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NON-EQUILIBRIUM MODEL OF LIQUID COLUMN CHROMATOGRAPHY.

II. EXPLICIT SOLUTIONS AND NON-IDEAL CONDITIONS

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SUMMARY

The analysis begun in the previous paper of a general model for liquid chromatography in a column is continued here. Explicit solutions are obtained for small-zone and large-zone non-equilibrium chromatography models both without and with diffusion. The effects on the moments of the elution profile of a distribution function which characterizes molecular heterogeneity (such as molecular size) or bead non-uniformities are analyzed. A first-order correction to the mean value of the elution profile when sorption–desorption kinetics are concentration dependent is derived.

Numerical simulations of the elution profile indicate the following. (1) The peak and mean may differ by as much as a factor of two for slow mass transfer ($k_1 \lesssim 0.01$). Since the mean is uniquely determined by the equilibrium constant but the peak is not, the use of the peak to characterize the equilibrium constant for broad asymmetric profiles may lead to serious errors. (2) When the rate of mass transfer from the void to penetrable volumes becomes comparable to u/h, a second peak will develop in the elution profile. This happens even for a completely homogeneous population under ideal conditions, and is caused by molecules that traverse the column without penetrating beads. The dispersion of this peak is therefore determined entirely by effects *other* than mass transfer. (3) In the non-linear regime (*i.e.*, when mass transfer rates are concentration dependent), the equilibrium constant is, in general, no longer uniquely determined by the mean. Uniqueness is, however, obtained in the limit as both mass transfer coefficients become very small, with their ratio remaining moderate.

INTRODUCTION

In the previous paper[1] we developed a non-equilibrium theory of chromatography which included diffusion, and we showed how the sorption–desorption kinetic parameters can be estimated from the moments of the elution profile. Expressions

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were derived for the mean, variance and skewness of the elution profile under ideal conditions of homogeneous molecules, uniform bead packing, and size- and concentration-independent rate constants. Here we extend that theory by considering other aspects of liquid column chromatography including nonideal conditions. The fundamental results derived here and in ref. 1 provide a basis for further quantitative development of chromatography as a method for thermodynamic and kinetic characterization of chemical reactions[2,3].

Solutions involving modified Bessel functions are given for both small-zone and large-zone chromatography models without diffusion. These solutions, together with a Gaussian kernel, are used to obtain solutions to a chromatography model with diffusion. Numerical simulations of the elution profile indicate that the peak and mean may differ by as much as a factor of two for slow mass transfer into the beads. Since the mean is uniquely determined by the sorption–desorption equilibrium constant, but the peak is not, the use of the peak to characterize the equilibrium constant for broad asymmetric profiles can lead to serious errors. For some low transfer rates the profile has two peaks. This happens even for homogeneous molecules under ideal conditions and is caused by molecules that traverse the bed without penetrating the beads. The dispersion in the first peak is determined by effects other than mass transfer.

We then consider heterogeneity or non-uniformity in the bed and in the molecules. When equilibrium constants are distributed, the expressions for the mean elution time involve the average equilibrium constant (or the average penetrable volume). If the sorption rate is constant, then the variance of the elution profile is proportional to the sum of the square of the average equilibrium constant and the variance of the distribution. A chromatography model with non-linear sorption–desorption kinetics is considered. When the mass transfer rates are concentration dependent, the sorption–desorption equilibrium constant is no longer uniquely determined by the profile mean. However, uniqueness is obtained in the limit as both mass transfer coefficients become small, with their ratio remaining moderate. Graphs reveal the remarkable dependence of the mean of the elution profile for the non-linear model on the mass transfer rates.

A CHROMATOGRAPHY MODEL WITHOUT DIFFUSION

Solutions for a very thin solute zone

The model discussed in ref. 1 consisted of the following diffusion–reaction–convection system

$$\frac{\partial p}{\partial t} = D\frac{\partial^2 p}{\partial x^2} + u\frac{\partial p}{\partial x} - k_1 p + k_{-1} q \qquad \qquad (1)$$

$$\frac{\partial q}{\partial t} = k_1 p - k_{-1} q \qquad \qquad (2)$$

together with appropriate boundary and initial conditions, where p and q are the probabilities per unit column length of finding solvent molecules at position x at time t, D is the diffusion constant, u is the convection velocity, and k_1 and k_{-1} are the rate

constants for penetrance of, and exit from, the beads. The bottom of the bed is at $x = 0$ and the top is at $x = h$ (see ref. 1 for notation). These equations were solved for quantities related to the moments of the density functions p and q. In particular, we obtained expressions for the mean, variance and skewness of the elution profile.

To obtain an expression for the entire profile, first consider eqns. 1 and 2 without diffusion ($D = 0$) subject to initial conditions

$$p(x,0) = \delta(x - h)$$

$$q(x,0) = 0 \qquad x \neq h \tag{3}$$

The number of molecules and the current must be continuous at the top of the bed so that

$$p(h,t) = 0 \qquad t > 0 \tag{4}$$

Instead of including the instantaneous source in the initial conditions (eqn. 3), it could have been included in eqn. 1 as a term $\delta(x - h)\,\delta(t)$ or in the boundary condition (eqn. 4) as $p(h, t) = \delta(u, t)$ for $t \geqslant 0$.

For the purpose of finding a solution, we assume that there is no solute buildup at the bottom of the bed; i.e., we assume that flow continues as though the bed were extended below $x = 0$. We thus take the eluted current (molecules per unit time) at the bottom of a bed of height h as $u A_0 C(0,t) = uIp(0,t)$. In this equation, I is the total number of solute molecules and $p(x,t)$ is the solution of the initial boundary value problem with a uniform bed on the semi-infinite interval $-\infty < x \leqslant h$, with p approaching zero as x approaches $-\infty$.

Now define $\Delta = ut + x - h$ and $\varrho = (k_1 k_{-1}/u^2)(h - x)$; then the solution (Appendix A) of eqns. 1–4 is

$$p(x,t) = \exp[-k_1(h - x)/u][\delta(\Delta) + H(\Delta)\exp(-k_{-1}\Delta/u)\sqrt{\varrho/\Delta}\,I_1(2\sqrt{\varrho\Delta})] \tag{5}$$

$$q(x,t) = (k_1/u)\exp[-k_1(h - x)/u]\,H(\Delta)\exp(-k_{-1}\Delta/u)\,I_0(2\sqrt{\varrho\Delta}) \tag{6}$$

where the Heaviside function $H(\Delta)$ is 0 for $\Delta < 0$ and 1 for $\Delta \geqslant 0$, and the symbols I_0 and I_1 are modified Bessel functions[4]. Thomas[5] found similar solutions and also found asymptotic approximations. Giddings and Eyring[6] and Giddings[7] obtained similar solutions using a stochastic (random walk) approach.

Solutions for a large solute zone

A large zone corresponds to an initial layer of macromolecules which is thick enough so that it cannot be considered an instantaneous source. To obtain a solution for this case we again begin with the initial boundary value problem without diffusion. The partial differential equations in the bed are eqns. 1 and 2 with $D = 0$, and the initial conditions are

$$p(x,0) = 0 \qquad q(x,0) = 0 \qquad 0 \leqslant x < h \tag{7}$$

If the thickness of the initial layer of molecules is T, then the boundary condition at the top of the bed is

$$p(h,t) = [1 - H(ut - T)]/T \tag{8}$$

for $t \geqslant 0$.

The following solutions of the initial boundary value problem described above are found by Laplace transforms (Appendix A).

$$p(x,t) = \begin{cases} 0 & \Delta < 0 \\ \dfrac{1}{T} \exp\left[\dfrac{-k_1(h-x)}{u}\right]\left[1 + \displaystyle\int_0^\Delta \exp\left(\dfrac{-k_{-1}w}{u}\right)\sqrt{\dfrac{\varrho}{w}}\, I_1(2\sqrt{\varrho w})\, dw\right] & 0 \leqslant \Delta \leqslant T \\ \dfrac{1}{T} \exp\left[\dfrac{-k_1(h-x)}{u}\right]\left[\displaystyle\int_{\Delta-T}^\Delta \exp\left(\dfrac{-k_{-1}w}{u}\right)\sqrt{\dfrac{\varrho}{w}}\, I_1(2\sqrt{\varrho w})\, dw\right] & \Delta \geqslant T \end{cases} \tag{9}$$

$$q(x,t) = \begin{cases} 0 & \Delta \leqslant 0 \\ \dfrac{k_1}{Tu} \exp\left[\dfrac{-k_1(h-x)}{u}\right]\displaystyle\int_0^\Delta \exp\left(\dfrac{-k_{-1}w}{u}\right) I_0(2\sqrt{\varrho w})\, dw & 0 \leqslant \Delta \leqslant T \\ \dfrac{k_1}{Tu} \exp\left[\dfrac{-k_1(h-x)}{u}\right]\displaystyle\int_{\Delta-T}^\Delta \exp\left(\dfrac{-k_{-1}w}{u}\right) I_0(2\sqrt{\varrho w})\, dw & \Delta \geqslant T \end{cases} \tag{10}$$

As T approaches 0, eqns. 9 and 10 approach eqns. 5 and 6. Using eqn. 9 in the definitions of the moments in ref. 1, we find that the mean and variance of the elution profile agree with eqns. 19 and 20 in ref. 1.

A MODEL WITH DIFFUSION

The procedure for finding a solution including diffusion can be understood best by considering a molecular interpretation of eqns. 5 and 6. In particular, we note that $p(x,t)$ could have been obtained by finding the probability that a molecule at (x,t) had moved freely for a total time $\tau \leqslant t$, multiplying that probability by the conditional probability that a molecule moving for time τ will be at x, and then integrating over τ[6,7]. In the absence of diffusion, the kernel in the integrand, $i.e.$, the probability that a molecule moving freely for total time τ is at x is $\delta(\tau - (h - x)/u)$ since motion by convection is completely deterministic. This procedure uncouples reaction from movement down the bed; something that can always be achieved for a linear system.

If now, rather than allowing movement only by convection, we include diffusion, then the kernel will be Gaussian. In particular, we take

$$G(x,\tau) = (4\pi D\tau)^{-1/2} \exp[-(u\tau + x - h)^2/4D\tau] \tag{11}$$

where $G(x,\tau)$ is the probability that a molecule having moved freely for $\tau \leqslant t$, will be

at x. The diffusion constant D should be interpreted broadly so that it not only includes the simple Brownian diffusion one would find in a homogeneous medium, but also includes eddy diffusion and velocity profile effects[1].

To find the probability density $P(x,t)$ for free molecules at (x,t), eqn. 11 must be multiplied by the probability that a molecule, having moved freely for $\tau \leqslant t$, will be free at (x,t) and the product must then be integrated over τ from 0 to t. The probability density $Q(x,t)$ for bound molecules at (x,t) is found similarly. But we already know the solutions for the reactive probabilities since eqns. 5 and 6 are simply those solutions integrated over a δ-function kernel. Hence we find that the solutions to the model with diffusion are

$$P(x,t) = \int_0^t G(x,\tau)\, p(h - u\tau,t)u\,d\tau \tag{12}$$

$$Q(x,t) = \int_0^t G(x,\tau)\, q(h - u\tau,t)u\,d\tau \tag{13}$$

More explicitly,

$$P(x,t) = G(x,t)e^{-k_1 t} + \int_0^t (4\pi D\tau)^{-1/2} \exp\left[- \frac{(u\tau + x - h)^2}{4D\tau} - k_1\tau - \right.$$
$$\left. k_{-1}(t - \tau) \right] \times \sqrt{\frac{k_1 k_{-1}}{u^2}\frac{\tau}{t - \tau}}\, I_1\left(2\sqrt{k_1 k_{-1}\tau(t - \tau)}\right)u\,d\tau \tag{14}$$

$$Q(x,t) = k_1 \int_0^t (4\pi D\tau)^{-1/2} \exp\left[- \frac{(u\tau + x - h)^2}{4D\tau} - k_1\tau - k_{-1}(t - \tau) \right] \times$$
$$I_0\left(2\sqrt{k_1 k_{-1}\,\tau(t - \tau)}\right)d\tau \tag{15}$$

The functions P and Q above satisfy the differential equations 1 and 2, the initial conditions (eqn. 3) and boundary conditions $P(\pm\infty,t) = 0$, $Q(\pm\infty,t) = 0$.

The main approximation in eqns. 14 and 15, for which we expect the error to be negligible, is that they hold on the interval $-\infty < x < \infty$, whereas the chromatographic bed only occupies $0 \leqslant x \leqslant h$. The contribution from molecules that move above h is expected to be only a second-order effect, since only a small fraction of solute will ever be above h when movement down the bed is dominated by convection. Similarly we expect the concentration of molecules just above $x = 0$, with no bed beneath $x = 0$, to be essentially the same as it would if the bed continued below $x = 0$. Approximate solutions to the large-zone problem with diffusion can be found as above by using eqns. 9 and 10 and the Gaussian kernel (eqn. 11).

PEAKS AND MEANS OF THE ELUTION PROFILE

The number of molecules per second leaving the bottom of the bed is the elution profile $uP(0,t) + D\dfrac{\partial P}{\partial x}(0,t)$ with $P(x,t)$ given by eqn. 14. From this elution

profile we can assess the approximation involved in using the peak of the profile rather than the mean to obtain the equilibrium constant.

A number of investigators have shown[1,8-10] that the mean depends only on the equilibrium constant $K = k_1/k_{-1}$. On the other hand, the peak is not uniquely determined by K, but depends on k_1 and k_{-1} separately. This is shown clearly in Fig. 1, where the time at which the peak occurs is plotted as a function of k_1. The parameters in this example are chosen so that the mean always occurs at 2000 sec. The peak and mean differ by less than 5% for $k_1 \geqslant 0.015$ sec^{-1}, but as k_1 drops the peak decreases rapidly so that it is within a few percent of its limiting value of 1000 sec at $k_1 = 0.002$ sec^{-1}. In the low k_1 limit, the mass transfer rate k_1 is sufficiently low relative to the time for a mobile molecule to traverse the bed that essentially no adsorption occurs.
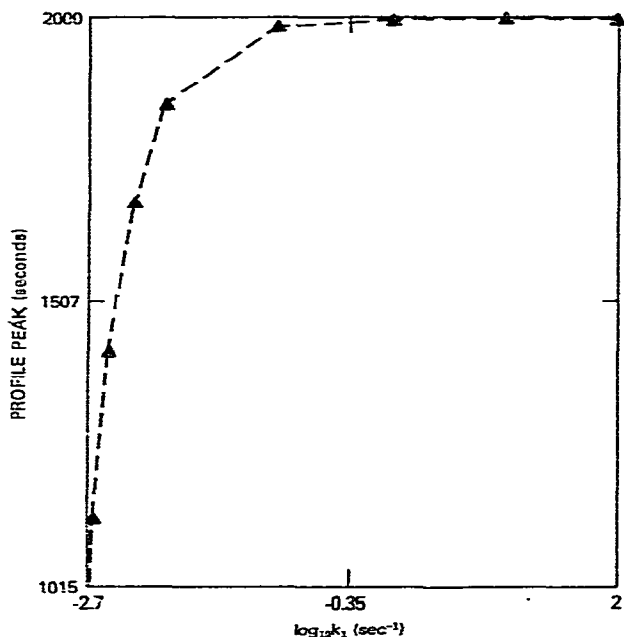

Fig. 1. The profile peak position is a function of the mass transfer rate (k_1 or k_{-1}) with K held constant. The profile mean, on the other hand, is determined only by K. The mean is at 2000 sec, $K = 1$, $h/u = 1000$ sec, $D = 0$.

As the low k_1 limit is approached an interesting effect arises: the profile begins to develop a second peak (Fig. 2). Mathematically, this peak arises from the first term in eqn. 14; physically it represents those particles that traverse the bed with no adsorption. The theory predicts that such a peak can be produced or eliminated by changing h/u so that it either approximates or exceeds $1/k_1$. The rate constant k_1 can be determined by methods discussed in ref. 1. Under usual circumstances one would want to perform separations so that an "artifactual peak" does not arise. However, if the second peak can be produced as readily as the theory suggests, it might be useful. Its breadth is free from mass transfer contributions and it therefore allows an assess-
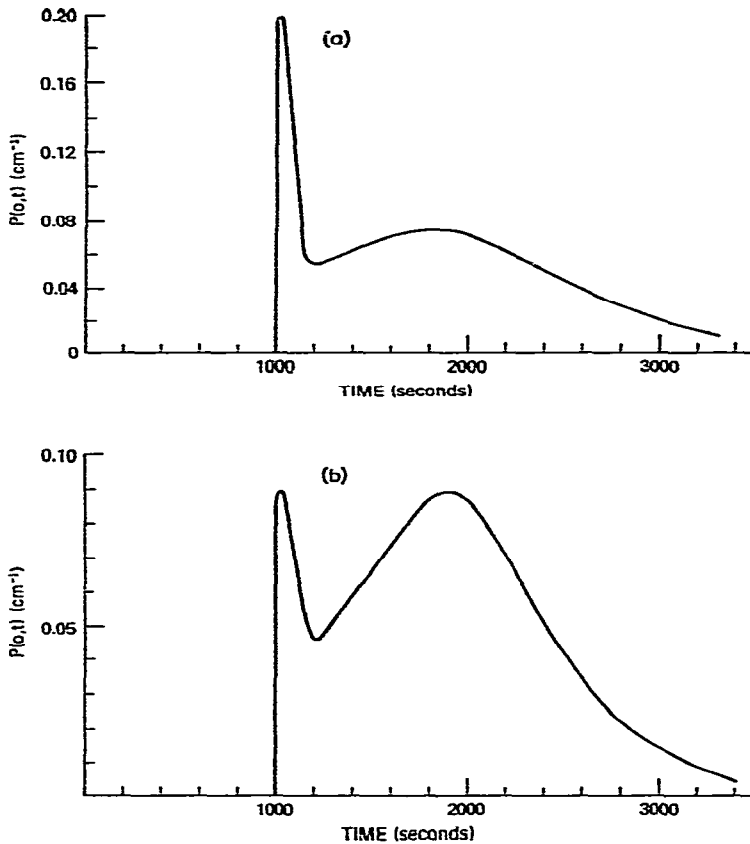
Fig. 2. The elution profile of a completely homogeneous molecular population under ideal conditions becomes bimodal when the rate of mass transfer from the void volume to interior bead volume is comparable to u/h. $D = 10^{-6}$ cm^2/sec, $u = 0.01$ cm/sec, $h = 10$ cm, $K = 1$. (a) $k_1 = 4 \times 10^{-3}$ sec^{-1}; (b) $k_1 = 5 \times 10^{-3}$ sec^{-1}.

ment of the relative contribution of diffusion and mass transfer to the overall profile dispersion.

HETEROGENEITY

The models formulated and analyzed here and in ref. 1 assume that the molecules are uniform in size, structure and weight and that the beads (gel particles are uniform in their packing, size and structure. Here we examine the effect of non-uniformities on the moments of the passage time. Assume that the equilibrium constant K is distributed with probability density function $n(K)$. Note that the distribution of K could be due to a distribution of k_1 or of k_{-1} or of both. The average over the distribution of K of the jth moment of the passage time at position x is defined as

$$T_j = \int_0^\infty n(K) \int_0^\infty t^j [up(x,t;K) + D\frac{\partial p}{\partial x}(x,t;K)]\, dt\, dK \qquad (16)$$

For a small-zone experiment for which diffusion is negligible, the analogs of the expressions in ref. 1 for the moments are

$$\bar{T}_e = (1 + \bar{K})h/u, \qquad \bar{S}_e = 2\overline{(K/k_{-1})}h/u \qquad (17)$$

$$\bar{V}_e = V_0 + \bar{V}_p, \qquad \bar{W}_e = 2FV_0 \overline{(K/k_{-1})} \qquad (18)$$

where $\bar{K} = \bar{V}_p/V_0$ and $\overline{(K/k_{-1})}$ is the expected value of K/k_{-1}.

If the main sources of equilibrium constant heterogeneity are non-uniformities in the beads or in their packing, then the average equilibrium constant $\bar{K}$ and the average penetrable volume $\bar{V}_p$ depend only on the column conditions. As long as the same column is used under the same conditions (for example, during molecular weight calibration and determination), this non-uniformity does not significantly affect the results since it is the same for all molecules passing through the column.

If the main sources of equilibrium constant heterogeneity are non-uniformities in the size, structure or weight of the molecules, then $\bar{K}$ and $\bar{V}_p$ are averages over these molecules. If the sorption rate k_1 is always the same for the molecules, but the desorption rate k_{-1} varies because of differences in the molecules, then $\overline{(K/k_{-1})} = \overline{K^2}/k_1$. In this case, if k_1 is known (e.g., from another experiment), then the second moment $\overline{K^2}$ can be estimated from the observed variance of the elution profile. Hence the variance W_e of the elution profile satisfies

$$W_e = \frac{2FV_0 \,\overline{K^2}}{k_1} = \frac{2FV_0}{k_{-1}}\{(\bar{K})^2 + [\overline{K^2} - (\bar{K})^2]\} \qquad (19)$$

where the first term in the brackets is the square of the mean of the equilibrium constant distribution and the second term is the variance. Thus if k_1 is constant, both the means and the variances of the distribution can be estimated.

NON-LINEAR KINETICS

Consider the chromatography model without diffusion for a thin solute zone described earlier. Assume that the sorption–desorption kinetic rates decrease near saturation, i.e., the kinetics are no longer linear. Then the eqns. 1 and 2 become

$$\frac{\partial p}{\partial t} = u\frac{\partial p}{\partial x} - k_1 p(1 - C/C^m) + k_{-1}q(1 - B/B^m) \qquad (20)$$

$$\frac{\partial q}{\partial t} = k_1 p(1 - C/C^m) - k_{-1}q(1 - B/B^m) \qquad (21)$$

where the parenthesized factors reflect saturation effects. The mobile and stationary phase concentrations C and B are less than the corresponding maximum concentrations C^m and B^m. Since $p = CA_0/I$ and $q = BA_p/I$, we find

$$C/C^m = ph(I/C^m A_0 h) \tag{22}$$

$$B/B^m = qh(I/B^m A_p h) \tag{23}$$

where $A_0 h$ and $A_p h$ are the void and penetrable volumes, respectively. If the total number of molecules I is much less than the molecular capacities $C^m A_0 h$ and $B^m A_p h$, then a suitable small parameter is

$$\varepsilon = I/C^m A_0 h \tag{24}$$

Since $K = V_p/V_0$, then

$$I/B^m A_p h = \varepsilon C^m V_0/B^m V_p = \varepsilon a/K \tag{25}$$

where $a = C^m/B^m$ is a constant near 1 since the saturation concentration C^m and B^m are nearly equal.

Let the expansion of p and q in powers of ε be

$$p + p_0 + p_1\varepsilon + p_2\varepsilon^2 + \dots$$
$$\tag{26}$$
$$q = q_0 + q_1\varepsilon + q_2\varepsilon^2 \dots$$

Substituting eqn. 26 into eqns. 20 and 21 modified to include ε by using eqns. 22–25, and equating the powers of ε, we find that p_0 and q_0 are given by eqns. 5 and 6 and p_1 and q_1 satisfy

$$\frac{\partial p_1}{\partial t} = u\frac{\partial p_1}{\partial x} - k_1 (p_1 - hp_0^2) + k_{-1}\left(q_1 - \frac{ah}{K}q_0^2\right)$$

$$\frac{\partial q_1}{\partial t} = k_1 (p_1 - hp_0^2) - k_{-1}\left(q_1 - \frac{ah}{K}q_0^2\right) \tag{27}$$

$$p_1(x,0) = 0, \; q_1(x,0) = 0, \; p_1(h,t) = 0$$

The first-order approximation to the mean elution time is

$$M_e = \int_0^\infty tu[p_0(0,t) + \varepsilon p_1(0,t)]dt = (1 + K)(h/u) + \varepsilon\int_0^\infty tup_1(0,t)dt \tag{28}$$

Following the procedure in the section "The moments of the elution profile" in ref. 1, we find

$$\int_0^\infty tup_1(x,t)dt = -\int_x^h [K\int_0^\infty hp_0^2(w,t) - \frac{a}{K}\int_0^\infty hq_0^2(w,t)dt]dw \tag{29}$$

Substituting eqns. 5 and 6 for p_0 and q_0 in eqn. 29 and using identities involving integrals and series[11], we obtain

$$
\int_0^x t u p_1(0,t) \mathrm{d}t = -(h/u) \left[\frac{2+\beta}{4\beta}(1 - \mathrm{e}^{-2z}) - \alpha \mathrm{e}^{-2z} + \frac{1}{2}\int_0^z \mathrm{e}^{-w} I_0(w)\mathrm{d}w - \right.
$$
$$
\left. \left(\frac{x}{2}\right) \mathrm{e}^{-2z} I_1^2(\sqrt{2\alpha}) - \frac{a}{2}\int_0^z \mathrm{e}^{-w} I_0(w)\mathrm{d}w \right] \tag{30}
$$

where $\alpha = k_1 h/u$ and $\beta = k_{-1} h/u$.

Numerical evaluation of the integral in eqn. 30 indicates that it is well approximated, over a wide range of α, by

$$
\int_0^z \mathrm{e}^{-w} I_0(w)\mathrm{d}w \cong -0.1895 + 0.855\sqrt{\alpha} \tag{31}
$$

In particular, this approximation holds to within 6% at $\alpha = 0.2$; 1% at $\alpha = 1$, and it becomes increasingly better as α increases. Therefore eqn. 28 can be written as

$$
M_c = (1 + K)(h/u) - \varepsilon(h/u) \left\{ \frac{2+\beta}{4\beta}(1 - \mathrm{e}^{-2z}) - \alpha \mathrm{e}^{-2z} \right.
$$

$$
\left. -\frac{\alpha}{2}\mathrm{e}^{-2z} I_1^2(\sqrt{2\alpha}) - \frac{1}{2}(1 - a)(0.1895 - 0.855\sqrt{\alpha}) \right\} \tag{32}
$$

If α and β are small, with K remaining moderate, the result simplifies to

$$
M_c \cong (1 + K)(h/u) - \frac{\varepsilon h K}{u} = [1 + K(1 - \varepsilon)](h/u) \tag{33}
$$

Combining eqns. 28 and 30 we find that the first-order approximation to the relative error in neglecting the non-linear kinetics is given by

$$
\left| \frac{M_c - (1 + K)(h/u)}{(1 + K)(h/u)} \right| \leqslant \frac{\varepsilon}{1 + K} \left[\frac{2+\beta}{4\beta} + (1 + a)\sqrt{\frac{\alpha}{2\pi}} \right] \tag{34}
$$

Eqn. 32 predicts that in the non-linear regime, the elution profile mean depends separately on the mass transfer rates k_1 and k_{-1}, not just on their ratio K. Thus with K held fixed, changes in $\alpha = k_1 h/u$ can cause changes in the mean (see Fig. 3). The percentage difference between the non-linear and linear means is usually small, generally not more than 100ε. The maximum percentage difference between the non-linear and linear means is shown in Fig. 4. Note that the linear mean is usually larger than the non-linear mean. More interesting are the maxima and minima that occur in some parts of Fig. 3. Fig. 3 clearly illustrates that when the sorption–desorption kinetics are non-linear, the mean is not uniquely determined by the equilibrium constant K, but depends on the sorption and desorption rate constants k_1 and k_{-1}.
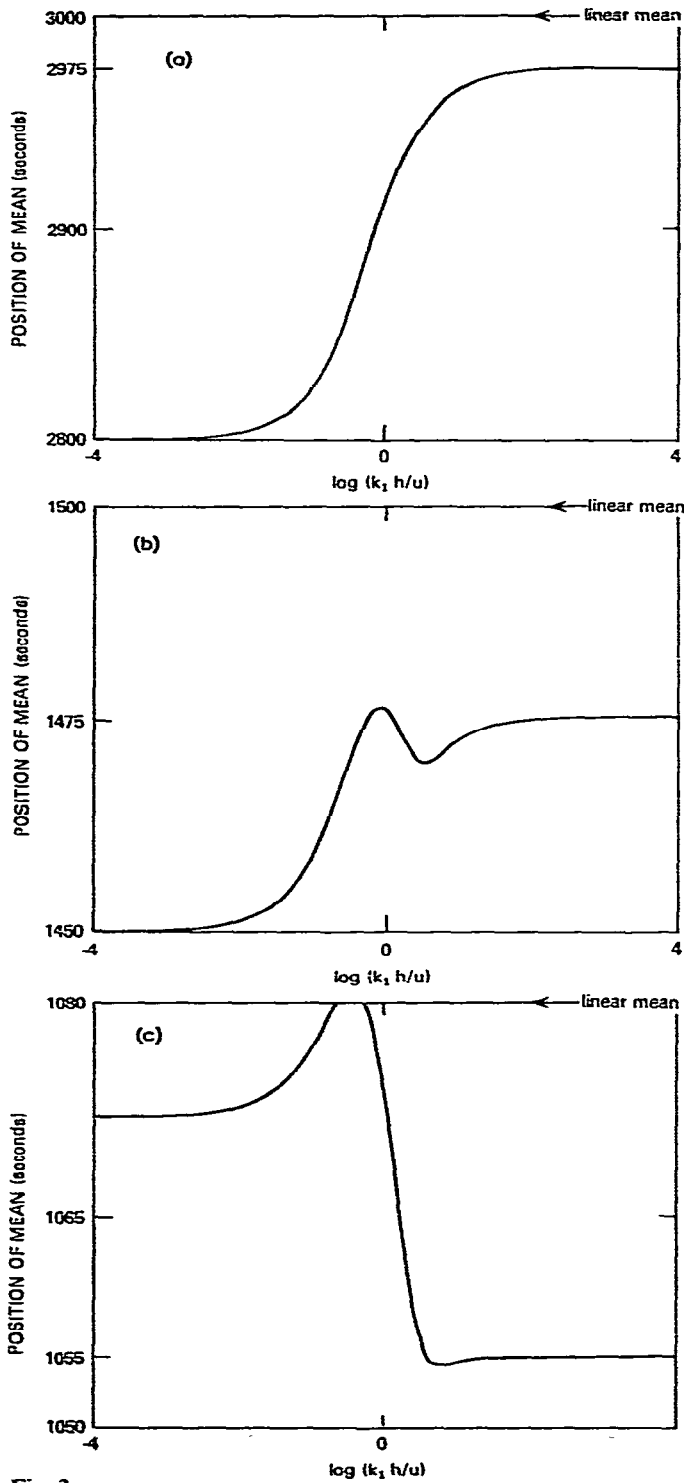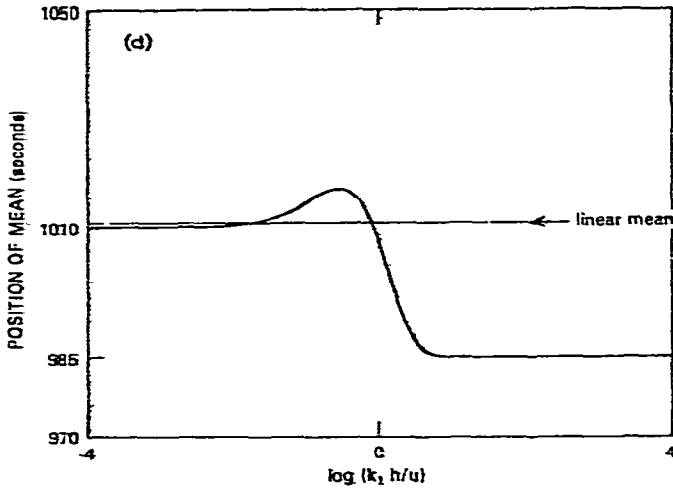
Fig. 3.

Fig. 3. The position of the mean in the non-linear problem is not uniquely determined by K. $a = 1$ and $\varepsilon = 0.1$ in all figures. (a) $K = 2$, (b) $K = 0.5$, (c) $K = 0.08$, (d) $K = 0.01$.
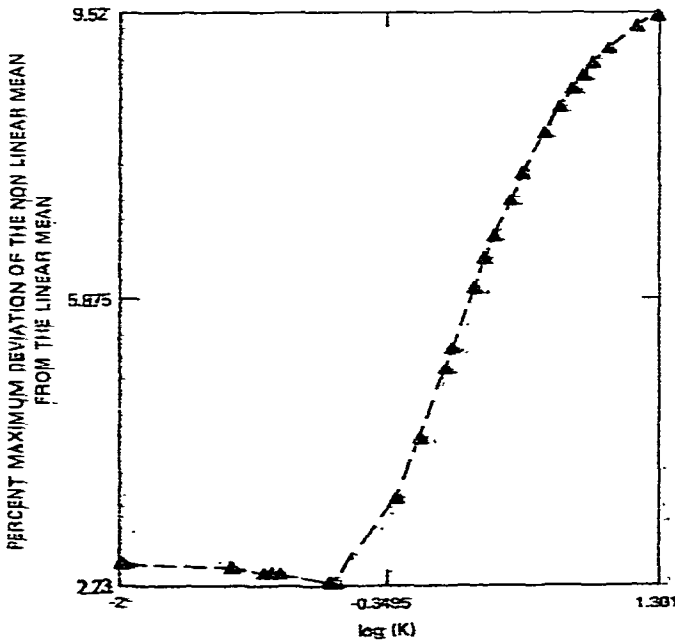

Fig. 4. Maximum deviation between the linear and non-linear means as a function of K. At high K, the maximum deviation is 10% (100s); at low K it is 2.5%.

APPENDIX A: DERIVATION OF EXPLICIT SOLUTIONS

Let $Lp(x,s)$ and $Lq(x,s)$ be the Laplace transforms of $p(x,t)$ and $q(x,t)$. From eqns. 1 and 2 we find that

$$u\frac{\partial Lp}{\partial x} - \left(s + k_1 - \frac{k_1 k_{-1}}{s + k_{-1}}\right)Lp = -\delta(x - h), \quad Lp(h,s) = 0 \tag{35}$$

$$Lq(x,s) = k_1 Lp/(s + k_{-1}) \tag{36}$$

The solution of the initial value problem (eqn. 35) is

$$Lp(x,s) = \frac{1}{u}\exp\left[\frac{-k_1(h - x)}{u} - \frac{s(h - x)}{u} + \frac{k_1 k_{-1}(h - x)}{u(s + k_{-1})}\right] \tag{37}$$

We will need the following Laplace transform formulas[12]:

$$e^{a/s} = L\{(a/t)^{1/2}\, I_1\,[2(at)^{1/2}] + \delta(t)\} \tag{38}$$

$$e^{a/s}/s = L[I_0\,(2at)^{1/2}] \tag{39}$$

Using eqns. 36–39 with the usual rules for Laplace transforms, we find the solution given by eqns. 5 and 6.

For the large-zone model

$$Lp(x,s) = \frac{(1 - e^{-Ts/u})}{Ts}\exp\left[\frac{-k_1(h - x)}{u} - \frac{s(h - x)}{u} + \frac{k_1 k_{-1}(h - x)}{u(s + k_{-1})}\right] \tag{40}$$

Using eqns. 36 and 38–40 and standard Laplace transform formulas, eqns. 9 and 10 are obtained.

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