of a high-concentration pulse of a solution of an additive by a pure mobile phase. $C_a = 1$ mM; $F_v = 1$ ml/min ($u = 0.12$ cm/s); $F = 0.215$; sample volume, 0.25 ml ($t_p = 15$ s); parameters of the Langmuir isotherm, $a = 30$, $b = 0.30$ mM^{-1}. Eqs. 8a–10 where used for calculation of the diffuse rear boundaries, and the position of the shocks, respectively. (a) Column length, L, 0.5 cm. (b) Column length, 10 cm.

to be anti-Langmuirian. The front of the band is a diffuse boundary and its rear is a shock.

Fig. 4 compares the band profiles obtained for three different pulse injections of the same volume, 0.25 ml, on the short column (Fig. 4a) and the long column (Fig. 4b). The first pulse (solid line) contains a 1 mM solution of the additive in the weak solvent. The second (dashed line) and third (dotted line) pulses contain a 2 mM solution. The first two injections are made in an "empty" column (i.e., a column containing the weak solvent without additive as the mobile phase), as in classical elution (experimental conditions of Fig. 1). The third injection is done in a column containing a mobile phase with 1 mM of the additive (experimental conditions of Fig. 2). When the column is short, and the injection plateau has not completely disappeared, the concentration level of the additive in the elution band is the same as in the injection pulse (Fig. 4a). The plateau of the first band is at the initial concentration level of the additive in the third case, i.e., 1 mM, while the plateau of the second and third bands are at the same level, 2 mM. The latter one, however, appears on a baseline at 1 mM, so its apparent height (i.e., above the baseline) is only 1 mM. The retention time of the front shock of these pulses increases in the order $t_{R,3}(M) < t_{R,2}(M) < t_{R,1}(M)$. Obviously, in elution in a column empty of additive, the retention time of a larger pulse is smaller than that of a smaller pulse. The difference between the retention times of the third pulse and of the other two pulses is accounted for by the differences between Eqs. 8b and 12b which give the retention times of their fronts. Because both the first and third pulse correspond to the actual injection of the same amount of the component (1 mM solution in a 0.25 ml volume,

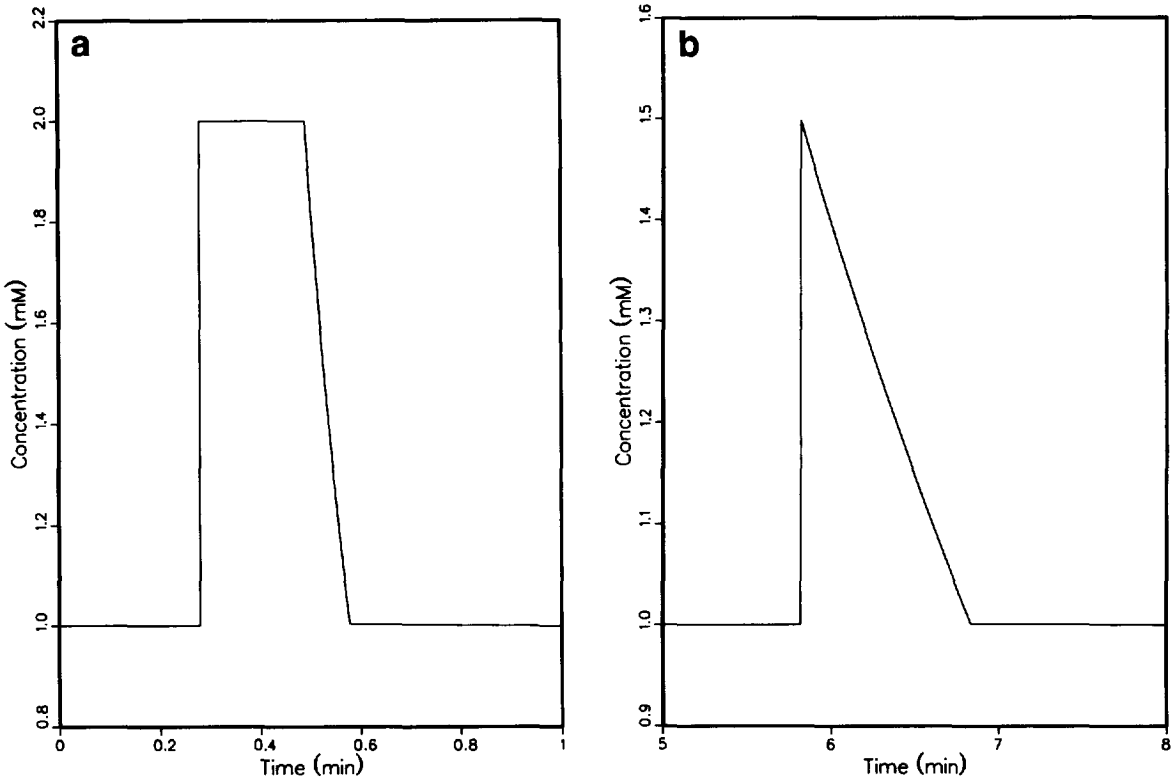

Fig. 2. Chromatograms calculated with the ideal model, for the elution of a high-concentration pulse of an additive by a mobile phase containing the additive. Eq. 11a was used for the calculation of the diffuse rear boundary, and Eqs. 12c and 13 for the calculation of the position of the front shock in (a) and (b), respectively. Additive concentration in the sample pulse, $C_a = 2$ mM, in the eluent, $C_0 = 1$ mM. Other conditions as in Fig. 1. (a) Column length, L, 0.5 cm. (b) Column length, 10 cm.

i.e., 0.25 μmole), their areas must be the same. Because the end of the third pulse profile comes at the retention time of a concentration of 1 mM (baseline concentration), it is eluted earlier than the end of the first pulse elution profile, at a concentration of 0. Its front should also elute earlier. In contrast, the rear boundaries of the three pulses overlay exactly, provided adjustment is made for the different concentration ranges, because they are all given by the same equation (Eqs. 9 and 11a).

When the same pulses are injected on the long column (Fig. 4b), their injection plateaus erode away before their elution and the band heights are lower. The system peak (third injection pulse) is eluted before the other two elution peaks. In the figure, the system peak is shown as it would appear above the baseline (i.e., the concentration $C - C_0$ is plotted versus time). The actual concentrations of the additive in this peak are obtained by adding 1 mM to the apparent concentrations displayed in Fig. 4b. The rear diffuse boundaries of the other two elution profiles overlay as they do in Langmuirian elution profiles. The system peak in Fig. 4b has the same area as the first injection pulse, since both peaks correspond to the same amount of material injected onto the column. However, the fact that the elution bands of the second and third injection pulses have the same height is co-incidental. Initially, the second elution band is twice as high as the third band (Fig. 4a). During their migration, the height of the second band decreases more rapidly than that of the third one. Because the injection plateau has been eroded away, the rear diffuse profile of the elution band is no longer directly connected to the same part of the system peak (as in Fig. 4a). However, these profiles are given by the same equation (with the t_0 correc-

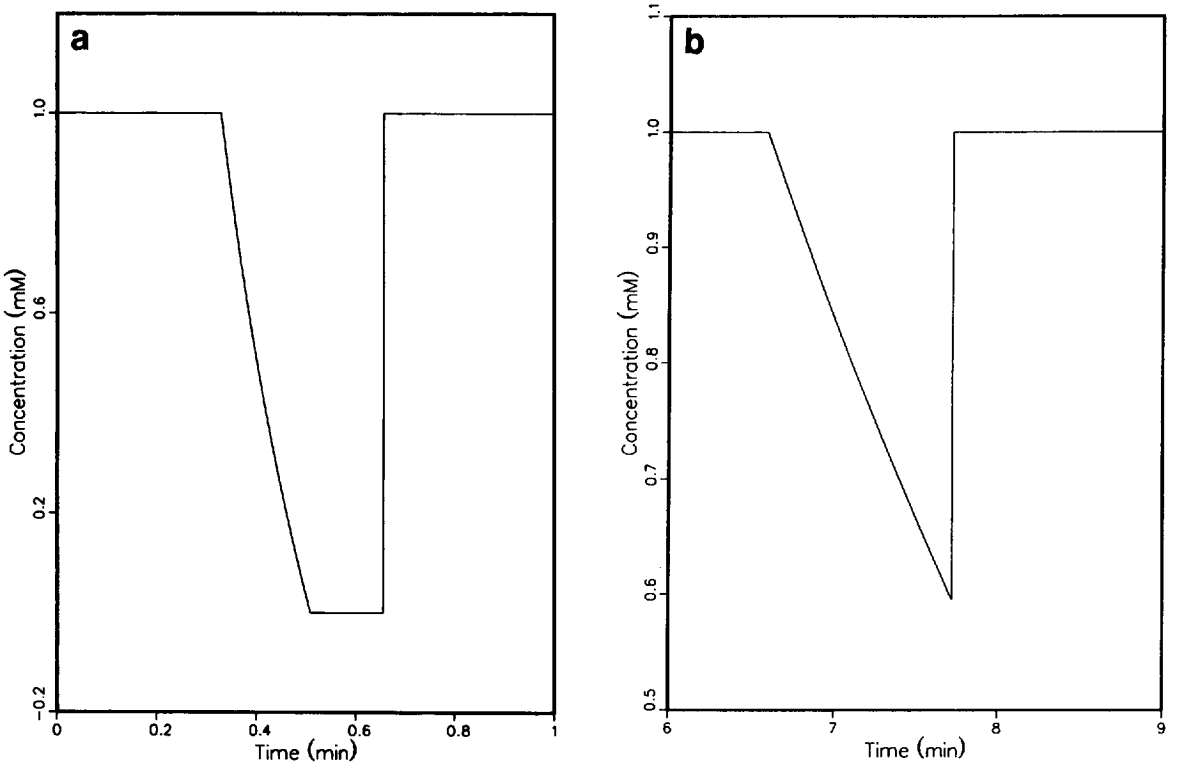

Fig. 3. Chromatograms calculated with the ideal model, for the elution of a large-size vacancy of an additive by a mobile phase containing the additive. Eq. 16a was used for the calculation of the diffuse front boundary, and Eqs. 17 and 18 for the calculation of the positions of the rear shocks of the bands, respectively. Additive concentration in the sample, $C_a = 0$, and in the eluent, $C_0 = 1$ mM. (a) Column length, L, 0.5 cm. (b) Column length, 10 cm.

tion) and the profiles appear, indeed, to be arcs of the same curve, as illustrated in Fig. 4c.

Now we want to compare the elution profiles of a pulse and a vacancy of the same size, but opposite signs. These profiles are plotted in Fig. 5, in the case of the long column (same experimental conditions as for Fig. 3b). The diffuse boundaries of the elution profiles of pulses and of vacancies of different sizes would overlay exactly. However, there are differences between these two series of diffuse boundaries. First, they originate from different points. This is clear in the equations of these boundaries (Eqs. 11b and 15b), which differ only by the presence of the term t_p in Eq. 11b and its absence from Eq. 15b. The reason for this lies in the origin of the diffuse boundary. In the case of a pulse, the diffuse boundary is at the band rear and results from the instability of the rear shock of the injection profile, which collapses into a flight of characteristics [26,28,36]. In the case of a vacancy, the diffuse boundary is on the front of the band, and results from the instability of the front shock of the injection. The shocks of the injection profile penetrate into the column at different times, the front followed by the rear at a distance t_p, which explains the different origin of the two sets of diffuse boundaries. Secondly, the two diffuse boundaries have the same curvature. In fact, they have the same equation, and would give two arcs of the same curve if one is moved towards the other in the direction parallel to the time axis, by a distance t_p. As a consequence, the profiles of a pulse and a vacancy of the same size cannot be overlaid. The rear of the pulse elution profile bends upwards, away from the baseline when moving towards the front shock, while the front of the vacancy elution profile bends in the direction of the baseline when going

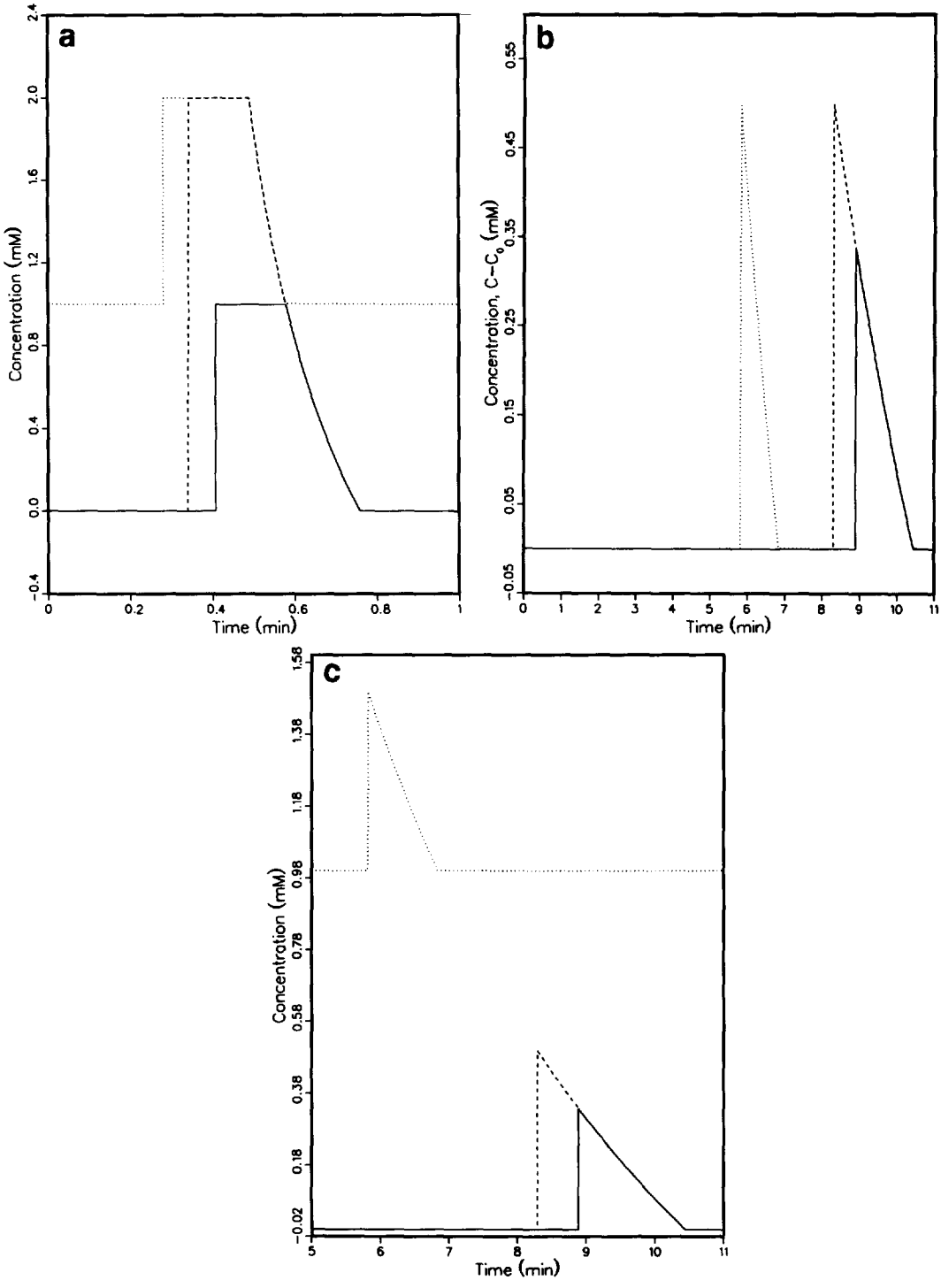

Fig. 4. Overlaid chromatograms showing the elution profiles calculated with the ideal model for three pulses of an additive eluted by different mobile phases on the same column. Solid line: $C_0 = 0$; $C_a = 1$ mM. Dashed line: $C_0 = 0$, $C_a = 2$ mM. Dotted line: $C_0 = 1$ mM, $C_a = 2$ mM. Same experimental conditions as in Figs. 1 and 2. (a) Column length, 0.5 cm. (b) Column length, 10 cm. Concentration origin for all profiles, the baseline, i.e., plot of $C - C_0$ versus time. (c) Same as for (b), but plot of C.

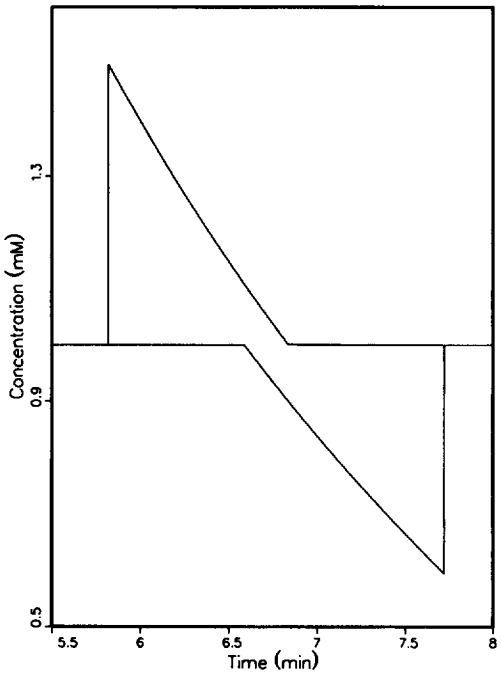

Fig. 5. Chromatograms calculated with the ideal model for a large pulse of an additive, and for a vacancy of the same amount, both eluted by a mobile phase containing the additive. $C_0 = 1$ mM; $C_a = 2$ mM (pulse) or $C_a = 0$ (vacancy). Column length, 10 cm.

towards the rear shock. In contrast to a superficial impression, the two series of profiles are not symmetrical with respect to the point at $C = C_0$, $t = t_p/2 + t_0[1 + k_0'/(1 + bC_0)^2]$.

The chromatograms shown in Figs. 1–5 have been derived using the ideal model and the equations given above, with a simple spreadsheet program which allows a rapid calculation of the numerical solutions and a fast drawing of the profiles. This procedure supplies an excellent approximation of the elution profile of a large-size system peak, positive or negative, as long as the column efficiency exceeds a few thousand plates, which is quite often the case in analytical applications. However, the ideal model assumes that the column efficiency is infinite while all actual columns have a finite efficiency. Thus, the procedure supplies only an idealized caricature of the actual profiles. In a companion paper we show how the equilibrium-dispersive model permits the calculation of profiles which are in close agreement with the experimental results [37].

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