

CHROM. 10,668

## THEORY OF NON-LINEAR FRONTAL CHROMATOGRAPHY

A. I. KALINICHEV, A. YA. PRONIN, K. V. CHMUTOV and N. A. GORYACHEVA

*Institute of Physical Chemistry, U.S.S.R. Academy of Sciences, Lenin Avenue 31, Moscow (U.S.S.R.)*

(Received September 9th, 1977)

---

### SUMMARY

Approximate analytical solutions describing the distribution of the concentration of the chromatographic fronts for arbitrary convex and concave isotherms are presented. The solutions, obtained by an integral method, make it possible to derive relationships describing the movement and broadening of chromatographic fronts at non-linear isotherms. In particular, the values of time (length) required for establishing the constant configuration of the chromatographic front (steady stage) can be derived.

The solutions obtained are compared with the known ones for slightly curved isotherms and those describing the stationary front at convex isotherms. The comparison shows the approximate solutions to have a good accuracy (*ca.* 5%). Theoretical and experimental curves are in good agreement.

---

### INTRODUCTION

The extent of broadening of chromatographic fronts accompanying the movement of solute through a porous medium is determined by the finite rate of mass transport between the phases (kinetics) and by the longitudinal diffusion coefficient. The degree of influence of these factors on broadening depends on the form of a distribution isotherm. The quantitative description of the effects of non-linearity of the isotherm can be estimated by solving the differential equations of the theory of chromatography, *i.e.* the mass balance equation and the sorption kinetic equation. These equations have been analytically solved for the case of a linear isotherm<sup>1,2</sup>. In the case of convex and concave isotherms with a small deviation from linearity the approximate analytical solutions describing the distribution of concentration in the chromatographic peak<sup>3,4</sup> and front<sup>5</sup> have been obtained. For the same non-linear isotherms the analytical relationships describing the movement and broadening of the peak<sup>4,6–8</sup> and front<sup>9,10</sup> have been derived by moment analysis. For convex isotherms the asymptotic ( $t \rightarrow \infty$ ) solutions of the running-wave type, *i.e.* steady stage of the front movement, are known<sup>11,12</sup>.

In this paper the distribution of concentration in the chromatographic front<sup>13</sup> is described. By using this distribution in the integral method one can calculate the concentration profile at any moment and describe the movement and broadening of the front for arbitrary convex and concave isotherms, including Freundlich isotherms.

Such a distribution of concentration is used here in two variants of the problem: equilibrium frontal chromatography at  $D \neq 0$  and non-equilibrium frontal chromatography at  $D = 0$ , where  $D$  is the coefficient of longitudinal diffusion.

### THEORETICAL

A basic equation of equilibrium frontal chromatography at  $D \neq 0$  for a semi-restricted column ( $0 \leq x < \infty$ ) is

$$\frac{\partial a}{\partial t} + \frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2}, \quad a = f(c) \quad (1)$$

with the initial and boundary conditions

$$c(0, t) = 1 \quad c(x, 0) = 0 \quad c(\infty, t) = 0 \quad (2)$$

where  $c = c'/c_0$ ;  $a = a'/c_0$ ;  $c'$  is the concentration of the solute in the mobile phase;  $a'$  is the mass of the solute in the stationary phase per unit volume of the mobile phase;  $c_0$  is the concentration of the solute at the column input (at  $x = 0$ );  $x$  is the coordinate;  $t$  is the time;  $u$  is the linear velocity of the mobile phase; and  $f(c)$  is the isotherm equation.

In dimensionless time  $\tau = 2ut/H$  and coordinate  $\eta = 2x/H$  the mass balance equation in eqn. 1 can be rewritten as

$$\frac{\partial f(c)}{\partial \tau} + \frac{\partial c}{\partial \tau} + \frac{\partial c}{\partial \eta} = \frac{\partial^2 c}{\partial \eta^2} \quad (3)$$

where  $H = 2D/u$ , the height of the equivalent theoretical plate (HETP).

To solve the non-linear eqn. 3 for the case of a non-linear isotherm  $f(c)$ , we can apply a method of integral ratios<sup>14,15</sup>, but with the difference that in place of the moving concentration boundary for the point of the front at height  $c = 0$ , we introduce the moving boundary  $\delta(\tau)$  for the point of the front at height  $c = 1$  (Fig. 1). Thus the concentration profile will be determined by the relationship<sup>13</sup>:

$$c(\eta, \tau) = 1, \quad \eta \leq \delta; \quad c(\eta, \tau) = \exp[-b^2(\tau)(\eta - \delta)^2] \quad \eta > \delta \quad (4)$$

The curvature of the concentration profile  $c(\eta, \tau)$  at any point  $\eta > \delta(\tau)$  is determined by the time-dependent coefficient  $b(\tau)$ . The width  $\sigma$  (dispersion) and the centre of gravity  $\bar{\eta}$  (Fig. 1) are determined by equations for the statistical moments of the curve  $-(\partial c/\partial \eta)$ :

$$\bar{\eta} = \frac{2\bar{x}}{H} = \int_{\delta}^{\infty} \eta \left(-\frac{\partial c}{\partial \eta}\right) d\eta = \delta + \frac{\sqrt{\pi}}{2b} \quad (5)$$

$$\sigma^2 = \overline{(\eta - \bar{\eta})^2} = \int_{\delta}^{\infty} (\eta - \bar{\eta})^2 \left(-\frac{\partial c}{\partial \eta}\right) d\eta = \left(1 - \frac{\pi}{4}\right) \cdot \frac{1}{b^2} \quad (6)$$

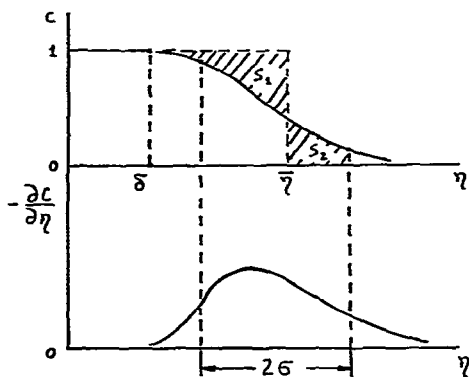


Fig. 1. Frontal concentration curve  $c(\eta, \tau)$  and the corresponding curve  $-(\partial c/\partial \eta)$ :  $\delta(\tau)$ , moving concentration boundary for  $c = 1$ ;  $\bar{\eta}$ , position of the gravity centre ( $S_1 = S_2$ );  $\sigma$ , dispersion of the curve  $-(\partial c/\partial \eta)$ .

The form of the function  $\delta(\tau)$ ,  $b(\tau)$  is determined by the requirement that eqn. 4 should satisfy two integral ratios of the zero and first orders describing the law of conservation of matter. An integral relationship of the  $n$ -th order is derived from eqn. 3 by multiplying the left- and right-hand sides of the equation by  $\eta^n$ , with a subsequent integration over  $\eta$  from  $\delta$  to  $\infty$ :

$$n = 0, \frac{d}{d\tau} \int_{\delta}^{\infty} (a + c) d\eta + [1 + f(1)] \frac{d\delta}{d\tau} = 1 \tag{7}$$

$$n = 1, \frac{d}{d\tau} \int_{\delta}^{\infty} \eta (a + c) d\eta + [1 + f(1)] \delta \frac{d\delta}{d\tau} = 1 + \delta + \int_{\delta}^{\infty} c d\eta \tag{8}$$

An arbitrary convex and concave isotherm can be approximated by a polynomial with an arbitrary degree  $m$ ,

$$f(c) = \gamma c + \gamma_1 \varepsilon_1 c^m \tag{9}$$

where  $\gamma$  is the Henry coefficient;  $\varepsilon_1$  and  $m$  characterize non-linearity of the isotherm, e.g. at  $\varepsilon_1 > 0$  and  $m > 1$ , or at  $\varepsilon_1 < 0$  and  $m < 1$ , the isotherm is concave, and at  $\varepsilon_1 < 0$  and  $m > 1$  or at  $\varepsilon_1 > 0$ ,  $m < 1$ , the isotherm is convex; if  $\gamma = 0$ ,  $\gamma_1 \varepsilon_1 > 0$ , and eqn. 9 becomes the Freundlich isotherm.

If eqn. 9 does not approximate a real isotherm closely enough, the number of terms may be increased and the degree  $m$  changed. The form of the obtained solutions (eqns. 4 and 10–12) remains unchanged, and only the constants  $\varepsilon$ ,  $m$ , and  $k$  vary.

By substituting eqn. 9 into eqns. 7 and 8 and taking integrals by means of eqn. 4, we get a solution of the ordinary differential eqns. 7 and 8 in the form<sup>13</sup>:

$$y - \ln |1 + y| = k \tau_1; \tau_1 = \frac{\tau}{(1 + \gamma)(1 + \varepsilon)}, \varepsilon = \frac{\gamma_1 \varepsilon_1}{1 + \gamma} \tag{10}$$

$$\frac{\sqrt{\pi}}{2b} = \frac{(1 + \varepsilon)y}{\varepsilon(1 - 1/\sqrt{m})} \tag{11}$$

where

$$y = \frac{\varepsilon(1 - 1/\sqrt{m})}{1 + \varepsilon/\sqrt{m}}(\tau_1 - \delta); k = \frac{[\varepsilon(1 - 1/\sqrt{m})]^2}{\frac{4}{\pi} \left(1 + \frac{\varepsilon}{m}\right) (1 + \varepsilon) - \left(1 + \frac{\varepsilon}{\sqrt{m}}\right)^2} \quad (12)$$

For the linear isotherm  $\varepsilon = 0$

$$\frac{1}{b} = \sqrt{\frac{2\tau_1}{1 - \pi/4}}, \quad \delta = \tau_1 - \sqrt{\frac{2\tau_1}{\frac{4}{\pi} - 1}}, \quad \bar{\eta} = \tau_1 \quad (13)$$

Eqn. 4, where the dependence of  $b(\tau)$ ,  $\delta(\tau)$  is determined from eqns. 11 and 12 and the transcendental eqn. 10, holds for convex and concave isotherms of any non-linearity  $\varepsilon, m$ . At  $\gamma = 0$ ,  $\gamma_1 \varepsilon_1 > 0$ , the solution is valid for the case of the Freundlich isotherm.

As the front begins to move, *i.e.* at short times,  $\tau_1 < (1/2k)$  (when  $|y| \ll 1$ ); using an expansion  $\ln |1 + y|$  in eqn. 10, we get from eqns. 10 and 11:

$$y = \sqrt{2k\tau_1}, \quad \frac{\sqrt{\pi}}{2b} = \frac{(1 + \varepsilon)\sqrt{2k\tau_1}}{\varepsilon(1 - 1/\sqrt{m})}, \quad \bar{\eta} = \tau_1 + \sqrt{2k\tau_1} \quad (14)$$

From eqns. 13 and 14 we can see that at the stage of initial movement, the width  $\sigma \sim |y|$  of the sorption front increases proportionally to  $\sqrt{t}$  not only for linear but also for convex and concave isotherms.

Let us consider in detail the dynamics of broadening of the chromatographic front for convex isotherms. It is well known<sup>11,12</sup> that for a convex isotherm, there exists an asymptotic ( $t \rightarrow \infty$ ) solution of the running wave type, *i.e.* a steady stage of the front movement with velocity  $v$ , when the function  $c$  depends on one variable  $z$  only, where  $z = x - vt$ . By using eqn. 10 it is easy to determine the time,  $\tau_1^{st}$  at which these conditions are established: at  $m > 1, \varepsilon_1 < 0$ , or  $m < 1, \varepsilon_1 > 0, \lim_{\tau \rightarrow \infty} y = -1$

$$\lim_{\tau \rightarrow \infty} \delta = \tau_1 + \frac{1 + \varepsilon/\sqrt{m}}{\varepsilon(1 - 1/\sqrt{m})}; \quad \lim_{\tau \rightarrow \infty} \frac{1}{b} = \frac{2(1 + \varepsilon)}{\sqrt{\pi} \varepsilon (-1 + 1/\sqrt{m})} \quad (15)$$

$$c(z) = \exp(-b^2 z^2); \quad z = \eta - \delta$$

Within an error limit of 1% ( $y_{st} = -0.99$ ), the width of the front  $\sigma \sim |y|$  (eqns. 6 and 11) becomes constant at  $\tau_1 > \tau_1^{st}$ ; from eqn. 10 we then obtain

$$\tau_1^{st} = \frac{\tau^{st}}{(1 + \gamma)(1 + \varepsilon)} = \frac{3.6}{k} \quad (16)$$

The moving boundary  $\delta$  and the centre of gravity  $\bar{\eta}$  of the front (Fig. 1) move with constant velocities

$$\frac{d\delta}{d\tau} = \frac{d\bar{\eta}}{d\tau} = \frac{1}{1 + f(1)}, \quad \frac{d\delta}{d\tau_1} = \frac{d\bar{\eta}}{d\tau_1} = 1 \quad (17)$$

This is the well-known Wilson relationship<sup>12,16</sup>, which determines the velocity of the front movement at the steady stage. The estimate of eqn. 16 indicates that the time at which the steady stage is established is proportional to  $H/\varepsilon^2$ , which agrees with the values obtained in refs. 5, 9 and 10 at  $m = 2$ ,  $\gamma = \gamma_1$  for convex isotherms of small non-linearity  $|\varepsilon| \ll 1$ . Eqn. 16 also holds for isotherms with large deviations from linearity, e.g.

$$m = 2, \gamma = \gamma_1; \varepsilon = -0.5, \tau_1^{st} = 9.2, \delta^{st} = \tau_1^{st} + \frac{1 + \varepsilon/\sqrt{m}}{\varepsilon(1 - 1/\sqrt{m})} = 4.8 \quad (18)$$

$$\varepsilon = -0.4, \tau_1^{st} = 39.6, \delta^{st} = 19$$

In the case of a concave isotherm ( $\varepsilon > 0$  and  $m > 1$ , or  $\varepsilon < 0$  and  $m < 1$ ) the sorption front widens progressively with time. From eqn. 12 it follows that  $y > 0$ , and at long times  $\tau_1 > (100/k)$  (when  $y \gg \ln |1 + y|$  in eqn. 10) we have

$$\tau_1 > \frac{100}{k} \quad y = k \tau_1$$

$$\sigma = \frac{1}{b} \sqrt{1 - \pi/4} = \sqrt{\frac{4}{\pi} - 1} \frac{(1 + \varepsilon) k \tau_1}{\varepsilon(1 - 1/\sqrt{m})} \quad (19)$$

The velocities of movement of the centre of gravity  $\bar{\eta}$  and moving boundary  $\delta$  are

$$\frac{d\delta}{d\tau_1} = 1 - \frac{(1 + \varepsilon/\sqrt{m})k}{\varepsilon(1 - 1/\sqrt{m})}; \quad \frac{d\bar{\eta}}{d\tau_1} = 1 + k \quad (20)$$

So, in the case of a concave isotherm the width of the sorption front,  $\sigma$ , increases proportionally to  $t$  (eqn. 19).

To check the accuracy of eqn. 4, where  $b(\tau)$  and  $\delta(\tau)$  are determined from eqns. 10–12, we have undertaken a comparison of that approximation with the known solution<sup>1</sup> for a linear isotherm:

$$\varepsilon = 0, c(\eta, \tau) = \frac{1}{2} \left[ \operatorname{erfc} \frac{\eta - \tau_1}{2\sqrt{\tau_1}} + e^\eta \operatorname{erfc} \frac{\eta + \tau_1}{2\sqrt{\tau_1}} \right] \quad (21)$$

and with a solution obtained in ref. 5 for the isotherm  $\gamma c + \gamma \varepsilon c^2$  with a small non-linearity  $|\varepsilon| \ll 1$ . The solution in ref. 5 was obtained by means of integral transformation of the function  $c(\eta, \tau)$ , which turns the non-linear mass balance equation into the linear one relative to a new function. Written in the terms of this paper, the solution<sup>5</sup> is:

$$c(\eta, \tau) = \frac{\exp \frac{\varepsilon p}{1 + \varepsilon} \operatorname{erfc} \frac{1}{2}(g + p/h)}{2 + \exp \frac{\varepsilon p}{1 + \varepsilon} \operatorname{erfc} \frac{1}{2}(g + p/h) - \operatorname{erfc} \frac{1}{2}(p/h - g)} \quad (22)$$

$$p = \eta - \tau_1, \quad h = \sqrt{\frac{\tau}{1 + \gamma} (1 + \varepsilon_1)}, \quad g = \frac{\varepsilon h}{1 + \varepsilon}$$

The solid line of Fig. 2 shows the concentration profiles at an arbitrary moment,  $\tau/(1 + \gamma) = 100$ , calculated for the linear isotherm from eqn. 21 (curve 2) and for slightly non-linear ( $\varepsilon = \pm 0.1$ ) isotherms  $\gamma(c + \varepsilon c^2)$  from eqn. 22 (curves 1 and 3). A comparison of these curves with the corresponding curves (dotted) calculated from eqns. 4 and 10–12 indicates a good approximation accuracy ( $\sim 5\%$ ) both for linear and slightly non-linear convex and concave isotherms. Note that at the given moment  $\tau/(1 + \gamma) = 100$  for a convex isotherm with  $m = 2$  and  $\varepsilon = -0.1$ , no steady stage of the front movement is yet established:  $(\tau^{st}/(1 + \gamma))_{\varepsilon=-0.1} = 860$ .

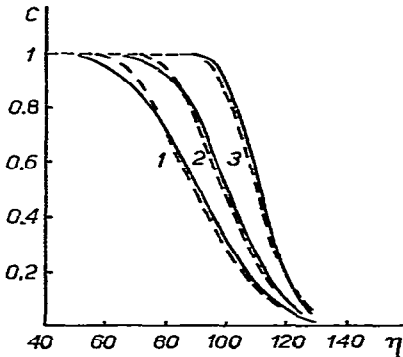


Fig. 2. Frontal concentration curve  $c(\eta, \tau)$  at  $\tau/1 + \gamma = 100$ ; 1, for the concave isotherm  $\varepsilon = 0.1$  ( $m = 2$ ); 2, for the linear isotherm  $\varepsilon = 0$ ; 3, for the convex isotherm  $\varepsilon = -0.1$  ( $m = 2$ ).

The accuracy of the approximate solution (eqn. 4) for isotherms with large non-linearity,  $|\varepsilon| > 0.3$ , can be established by comparing it with an asymptotic solution obtained from eqn. 3 at long times for convex isotherms  $\gamma(c + \varepsilon c^2)$ , when the front movement is in its steady stage:

$$\varepsilon < 0, \quad t \rightarrow \infty \quad \frac{\partial c}{\partial \tau} = -\frac{1}{1 + f(1)} \cdot \frac{dc}{dz}, \quad \frac{\partial c}{\partial \eta} = \frac{dc}{dz} \tag{23}$$

$$m = 2 \quad \ln c - \ln |1 - c| = \frac{\varepsilon z}{1 + \varepsilon} + \text{constant}$$

From the estimates given in eqns. 16 and 18, the steady stage occurs at  $m = 2$ ;

$$\left(\frac{\tau^{st}}{1 + \gamma}\right)_{\varepsilon=-0.5} = 4.2, \quad \left(\frac{\tau^{st}}{1 + \gamma}\right)_{\varepsilon=-0.1} = 860.$$

The solid lines in Fig. 3 show the concentration fronts calculated from eqn. 23 for strongly non-linear ( $\varepsilon = -0.5$ , curve 1) and slightly non-linear ( $\varepsilon = -0.1$ , curve 2) isotherms. The dotted lines are those calculated from eqns. 4 and 10–12. The agreement is good for isotherms with both large and small non-linearity.

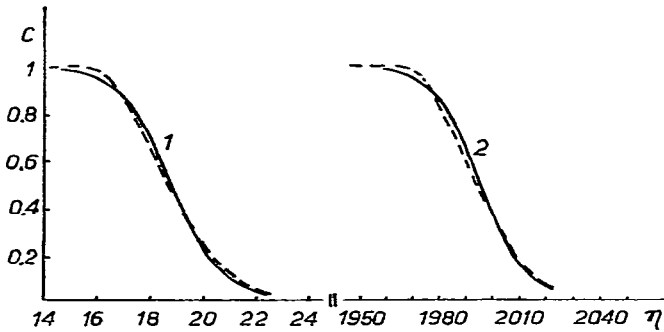


Fig. 3. Concentration fronts in the stationary regime: (1) for strongly non-linear convex isotherm  $\varepsilon = -0.5$ ,  $m = 2$ ,  $\tau/1 + \gamma = 10$ ; (2) for slightly non-linear convex isotherm  $\varepsilon = -0.1$ ;  $m = 2$ ,  $\tau/1 + \gamma = 1800$ .

Non-equilibrium frontal chromatography will be exemplified by means of the mass balance equation at  $D = 0$ :

$$\frac{\partial a}{\partial t} + \frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = 0 \quad (24)$$

and the kinetics equation, where the non-equilibrium of sorption processes is expressed through the parameter  $l$ , the delay path<sup>12</sup>:

$$a = f(c) - l \frac{df}{dc} \cdot \frac{\partial c}{\partial x} \quad (25)$$

To solve eqns. 24 and 25, let us substitute the latter into the former and write down the resulting equation in the dimensionless coordinate  $\eta = x/l$  and time  $\tau = ut/l$ :

$$\frac{\partial f(c)}{\partial \tau} + \frac{\partial c}{\partial \tau} + \frac{\partial^2 f(c)}{\partial \tau \partial \eta} = - \frac{\partial c}{\partial \eta} \quad (26)$$

Integral ratios are derived from eqn. 26 by means of eqns. 4 and 9, using the procedure described. In the practically important case of  $\gamma, \gamma_1 \gg 1$ , the equations for  $b(\tau)$ ,  $\delta(\tau)$  derived from eqns. 26 have the form of eqn. 10–12, with the difference that coordinate and time are expressed not in  $D/u$  values, but in terms of  $l$ . All the conclusions and estimates obtained for equilibrium frontal chromatography are applicable without alteration to non-equilibrium frontal chromatography.

Let us consider an approximate solution describing the leading (sorption) and trailing (desorption) fronts of the wide feed band at the column outlet in the case of arbitrary convex and concave isotherms. Here we write the mass balance equation in the form of eqn. 24 and the kinetic equation, where the non-equilibrium of the sorption process is expressed through the delay time  $\tau^*$  of establishing equilibrium between mobile and stationary phases<sup>2,17</sup>, in the form of

$$a = f(c) - \tau^* \frac{df}{dc} \cdot \frac{\partial c}{\partial t} \quad (27)$$

By substituting eqn. 27 into eqn. 24 and using the dimensionless variables  $T = t/\tau^*$  and  $X = x/\nu\tau^*$ , we obtain the main equation

$$\frac{\partial f(c)}{\partial T} + \frac{\partial c}{\partial T} + \frac{\partial c}{\partial X} = \frac{\partial^2 f(c)}{\partial T^2} \quad (28)$$

For an approximate solution of eqn. 28 we use, as previously, the integral method with the moving boundary for the point of the front at height  $c = 1/T_s$  for the sorption front  $c_s$ , and  $T_d$  for the desorption  $c_d$  (Fig. 4). The moving boundaries  $T_s$  and  $T_d$  for the outlet curves depend not on time but on the distance  $X - T_{s,d}(X)$ .

The solutions  $c_{s,d}$  have a form similar to eqn. 4:

$$T < T_s \quad c_s = \exp[-b_s^2(X)(T - T_s)^2]; \quad T > T_s \quad c_s = 1 \quad (29)$$

$$T < T_d \quad c_d = 1; \quad T > T_d \quad c_d = \exp[-b_d^2(X)(T - T_d)^2]$$

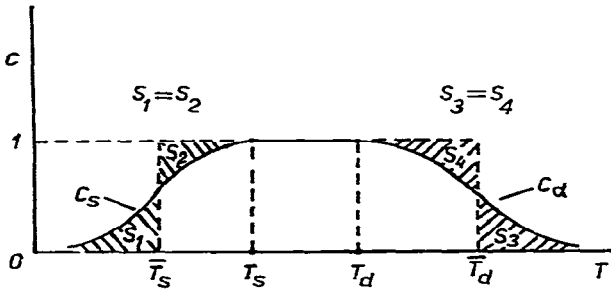


Fig. 4. Output concentration curve for the wide feed band:  $T_{s,d}$ , moving boundaries of concentration  $c_{s,d} = 1$ ;  $\bar{T}_{s,d}$ , position of the gravity centres of the fronts  $c_{s,d}$ .

The dependences  $b_i(X)$ ,  $T_i(X)$  ( $i = s$  or  $d$ ) are derived from two integral ratios of the zeroth and first orders ( $n = 0$  and  $n = 1$ ) for each front of  $c_s$  and  $c_d$ , respectively,

$$n = 0, \quad \frac{d}{dX} \int_{p_i}^{q_i} c_i dT + (-1)^g \frac{dT_i}{dX} = (-1)^g [1 + f(1)] \quad (30)$$

$$\begin{aligned} n = 1, \quad \frac{d}{dX} \int_{p_i}^{q_i} T c_i dT + (-1)^g T_i \frac{dT_i}{dX} - \int_{p_i}^{q_i} [c_i + f(c_i)] dT = \\ = (-1)^g \{f(1) + [1 + f(1)] T_i\} \quad (31) \end{aligned}$$

$$i = s, \quad g = 1, \quad (p_s \ q_s) = (-\infty \ T_s); \quad i = d, \quad g = 2, \quad (p_d \ q_d) = (T_d \ \infty)$$

An integral ratio of the  $n$ -th order is derived from eqn. 28 by a multiplication by  $T^n$  and further integration over  $T$  from  $p_i$  to  $q_i$ . At the outlet of the column the sorption front  $c_s$  appears at  $T > 0$ , and with a very small error the integration limits  $(0, T_s)$  can be replaced by the limits  $(-\infty, T_s)$ .



By substituting eqn. 29 into eqn. 31 and using the isotherm eqn. 9, we obtain the solutions of ordinary differential equations:

$$\frac{\sqrt{\pi}}{2b_i} = (-1)^s (L_i - T_i), L_i = [1 + f(1)] X_i \quad (32)$$

$$X_i = \frac{2\gamma \mathcal{L}_i}{H(1+\gamma)^2}, H = \frac{2u\gamma\tau^*}{(1+\gamma)^2} \text{ (HETP)}$$

where  $\mathcal{L}_i$  is the distance from the initial position of the front  $c_i$  to the place of its outlet. The moving boundaries  $T_i$  in eqn. 32 are determined from a transcendental equation

$$y_i - \ln |1 + y_i| = K L_i, K = \frac{\varepsilon^2 (1 - 1/\sqrt{m})^2}{(1 + \varepsilon) \left( \frac{\gamma}{1 + \gamma} + \varepsilon \right) \left( \frac{4}{\pi} - 1 \right)} \quad (33)$$

where

$$y_i = \frac{\varepsilon (1 - 1/\sqrt{m})}{\frac{\gamma}{1 + \gamma} + \varepsilon} (T_i - L_i) \quad (34)$$

The time of outlet,  $\bar{T}_i$ , and the width,  $\sigma_i$ , of the front  $c_i$  are determined by the first  $\bar{T}_i$  (centre of gravity) (Fig. 4) and second central  $\sigma_i^2$  (dispersion) moments<sup>10,18</sup>. By substituting eqn. 29 into the known ratios determining statistical moments, we get:

$$\bar{T}_i = \int_{p_i^1}^{q_i} T \frac{\partial c_i}{\partial T} dT / \int_{p_i^1}^{q_i} \frac{\partial c_i}{\partial T} dT = L_i \quad (35)$$

$$\sigma_i = \sqrt{(T - \bar{T}_i)^2} = \frac{1}{b_i} \sqrt{1 - \frac{\pi}{4}} \quad (36)$$

The relationship 35 coincides with that obtained in refs. 10 and 18 for slightly curved isotherms, but eqn. 35 is also applicable to isotherms with large non-linearity.

By using eqns. 32–34, it is easy to determine the length,  $L^{st}$ , at which the steady stage of the front movement is established. This takes place for the sorption front  $c_s$  when the isotherm is convex and for the desorption front  $c_d$  where the isotherm is concave. From eqn. 32 it follows that, within 1%, the frontal width  $\sigma \sim |y|$  (eqns. 32 and 36) becomes constant ( $y^{st} = -0.99$ ) at  $L > L_i^{st}$ :

$$L_i^{st} = \frac{3.6}{K}, \sigma_i^{st} = \frac{1 + \varepsilon}{|\varepsilon (1 - 1/\sqrt{m})|} \sqrt{\frac{4}{\pi} - 1} \quad (37)$$

$i = s$  at  $\varepsilon < 0, m > 1$  or  $\varepsilon > 0, m < 1$ ;  $i = d$  at  $\varepsilon > 0, m > 1$  or  $\varepsilon < 0, m < 1$ .

At large distances,  $L_i > 100/K$  (when  $y_i \gg \ln |1 + y_i|$ ), a progressive widening of the front is described by the ratios derived from eqns. 32–36 ( $\gamma \gg 1$ )

$$y > 0, y_i = K L_i, \sigma_i = \frac{|\varepsilon(1 - 1/\sqrt{m})| L_i}{\sqrt{\frac{4}{\pi} - 1} (1 + \varepsilon)} \quad (38)$$

$i = s$  at  $\varepsilon > 0, m > 1$  or  $\varepsilon < 0, m < 1$ ;  $i = d$  at  $\varepsilon < 0, m > 1$  or  $\varepsilon > 0, m < 1$ .

## EXPERIMENTAL

To test experimentally the theoretical eqns. 29 and 32–34, the outlet chromatographic curves were obtained for the wide feed band on ion-exchange columns (0.435 cm<sup>2</sup> in cross-section,  $H = 0.8$  cm) of different length  $\mathcal{L}$  during Ca<sup>2+</sup>–Mg<sup>2+</sup> exchange. A detailed description of experimental procedure is given in refs. 18 and 19. The experimental ion exchange isotherm Ca<sup>2+</sup>–Mg<sup>2+</sup> is shown in Fig. 5 (points). The curve of Fig. 5 is approximated by eqn. 9 (solid line) with the parameters  $\gamma = \gamma_1 = 25$ ,  $\varepsilon_1 = -0.31$ ,  $m = 1.4$ .

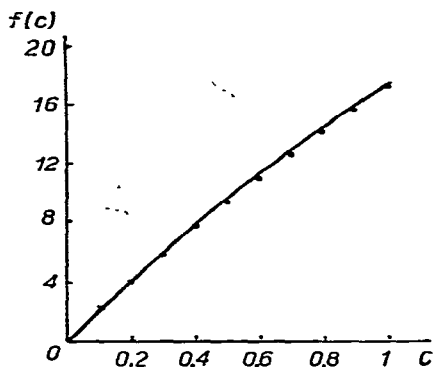


Fig. 5. Calcium–magnesium exchange isotherm: points, experimental; line,  $\gamma(c + \varepsilon_1 c^m)$  dependence,  $\gamma = 25$ ,  $\varepsilon_1 = -0.31$ ,  $m = 1.4$ .

## RESULTS AND DISCUSSION

From the parameters of the isotherm,  $\gamma$ ,  $\varepsilon$  and  $m$ , it is easy to calculate the coefficient  $K$  in eqn. 33. By substituting into eqn. 33 the known values of  $\mathcal{L}_i$  (the distances travelled by the sorption  $c_s$  and desorption  $c_d$  fronts), one can find a solution for  $y_i$ . Then from eqn. 34 one can evaluate  $T_i(L_i)$  and from eqn. 32 determine the coefficient  $b_i(L_i)$ . The concentration profile  $c_i$  is calculated from eqn. 29.

Figs. 6 and 7 show concentration curves calculated for different  $\mathcal{L}_i$  as described above (solid line). The points show experimental outlet curves obtained from columns of different length  $\mathcal{L}$ . The agreement between theoretical and experimental curves  $c_i$  indicates that the approximate solutions of eqns. 29 and 32–34 have a good accuracy.

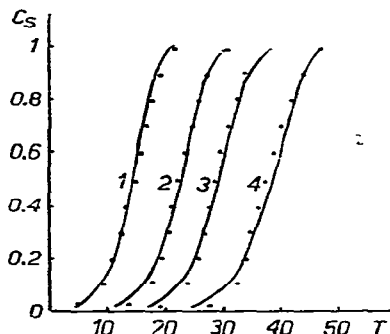


Fig. 6. Output concentration front  $c_s$ : points, experimental; line, calculation; 1,  $L_s = 8.4$  cm; 2,  $L_s = 13.4$  cm; 3,  $L_s = 17.7$  cm; 4,  $L_s = 22.8$  cm.

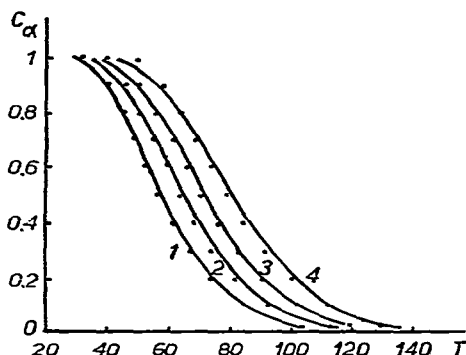


Fig. 7. Output concentration front  $c_\alpha$ : points, experimental; line, dependence; 1,  $L_d = 36.3$  cm; 2,  $L_d = 41$  cm; 3,  $L_d = 45.3$  cm; 4,  $L_d = 50.4$  cm.

From eqns. 10–12 or 32–34, the simple ratios 16 and 37 follow, and these determine the time (length) required for the steady stage of chromatographic front movement to be established. The parameters  $\tau^{st}$  and  $L^{st}$  are proportional to HETP- $H$  and inversely proportional to  $\varepsilon^2$ . A criterion of the steady stage is constant width of the front. This width is determined by a dispersion,  $\sigma$ , of the corresponding concentration curve (Fig. 1).

While the fronts are widening the width depends on the time or the distance travelled by the front (eqns. 19 and 38).

Regularities of movement and widening of the front are described at short times by eqns. 13 and 14, and at long times by eqns. 15, 17, 19 and 20.

The solutions 4 and 10–12, and 29 and 32–34 permit the calculation of the distribution of concentration along the column, or the concentration curve at the column outlet, if the parameters of the HETP- $H$  column and the isotherm ( $\gamma$ ,  $\varepsilon$ ,  $m$ ) are used.

## CONCLUSIONS

Comparison with the known theoretical solutions, eqns. 21–23, and with the experimental data shows that to a good accuracy ( $\sim 5\%$ ) the obtained approximate solutions, eqns. 4 and 10–12, and 29 and 32–34, describe chromatographic fronts for the linear and non-linear (convex or concave) isotherms.

The proposed method can also be used to obtain the equation that describes the chromatographic front in the case of S-shaped isotherms<sup>20,21</sup>.

## REFERENCES

- 1 L. Lapidus and N. R. Amun'sen, *J. Phys. Chem.*, 56 (1952) 984.
- 2 S. E. Bresler and Ya. S. Ufljand, *Zh. Tekh. Fiz.*, 28 (1953) 1443.
- 3 G. Houghton, *J. Phys. Chem.*, 67 (1963) 84.
- 4 P. P. Zolotarev and A. I. Kalinichev, *Dokl. Akad. Nauk SSSR*, 204 (1972) 630.
- 5 M. S. Safonov and V. A. Potechnov, *Theor. Osnov. Khim. Tekhnol.*, 3 (1969) 42.

- 6 K. de Clerk and T. S. Buys, *J. Chromatogr.*, 63 (1971) 193.
- 7 T. S. Buys and K. de Clerk, *J. Chromatogr.*, 67 (1972) 1.
- 8 A. I. Kalinichev and P. P. Zolotarev, *Zh. Fiz. Khim.*, 48 (1974) 138.
- 9 A. I. Kalinichev and P. P. Zolotarev, *Zh. Fiz. Khim.*, 47 (1973) 1583.
- 10 A. I. Kalinichev, *Zh. Fiz. Khim.*, 50 (1976) 1839, 3135.
- 11 E. Glueckauf, *Trans. Farad. Soc.*, 51 (1955) 1540.
- 12 V. V. Rachinsky, *Vvedenie v Obshchuyu Teoriyu Dinamiki Sorbitsii i Khromatografii*, Nauka, Moscow, 1964.
- 13 A. I. Kalinichev, *Ing. Fiz. Zh.*, (1978) in press.
- 14 G. I. Barenblatt, *Izv. Akad. Nauk SSSR, Ser. tekhn.*, 9 (1954) 35.
- 15 T. Gudman, in T. F. Irvine and J. P. Hartnett (Editors), *Advances in Heat Transfer, Vol. 1*, Academic Press, New York, London, 1964.
- 16 I. N. Wilson, *J. Amer. Chem. Soc.*, 62 (1940) 1583.
- 17 S. E. Bresler, *Dokl. Akad. Nauk SSSR*, 97 (1954) 699.
- 18 A. I. Kalinichev, A. Ya. Pronin, P. P. Zolotarev, N. A. Goryacheva, K. V. Chmutov and V. Ya. Filimonov, *J. Chromatogr.*, 120 (1976) 249.
- 19 A. I. Kalinichev, A. Ya. Pronin, N. A. Goryacheva, K. V. Chmutov and V. Ya. Filimonov, *Zh. Fiz. Khim.*, 51 (1977) 1785.
- 20 A. I. Kalinichev, *Zh. Fiz. Khim.*, 51 (1977) 2961.
- 21 A. I. Kalinichev and V. V. Belov, in V. A. Tulupov (Editor), *Sorptisia i Khromatographia*, Nauka, Moscow, 1978, in press.