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INFLUENCE OF SORPTION ON THE SHAPE OF CHROMATOGRAPHIC ELUTION CURVES

G. V. YEROSHENKOVA, S. A. VOLKOV and K. I. SAKODYNSKII*

Karpov Institute of Physical Chemistry, M. Obukha 10, 107125 Moscow (U.S.S.R.)

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SUMMARY

An expression for the chromatographic elution curve in the presence of the sorption effect and axial diffusion is obtained, and corresponding expressions for the first three statistical moments are derived. The shape of the chromatographic elution curve is considered for different values of the initial parameters, and the influence of non-linearity of the adsorption isotherm is also discussed.

INTRODUCTION

Recently, attention was paid again¹ to the importance of the sorption effect in chromatographic peak broadening and distortion when the concentration of the solute in the mobile phase becomes large. The band shape problem was considered for the case when the sorption effect and non-linearity of the adsorption isotherm were taken into account, but axial diffusion and kinetic effects were excluded.

An attempt to develop a general approach to such a problem, including the sorption effect, non-linearity of the isotherm and band broadening due to non-ideality (in terms of the concept of theoretical plates) was made by Haarhoff and Van der Linde² for the case when the column length tends to infinity.

The influence of the sorption effect on retention time in chromatography with a non-linear isotherm was evaluated by moments analysis by De Clerk and Buys³.

In this paper we present a solution of the basic chromatography equation which includes the sorption effect and effective axial diffusion, first for the case of a linear isotherm. Although it seems that the combination of sorption effect with linearity of the isotherm is difficult to realize in practice, it is useful to start with this case for a clear and rigorous analysis of the influence of the sorption effect on the shape of chromatographic elution peaks. Moreover, the above solution describes an important case of chromatography with a vapour-phase eluent when sorption of the latter should be taken into account. Further, we have studied the shape of chromatographic peaks when both the sorption effect and non-linearity of the isotherm are present.

THE BASIC DIFFERENTIAL EQUATION

In gas chromatography, the flow velocity is known to depend on the solute concentration⁴⁻⁷, and it therefore varies throughout the column length. When both solute and eluent adsorption with linear isotherms is allowed, the mobile phase flow velocity in the solute zone is given by the following expression^{8,9*}:

$$u = \frac{u_0}{1 - (1 - \Gamma_2/\Gamma_1) N_1} \quad (1)$$

where u_0 is the mobile phase flow velocity in the absence of solute ($N_1 = 0$) and Γ_1, Γ_2 are Henry coefficients for the solute and eluent, respectively ($\Gamma = \varepsilon + \mu k$, where ε and μ are the column volume fractions for the mobile and stationary phases, respectively, and k is the distribution coefficient for the latter).

If $\alpha = 1 - \Gamma_2/\Gamma_1$, then for the usual case, when adsorption of the eluent is absent, $\Gamma_2 = \varepsilon < \Gamma_1$, so $\alpha > 0$. However, for chromatography with a vapour-phase eluent, α may be of arbitrary sign.

The equation describing the mass transport of the mobile phase in a chromatographic column when non-equilibrium effects are taken into account by an effective diffusion coefficient, D , has the following form for the linear isotherm:

$$\Gamma_1 \cdot \frac{\partial}{\partial t} \cdot N_1 + \frac{\partial}{\partial x} (uN_1) = D \cdot \frac{\partial^2}{\partial x^2} \cdot N_1 \quad (2)$$

where t is time and x is an axial distance coordinate. It should be noted that eqn. 2 is equivalent to the following for eluent N_2 :

$$\Gamma_2 \cdot \frac{\partial}{\partial t} \cdot N_2 + \frac{\partial}{\partial x} (uN_2) = D \cdot \frac{\partial^2}{\partial x^2} \cdot N_2 \quad (3)$$

if one takes into account eqn. 1 and the relationship

$$N_1 + N_2 = 1 \quad (4)$$

for the molar fractions of the solute and eluent⁸. Let us suppose the value of $|\alpha| N_1$ to be small: $|\alpha| N_1 \ll 1$; then, from eqns. 1 and 2 one obtains the basic differential equation

$$\frac{\partial}{\partial t} \cdot N_1 + \frac{u_0}{\Gamma_1} (1 + 2\alpha N_1) \frac{\partial}{\partial x} \cdot N_1 = \frac{D}{\Gamma_1} \cdot \frac{\partial^2}{\partial x^2} \cdot N_1 \quad (5)$$

We use it in this paper for studying chromatographic band development started by releasing a solute pulse into a stream of eluent at $t = 0$ (initial condition):

$$N_1(t = 0, x) = f(x) \quad (6)$$

* A brief derivation of eqn. 1 is given in the Appendix.

with the boundary conditions

$$N_1(t, x = \pm \infty) = 0 \tag{7}$$

Therefore, we consider here for convenience an infinite column but assume that $f(x) \geq 0$ only for $0 \leq x$.

After redefining the variables (moving reference frame)

$$\tau = t, \xi = \frac{\Gamma_1}{u_0} \cdot x - t$$

eqn. 5 for the function

$$C(\tau, \xi) = 2\alpha N_1[t(\tau, \xi), x(\tau, \xi)] \tag{8}$$

reduces to the well known non-linear Burgers equation¹⁰:

$$\frac{\partial}{\partial \tau} \cdot C + C \cdot \frac{\partial}{\partial \xi} \cdot C = \frac{\Gamma_1 D}{u_0^2} \cdot \frac{\partial^2}{\partial \xi^2} \cdot C \tag{9}$$

with the initial condition

$$C(\tau = 0, \xi) = 2\alpha f(\xi) \equiv F(\xi) \tag{10}$$

and the zero boundary conditions at infinity. Let $\nu = \Gamma_1 D / u_0^2$, then the Cole-Hopf transformation¹⁰

$$C(\tau, \xi) = -2\nu \cdot \frac{1}{\varphi} \cdot \frac{\partial}{\partial \xi} \cdot \varphi \tag{11}$$

reduces eqn. 9 to the parabolic diffusion-type equation:

$$\frac{\partial}{\partial \tau} \cdot \varphi = \nu \cdot \frac{\partial^2}{\partial \xi^2} \cdot \varphi$$

with the initial condition (see eqns. 10 and 11)

$$\varphi(\tau = 0, \xi) = \varphi_0 \exp \left[-\frac{1}{2\nu} \int_0^\xi d\eta F(\eta) \right] \tag{12}$$

The Cole-Hopf procedure¹¹ allows one to obtain a general solution of the non-linear problem (eqns. 5-7):

$$N_1(t, x) = \frac{1}{2\alpha t} \frac{\int_{-\infty}^{+\infty} d\omega \varphi(0, \omega) \left(\frac{\Gamma_1}{u_0} \cdot x - t - \omega \right) \exp \left[-\left(\frac{\Gamma_1}{u_0} \cdot x - t - \omega \right)^2 / 4\nu t \right]}{\int_{-\infty}^{+\infty} d\omega \varphi(0, \omega) \exp \left[-\left(\frac{\Gamma_1}{u_0} \cdot x - t - \omega \right)^2 / 4\nu t \right]} \tag{13}$$

For $\alpha \rightarrow 0$ the solution in eqn. 13 correctly reduces to the one corresponding to eqn. 5 with $\alpha = 0$ and initial condition 6.

SOLUTIONS AND MOMENTS ANALYSIS

In this section we study the shape of outlet chromatographic peaks for the particular initial condition

$$f(x) = \begin{cases} N_0, & 0 \leq x \leq x_0 \\ 0, & x < 0, x_0 < x \end{cases} \quad (14)$$

This inlet solute band approximates the rapid sample injection technique used in gas chromatography. From the general solution 13 for initial condition 14 one obtains

$$N_1(t, x) = \frac{N_0}{2\alpha} \cdot \frac{[\operatorname{erf}(a+d) - \operatorname{erf}(b+d)] \exp c}{1 - \operatorname{erf} a + [\operatorname{erf}(a+d) - \operatorname{erf}(b+d)] \exp c + [1 + \operatorname{erf} b] \exp h} \quad (15)$$

where

$$\operatorname{erf} y = \frac{2}{\sqrt{\pi}} \int_{-\infty}^y d\zeta e^{-\zeta^2}$$

and

$$\left. \begin{aligned} a &= \xi / \sqrt{4vt} \\ b &= \left(\xi - \frac{\Gamma_1}{u_0} \cdot x_0 \right) / \sqrt{4vt} \\ c &= -2\alpha N_0 \left(2t\xi - 2\alpha N_0 t^2 + \frac{\Gamma_1}{u_0} \cdot x_0 t \right) / 4vt \\ d &= -2\alpha N_0 t / \sqrt{4vt} \\ h &= -2\alpha N_0 \cdot \frac{\Gamma_1}{u_0} \cdot x_0 / 2v \end{aligned} \right\} \quad (16)$$

Solution 15 and 16 takes into account a finite inlet volume effect: $x_0 > 0$. This is very important for a rapid development because in this instance the shape of a chromatographic peak depends crucially on the width of the inlet solute band (eqn. 14).

If $x_0 \rightarrow 0$ with the condition $x_0 N_0 = \text{constant}$ (infinitely narrow inlet solute band), then the finite inlet volume effect disappears and solution 15 and 16 takes the following form⁹:

$$N_1(t, x) = \frac{1}{2\alpha} \sqrt{\frac{\Gamma_1 D}{t u_0^2}} \cdot \frac{(e^R - 1) \exp \left[-\frac{(x - u_0 t / \Gamma_1)^2}{4Dt / \Gamma_1} \right]}{\sqrt{\pi} + (e^R - 1) \sqrt{\pi} \left[1 - \frac{1}{2} \cdot \operatorname{erf} \left(\frac{x - u_0 t / \Gamma_1}{\sqrt{4Dt / \Gamma_1}} \right) \right]} \quad (17)$$

where

$$R = \frac{Q}{D} \equiv \frac{\alpha N_0 x_0 u_0}{D} \quad (18)$$

Let the diffusion be more essential than the sorption effect, *i.e.*, $|R| \ll 1$. Then solution 17 gives a Gaussian-type shape for the outlet chromatographic peak:

$$N_1(t, x) = \frac{N_0 x_0}{\sqrt{4\pi D t / \Gamma_1}} \cdot \exp \left[-\frac{(x - u_0 t / \Gamma_1)^2}{4 D t / \Gamma_1} \right] \quad (19)$$

In contrast, for $|R| \gg 1$ solution 17 gives an essentially asymmetric outlet peak (for details, see ref. 9). It should be noted that the above asymmetry depends crucially on the sign of α . For $\alpha > 0$ (sorption of the solute is easier than that of the eluent) tailing of the outlet peak is observed:

$$N_1(t, x) = \left\{ \begin{array}{l} 0(R^{-1/2}) \text{ for } Z = \frac{x - u_0 t / \Gamma_1}{\sqrt{4 Q t / \Gamma_1}} < 0 \\ \frac{1}{2\alpha u_0} \sqrt{\frac{4 Q \Gamma_1}{t}} \cdot \frac{Z}{1 + 2Z \sqrt{\pi R} \exp [R(Z^2 - 1)]} \text{ for } 0 \leq Z \end{array} \right\} \quad (20)$$

If $R \rightarrow \infty$ the outlet peak (eqn. 20) has a shock-wave shape:

$$N_1(t, x) = \left\{ \begin{array}{l} \frac{\Gamma_1}{2\alpha u_0} \cdot \frac{(x - u_0 t / \Gamma_1)}{t} \text{ for } 0 < \frac{x - u_0 t / \Gamma_1}{\sqrt{4 Q t / \Gamma_1}} < 1 \\ 0 \text{ for other } t, x \end{array} \right\} \quad (21)$$

For $\alpha < 0$ (sorption of the eluent is easier than that of the solute) asymmetry of the outlet peak is of the opposite type:

$$N_1(t, x) = \left\{ \begin{array}{l} 0(|R|^{-1/2}) \text{ for } Z = \frac{x - u_0 t / \Gamma_1}{\sqrt{4 |Q| t / \Gamma_1}} > 0 \\ \frac{1}{2\alpha u_0} \sqrt{\frac{4 |Q| \Gamma_1}{t}} \cdot \frac{Z}{1 - 2Z \sqrt{\pi |R|} \exp [|R|(Z^2 - 1)]} \text{ for } Z \leq 0 \end{array} \right\} \quad (22)$$

and for $R \rightarrow \infty$ one obtains

$$N_1(t, x) = \left\{ \begin{array}{l} \frac{\Gamma_1}{2|\alpha|u_0} \cdot \frac{|x - u_0 t / \Gamma_1|}{t} \text{ for } -1 < \frac{x - u_0 t / \Gamma_1}{\sqrt{4 |Q| t / \Gamma_1}} < 0 \\ 0 \text{ for other } t, x \end{array} \right\} \quad (23)$$

The outlet peaks for different values of parameters and fixed coordinates x (the column length) are shown in Fig. 1.

The explicit solution 17 allows us to develop moments analysis for the outlet peak. This gives information about the shape of the chromatographic elution curves. We start with dispersion (the second moment), $\sigma^2 = \langle (x - \langle x \rangle)^2 \rangle$, which has the following expression:

$$\sigma^2 = \frac{4D(e^R - 1) t}{R \Gamma_1} \left\{ I_2 - \frac{e^R - 1}{R} \cdot I_1^2 \right\} \quad (24)$$

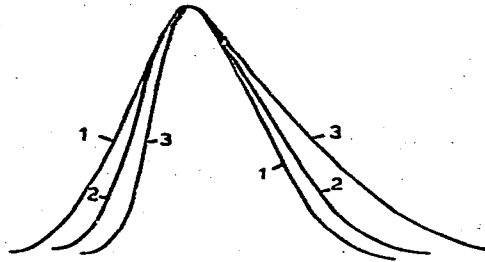


Fig. 1. Peaks at $\mu k_1 = 5.0$; $u_0 = 2$ cm/sec; $x = 50$ cm; $\varepsilon = 0.2$; $D = 0.1$ cm²/sec. 1, $N_0 = 0.01$ ($R = 0.384$); 2, $N = 0.1$ ($R = 3.84$); 3, $N = 0.3$ ($R = 11.52$).

Here, by definition

$$\langle x^k \rangle = \frac{\int_{-\infty}^{+\infty} dx x^k N_1(t, x)}{\int_{-\infty}^{+\infty} dx N_1(t, x)}$$

and therefore

$$I_k = \int_{-\infty}^{+\infty} dx \cdot \frac{x^k \exp(-x^2)}{\sqrt{\pi} + (e^R - 1) \sqrt{\pi} \left(1 - \frac{1}{2} \operatorname{erf} x\right)} \quad (25)$$

As a consequence of eqn. 24, dispersion of the outlet elution curves in the presence of a sorption effect increases linearly with time. A detailed analysis shows that for $|R| \gg 1$ (with good accuracy for $R > 13$) one has

$$\sigma^2 = \frac{2|Q|t}{9\Gamma_1} \quad (26)$$

When diffusion dominates, *i.e.*, $|R| \ll 1$, one has correspondingly (see eqn. 19)

$$\sigma^2 = \frac{4Dt}{\Gamma_1} \quad (27)$$

The second moment, σ^2 , gives the law of outlet band broadening, and the third moment, $\chi = \langle (x - \langle x \rangle)^3 \rangle$, its degree of asymmetry:

$$\chi = \left(\frac{4Dt}{\Gamma_1}\right)^{3/2} \frac{e^R - 1}{R} \left\{ I_3 + 2 \cdot \frac{(e^R - 1)^2 I_1^3}{R^2} - 3 \cdot \frac{(e^R - 1) I_1 I_2}{R} \right\} \quad (28)$$

For $|R| \ll 1$ the third moment, χ , is naturally zero, (see eqn. 19), but for $|R| \gg 1$ one obtains from eqn. 28 the following expression:

$$\chi = -(\operatorname{sign} R) \frac{1}{5} \left(\frac{4|Q|t}{9\Gamma_1}\right)^{3/2} \quad (29)$$

where $\operatorname{sign} R$ corresponds to two different situations (eqn. 21 and 23).

NON-LINEAR CHROMATOGRAPHY

A well known standard approach for explaining the real shape of gas chromatographic elution curves is based on the isotherm non-linearity assumption (non-linear chromatography)¹¹⁻¹³. In spite of the significant attention paid in many papers to non-linearity of the isotherm an exhaustive description of experimental data cannot be given without taking into account the above-mentioned sorption effect. An explicit example has been described^{14,15} for a solute which, with high accuracy, has a linear isotherm but an asymmetric outlet chromatographic peak. Therefore, it is important to study the sorption effect in non-linear chromatography.

Let a non-linear solute isotherm to be of the polynomial form

$$a_1 = g_1(N_1) = \mu k_1 N_1 + \delta_1 N_1^2 \quad (30)$$

Then eqn. 2 changes to

$$(\Gamma_1 + 2\delta_1 N_1) \frac{\partial}{\partial t} \cdot N_1 + \frac{\partial}{\partial x} (u N_1) = D \cdot \frac{\partial^2}{\partial x^2} \cdot N_1 \quad (31)$$

Here we again assume adsorption of the eluent with $N_2 = 1 - N_1$, so that equations similar to eqns. 30 and 31 can be written. As in the section The Basic Differential Equation, these equations together with eqns. 31 and 4 immediately give us the expression for the mobile phase flow velocity, u :

$$u = u_0 \exp \left(- \int_0^{N_1} dy \cdot \frac{n + my}{k + ly + my^2} \right) \quad (32)$$

where

$$k = \Gamma_1; l = \Gamma_2 - \Gamma_1 + 2(\delta_1 + \delta_2); m = -2(\delta_1 + \delta_2); n = \Gamma_2 - \Gamma_1 + 2\delta_2 \quad (33)$$

Let $\Delta = 4km - l^2$ and $4\Gamma_1\Gamma_2 < (\Gamma_1 + \Gamma_2 - m)^2$, then $\Delta < 0$, and therefore

$$u = u_0 \exp \left\{ - \frac{n}{\sqrt{-\Delta}} \cdot \ln \left| \frac{(l + 2mN_1 - \sqrt{-\Delta})(l + \sqrt{-\Delta})}{(l + 2mN_1 + \sqrt{-\Delta})(l - \sqrt{-\Delta})} \right| \right. \\ \left. - \frac{1}{2} \ln \left| \frac{k + lN_1 + mN_1^2}{k} \right| + \frac{1}{2} \cdot \frac{l}{\sqrt{-\Delta}} \right. \\ \left. \cdot \ln \left| \frac{(l + 2mN_1 - \sqrt{-\Delta})(l + \sqrt{-\Delta})}{(l + 2mN_1 + \sqrt{-\Delta})(l - \sqrt{-\Delta})} \right| \right\} \quad (34)$$

The general expression 34 seems to be difficult to handle, but it shows that with the approximations

$$|\delta_1| + |\delta_2| \ll |\Gamma_1 - \Gamma_2|, |\delta_1 N_1| \ll \Gamma_1 \quad (35)$$

eqn. 1 remains unchanged. Hence, the basic differential equation takes the following form (compare eqn. 5):

$$\frac{\partial}{\partial t} N_1 + \frac{u_0}{\Gamma_1} \left[1 + 2 \left(\alpha - \frac{\delta_1}{\Gamma_1} \right) N_1 \right] \frac{\partial}{\partial x} N_1 = \frac{D}{\Gamma_1} \cdot \frac{\partial^2}{\partial x^2} N_1 \quad (36)$$

A similar equation was considered by De Clerk and Buys³, where only adsorption of a solute was allowed and the investigation was based on moments analysis.

From eqn. 36 it follows that the theory developed above can be adapted to include isotherm non-linearity with the approximation (eqn. 35) by introducing

$$\bar{\alpha} = \alpha - \delta_1/\Gamma_1 = 1 - (\Gamma_2 + \delta_1)/\Gamma_1 \quad (37)$$

Therefore, there are no drastic changes in the shape of the outlet band in comparison with the case $\delta_1 = 0$, because $\bar{\alpha}$ has the same sign as α . Hence for the approximations 35 the sorption effect has a prevailing effect on the non-linearity of the isotherm, which gives only small corrections to the solution 15 or 17.

In the opposite case:

$$|\delta_1| + |\delta_2| \gg |\Gamma_1 - \Gamma_2|, \quad |\delta_1 N_1| \ll \Gamma_1 \quad (38)$$

one obtains from eqn. 34 for the mobile phase flow velocity:

$$u = \frac{u_0}{1 + N_1(\delta_1 + \delta_2)/\Gamma_1} \quad (39)$$

Then the basic differential equation 31 takes the form

$$\frac{\partial}{\partial t} \cdot N_1 + \frac{u_0}{\Gamma_1} [1 + 2(\beta_1 + \beta_2) N_1] \frac{\partial}{\partial x} \cdot N_1 = \frac{D}{\Gamma_1} \cdot \frac{\partial^2}{\partial x^2} N_1 \quad (40)$$

As above, this case can be easily adapted by introducing the parameter

$$\begin{aligned} \hat{\alpha} &= \beta_1 + \beta_2 \\ \beta_1 &= -(\delta_1 + \delta_2)/\Gamma_1, \quad \beta_2 = -\delta_1/\Gamma_1 \end{aligned} \quad (41)$$

An important consequence of eqns. 38 and 40 is a non-trivial interference of the sorption effect, when both solute and eluent adsorption are allowed, with non-linearity of the isotherm. When the sorption effect is excluded, $\beta_1 = 0$, and

$$\hat{\alpha} = -\delta_1/\Gamma_1 \quad (42)$$

The sorption effect (see eqns. 38 and 41) can change the value and sign of $\hat{\alpha}$ (eqn. 42) and, as a consequence, the shape of the outlet peak (see Solutions and Moments Analysis). This means that the investigation of the sorption effect in non-linear chromatography for the case in eqn. 38 is very relevant.

CONCLUSION

In contrast to other papers (*e.g.*, ref. 13) this work takes into account a new aspect of the sorption effect by allowing both solute and eluent sorption within the framework of non-ideal and non-linear chromatography. This case can be realized experimentally in chromatography with a vapour-phase eluent^{14,15}.

The main results of our research are the following.

(i) The above-mentioned sorption effect allows the elution curve to have both types of asymmetry (even in the case of linear isotherms) which depends on the relationship between the Henry coefficients Γ_1 and Γ_2 corresponding to the solute and eluent.

(ii) There is a non-trivial interference between the sorption effect and the isotherm non-linearity, which for appropriate conditions can change the initial asymmetry due to isotherm non-linearity into the opposite one for different signs of α . These results are obtained on the basis of the following main assumptions:

(a) the chromatographic process is supposed to be non-ideal, which is taken into account by means of a standard concept of effective diffusion with a longitudinal coefficient D incorporated into the well known sorption dynamic equations (eqns. 2, 3 and 31) (in general, the coefficients should be different for the solute and the eluent);

(b) the chromatographic process corresponds to a constant mass flow-rate of carrier gas at the column inlet;

(c) non-linear distribution isotherms (non-linear chromatography) with a small deviation from linearity are allowed for solute and eluent (see eqn. 30).

In this paper, our main purpose has been to obtain an explicit solution of the problem instead of, *e.g.*, pure moments analysis. This is possible, of course, only with some limitations as defined by the model. Our study of the sorption effect in non-linear chromatography is performed, for instance, only in the two extremal cases. The approximations implied can be illustrated in detail (see also Appendix) by the second case. The sorption dynamic equation 31 for the solute contains two types of non-linearity:

$$(\Gamma_1 + 2\delta_1 N_1) \frac{\partial N_1}{\partial t} + \frac{\partial}{\partial x} \left[\frac{u_0}{1 + N_1(\delta_1 + \delta_2)/\Gamma_1} \cdot N_1 \right] = D \cdot \frac{\partial^2}{\partial x^2} \cdot N_1 \quad (43)$$

The first corresponds to isotherm non-linearity (eqn. 30) and the second to the sorption effect (eqn. 39), when linear terms of the isotherms are close (eqn. 38). The assumption (c) [here $|\delta_1 N_1| \ll \Gamma_1$ and $|\delta_1 + \delta_2| N_1 \ll \Gamma_1$] allows one to rewrite eqn. 43 in the form of eqn. 40. It is for this case that the result (ii) follows for appropriate values of the parameters. The assumptions above are known to be natural and easily realized for gas-liquid chromatography^{7,14}. Therefore, results (i) and (ii) are readily applicable to an explanation of experiments described elsewhere^{14,15}, where "shock-wave"-type elution curves (for $|R| \gg 1$) and asymmetry inconsistent with non-linear chromatography without a sorption effect were observed.

Now, it should be noted that the considerations in the last two sections essentially reduce to analysis of the Burgers-type equations. Therefore, the validity of our approximations has been adequately tested by means of computer simulation^{3,12,13}. For intermediate cases, which are not discussed in the previous section,

the vindications of our approach will have to await both computer and experimental verification.

APPENDIX

We turn now to the sorption effect when both solute and eluent adsorption are allowed. For the convenience of readers we derive here the expression for the mobile phase flow velocity, $u = u(N_1)$, in the sorption zone (see eqns. 1 and 32).

For the last stage of the chromatographic process, owing to the broadening of the elution zone, diffusion is expected to be of secondary importance in the equations of sorption dynamics⁸. Therefore, they can be rewritten in the form

$$\left. \begin{aligned} \frac{\partial}{\partial t} a_1(N_1) + \frac{\partial}{\partial x} (uN_1) &= 0 \\ \frac{\partial}{\partial t} a_2(N_2) + \frac{\partial}{\partial x} (uN_2) &= 0 \end{aligned} \right\} \text{(A1)}$$

where $a_1 = g_1(N_1)$ and $a_2 = g_2(N_2)$ are the distribution isotherms for the solute and eluent, respectively. The molar fractions of the latter satisfy eqn. 4, so from eqn. A1 one obtains

$$\frac{da_2}{dN_2} \cdot \frac{\partial}{\partial x} (uN_1) + \frac{da_1}{dN_1} \cdot \frac{\partial}{\partial x} (uN_2) = 0 \quad \text{(A2)}$$

Eqn. A2 is equivalent to the equation

$$(B - A) u \cdot \frac{\partial N_1}{\partial x} + (BN_1 + AN_2) \frac{\partial u}{\partial x} = 0$$

where

$$A = \frac{da_1}{dN_1} \quad \text{and} \quad B = \frac{da_2}{dN_2},$$

which can be easily integrated for $u = u(N_1)$ with initial condition $u_0 = u(N_1 = 0)$:

$$u = u_0 \exp \left(- \int_0^{N_1} dN_1 \cdot \frac{B - A}{BN_1 + AN_2} \right) \quad \text{(A3)}$$

As a consequence, one obtains eqn. 1 for linear isotherms and eqn. 32 for non-linear isotherms (eqn. 30).

LIST OF SYMBOLS

- a = convenient parameter in eqn. 16;
 a_1 = solute concentration in stationary phase (eqn. 30);
 b = convenient parameter in eqn. 16;

c	= convenient parameter in eqn. 16;
C	= convenient function in eqn. 8;
d	= convenient parameter in eqn. 16;
D	= effective longitudinal diffusion coefficient;
g_1	= solute concentration in stationary phase (eqn. 30);
f	= value of solute concentration at time $t = 0$;
F	= value of C at time $\tau = 0$;
k	= Γ_1 , Henry coefficient for solute (eqn. 33);
$k_i (i = 1,2)$	= mass distribution coefficients for solute and eluent;
$I_k (k = 1,2,3)$	= value of integrals (eqn. 25);
l	= convenient parameter in eqn. 33;
m	= convenient parameter in eqn. 33;
n	= convenient parameter in eqn. 33;
N_0	= amplitude of solute concentration for inlet band;
$N_i (i = 1,2)$	= concentration of solute and eluent in mobile phase;
Q	= convenient parameter in eqn. 18;
R	= convenient parameter in eqn. 18;
t	= time;
u_0	= mobile phase flow velocity in the absence of solute;
u	= mobile phase flow velocity;
x	= axial distance coordinate;
x_0	= width of inlet solute band (eqn. 14);
$\langle x \rangle$	= mean (first moment) of concentration-distance distribution;
Z	= convenient parameter in eqns. 20 and 22;
α	= $(1 - \Gamma_2/\Gamma_1)$, convenient parameter;
$\bar{\alpha}$	= convenient parameter in eqn. 37;
$\hat{\alpha}$	= convenient parameter in eqn. 41;
$\beta_i (i = 1,2)$	= parameters in expression for $\hat{\alpha}$;
Γ_i	= $\varepsilon + \mu k_i (i = 1,2)$ = Henry coefficients for solute and eluent;
Δ	= determinant (eqn. 34);
$\delta_i (i = 1,2)$	= isotherm non-linearity parameters;
ε	= column volume fraction for mobile phase;
μ	= column volume fraction for stationary phase;
ν	= $\Gamma_1 D/u_0^2$, convenient parameter in eqn. 11;
ξ	= moving reference frame;
σ^2	= second moment;
τ	= t , moving reference frame;
φ	= convenient function in Cole-Hopf transformation (eqn. 11);
φ_0	= $\varphi(0,0)$, initial value of φ ;
χ	= third moment.

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