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THE EFFECT OF SORPTION ON RETENTION TIMES IN NON-LINEAR CHROMATOGRAPHY

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SUMMARY

An approximate expression is derived to account for the effects of non-linearity, sorption, finite inlet width, mobile phase non-equilibrium and gas phase compressibility on retention times in gas chromatography.

INTRODUCTION

In a recent series of papers[1–4], the effect of a non-linear distribution isotherm

$$C_s = \varepsilon k_1 C + \varepsilon k_2 C^2 \tag{1}$$

on the lower statistical moments of chromatographic peaks has been evaluated. There is, however, another important effect which also manifests itself at higher solute concentrations, *viz.*, the increase in mobile phase velocity within the solute zone. This phenomenon is known in the literature as the sorption effect and the purpose of this paper is to show how it can be incorporated within the existing framework mentioned above.

THEORETICAL

In the basic partial differential equation considered in refs. 1–3:

$$\frac{\partial C}{\partial t} = -\frac{u}{(1+k_1)(1+\lambda C)} \cdot \frac{\partial C}{\partial z} + \frac{D_p}{(1+k_1)(1+\lambda C)} \cdot \frac{\partial^2 C}{\partial z^2} \tag{2}$$

u represented the carrier flow velocity and was considered to be constant throughout the column length. Actually, flow continuity requires that regions in which $k \neq 0$ should have a mobile phase flow velocity in excess of that in which no solute interchange with the stationary phase is taking place. In order to give a quantitative description to this effect, consider two regions at identical pressures, one within the solute zone and the other in a pure carrier region (Fig. 1).

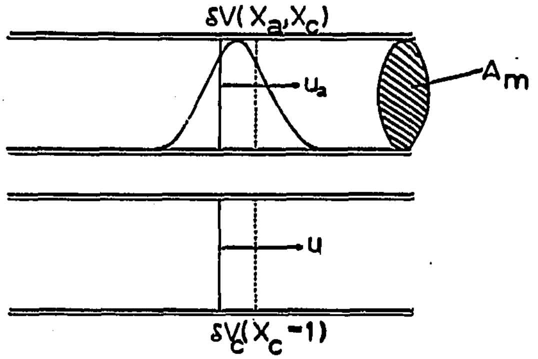

Fig. 1. Volume elements considered in model.

In a time δt, the pure carrier sweeps out a volume

$$\delta V_c = u \delta t A_m \tag{3}$$

while in the same time a section, containing X_a and X_c mole fractions of solute (a) and carrier (c), respectively, will sweep through a volume

$$\delta V = \delta V_a + \delta V_c^a \tag{4}$$

The volume associated with solute (δV_a) can be calculated by using the probability f_a of a solute molecule being in the mobile phase:

$$f_a = \frac{1}{(1+k_1)(1+\lambda C/2)} \tag{5}$$

Eqn. 5 follows from the distribution isotherm (eqn. 1) used in the non-linear chromatographic model (*e.g.*, ref. 1). As solute molecules constitute only a fraction X_a of the number of mobile phase molecules within this specific section, δV_a follows as

$$\delta V_a = \frac{X_a \delta t u_a A_m}{(1+k_1)(1+\lambda C/2)} \tag{6}$$

where ideal gas behaviour has been assumed. δV_c^a is simply given by

$$\delta V_c^a = X_c \delta t u_a A_m \tag{7}$$

Compressibility effects need not be considered at this stage so that a simple volume balance ($\delta V = \delta V_c$) yields the following relationship between u_a and u:

$$u_a = \frac{u}{1-\gamma' X_a} \tag{8}$$

where

$$\gamma' = 1 - \frac{1}{(1+k_1)(1+\lambda C/2)} \tag{9}$$

For $\lambda=0$, this result reduces to the existing expression for linear chromatography (*e.g.*, ref. 5).

For an ideal gas

$$X_a = \frac{CRT}{P} \tag{10}$$

so that

$$u_a = \frac{u}{1-\gamma C} \tag{11}$$

where

$$\gamma = \gamma' RT/P \tag{12}$$

and P is the local total pressure. (Gas phase imperfections could have been introduced at this stage via the virial coefficients —see, *e.g.*, Conder and Purnell[5].) The value of u_a given by eqn. 8 should be used in place of u in eqn. 2 if the latter equation is to describe the effects of sorption. Actually, D_p is also a function of the mobile phase flow velocity and a more exact description should include a corresponding flow correction. This is expected to be of secondary importance, however, and will not be considered in the present study.

When u in eqn. 2 is replaced by u_a, it follows that

$$\frac{\partial C}{\partial t} = -\frac{u}{(1+k_1)(1-\gamma C)(1+\lambda C)} \cdot \frac{\partial C}{\partial z} + \frac{D_p}{(1+k_1)(1+\lambda C)} \cdot \frac{\partial^2 C}{\partial z^2} \tag{13}$$

where the three factors in the coefficient of $\partial C/\partial z$, *viz.*, $\frac{1}{1+k_1}$, $\frac{1}{1-\gamma C}$ and $\frac{1}{1+\lambda C}$, represent the effects of linear partitioning, sorption and non-linearity, respectively. As γC is always smaller than unity and assuming that this also applies to λC, a binomial series expansion yields, in first order approximation,

$$\frac{\partial C}{\partial t} = -U\left[1-\left(\lambda - \frac{RTk_1}{P(1+k_1)}\right)C\right] \cdot \frac{\partial C}{\partial z} + D_e[1-\lambda C] \cdot \frac{\partial^2 C}{\partial z^2} \tag{14}$$

where

$$U = u/(1+k_1) \tag{15}$$

and

$$D_e = D_p/(1+k_1) \tag{16}$$

It therefore follows that the existing moment theory can be adapted to include sorption effects by simply substituting $\lambda - RTk_1/[P(1+k_1)]$ for λ in the appropriate velocity terms. For the first moment, it thus follows[1] that

$$\frac{\mathrm{d}\langle z\rangle}{\mathrm{d}t} = U - \frac{(\lambda C_i)m_i U}{2\sqrt{2}(1+4\pi D_e t/w_i^2)^{\frac{1}{2}} m_0} + \left[\frac{C_i RTk_1}{P(1+k_1)}\right] \cdot \frac{m_i U}{2\sqrt{2}(1+4\pi D_e t/w_i^2)^{\frac{1}{2}} m_0} - \frac{(\langle z\rangle - Ut)}{m_0} \cdot \frac{\mathrm{d}m_0}{\mathrm{d}t} \tag{17}$$

where the deviation due to sorption is clearly seen to be in the same direction as non-linear effects arising from $\lambda < 0$.

If it is assumed that $m_0 = m_l$, then

$$\frac{\mathrm{d}\langle z\rangle}{\mathrm{d}t} = U - \frac{(\lambda C_l)U}{2\sqrt{2}(1+4\pi D_e t/w_i^2)^{\frac{1}{2}}} + \left[\frac{C_l RTk_1}{P(1+k_1)}\right]\frac{U}{2\sqrt{2}(1+4\pi D_e t/w_i^2)^{\frac{1}{2}}} \tag{18}$$

Eqn. 18 can now be integrated and solved for t, where the retention time, t_R corresponds to $\langle z\rangle = l$. In the integration itself, the compressibility of the gas phase should be taken into account. This implies that U, P and D_e (via u) are written as functions of $\langle z\rangle$ by using Poiseuille's law and assuming ideal gas behaviour (see, *e.g.* ref. 6). The influence of the $\langle z\rangle$ dependence of k_1 is expected to be less pronounced and will not be investigated here. (For convenience $\langle z\rangle$ will from now on be replaced by z.) It then follows that

$$U = U(z) = \frac{u(z)}{1+k_1} = \frac{u_l}{(1+k_1)\left\{1 - \frac{z}{l}\left[\frac{p^2-1}{p^2}\right]\right\}^{\frac{1}{2}}} \tag{19}$$

$$P = P(z) = \frac{P_l u_l}{u(z)} = P_l\left\{1 - \frac{z}{l}\left[\frac{p^2-1}{p^2}\right]\right\}^{\frac{1}{2}} \tag{20}$$

and

$$D_e = D_e(z) = A + B_1 u(z) + B_2[u(z)]^2 + \ldots \tag{21}$$

where

$$p = P_l/P_o \tag{22}$$

To a good approximation, however, $P(z)$ and $D_e(z)$, which appear in correction terms, can be replaced by the mean total pressure[7]:

$$P_m = P_o J_2^3 \tag{23}$$

where

$$J_n^m = \frac{n}{m}\left[\frac{p^m-1}{p^n-1}\right] \tag{24}$$

and the effective diffusion coefficient in terms of the inlet velocity (*e.g.*, ref. 6), *i.e.*,

$$D_e = D_{el} = A + B_1 u_l + B_2 u_l^2 + \ldots \tag{25}$$

Eqn. 18, rearranged for integration, now becomes

$$(1+k_1)\int_0^l \frac{\mathrm{d}z}{u(z)} = \int_0^{t_R}\left\{1 - \frac{1}{2\sqrt{2}}\,Y\left[1 + \frac{t}{2B^2}\right]^{-\frac{1}{2}}\right\}\mathrm{d}t \tag{26}$$

where

$$Y = \lambda C_l - \frac{C_l RTk_1}{P_m(1+k_1)} \tag{27}$$

and

$$B = \frac{w_i}{2(2\pi D_{ei})^{\frac{1}{2}}} \tag{28}$$

Integration gives

$$\frac{l(1+k_1)}{u_i\, p} J_2^3 = t_R - \sqrt{2}B^2Y\left[\left(1+\frac{t_R}{2B^2}\right)^{\frac{1}{2}} - 1\right] \tag{29}$$

from which t_R follows as

$$t_R = \frac{l(1+k_1)}{u_o} J_2^3 - \sqrt{2}B^2Y + \tfrac{1}{2}B^2Y^2\left\{1+\left[1-\frac{4\sqrt{2}}{Y}+\left(\frac{l(1+k_1)}{u_o}J_2^3+2B^2\right)\frac{4}{B^2Y^2}\right]^{\frac{1}{2}}\right\} \tag{30}$$

where $u_i p$ has been replaced by u_o (assumption of ideal gas phase).

DISCUSSION

Eqn. 30 gives an expression for the retention time in which non-linearity, sorption, finite inlet width, non-equilibrium and gas phase compressibility have been taken into account within the limitations as defined by the model. In the case of the non-linear effects, these have been adequately tested by means of computer simulation and it remains to carry out a similar procedure for the phenomena associated with sorption in order to define the relative importance of the terms in the series expansions. Even then, conclusive vindication of the equation will have to await experimental verification.

Of the remaining effects that affect retention times, local temperature variations accompanying solute distribution, interaction between solute components and deviations from perfect gas phase behaviour, the first two promise to be the most formidable to describe theoretically. In particular, interaction between the components of the sample should receive attention. A framework for such a theoretical analysis has already been formulated by Helfferich and Klein[8] and it is hoped that the present methods will be of help in giving quantitative substance to this description.

LIST OF SYMBOLS

A = parameter in expression for D_e (eqn. 21)
A_m = cross-sectional area of the mobile phase
B = $w_i/[2(2\pi D_{ei})^{\frac{1}{2}}]$, a convenient parameter
B_1, B_2 = parameters in expression for D_e (eqn. 21)
C = solute concentration in mobile phase (with respect to mobile phase volume)
C_i = value of C at $t=0$ at the inlet
C_s = solute concentration in stationary phase (with respect to total column volume)
D_e = $D_p/(1+k_1)$
D_{ei} = D_e in terms of the inlet flow velocity (eqn. 25)
D_p = effective longitudinal diffusion coefficient in mobile phase
f_a = probability for a solute molecule to be in the mobile phase (eqn. 5)
$J_n{}^m$ = $\frac{n}{m}\left[\frac{p^m-1}{p^n-1}\right]$, convenient (compressibility) parameter
k = mass distribution coefficient (in general)
k_j = ($j=1,2$) parameters in non-linear distribution isotherm (eqn. 1)

l = column length
m_i = mass of solute per unit cross section of the mobile phase at the inlet at time $t=0$
m_0 = zeroth moment
p = P_i/P_o
P = local total pressure
P_i = pressure at the column inlet
P_o = pressure at the column outlet
P_m = mean total pressure (eqn. 23)
R = gas constant
t = time
δt = time interval
t_R = retention time (*i.e.*, t when $<z> = l$)
T = absolute temperature
u = mobile phase flow velocity in the absence of solute ($X_c = 1$)
u_a = mobile phase flow velocity in solute zone ($X_a \neq 0$)
u_i = carrier flow velocity at the column inlet
u_o = carrier flow velocity at the column outlet
U = $u/(1+k_1)$
δV = $\delta V_a + \delta V_c^a$, volume of mobile phase displaced in solute zone in time δt
δV_a = solute contribution to δV
δV_c^a = carrier contribution to δV
δV_c = volume of mobile phase displaced in time δt when no solute is present ($X_c = 1$)
w_i = width of plug inlet sample profile
X_a = mole fraction of solute
X_c = mole fraction of carrier
Y = convenient parameter (eqn. 27)
z = axial distance coordinate
$<z>$ = mean (first moment) of concentration-distance distribution
γ = $\gamma' RT/P$, convenient parameter
γ' = convenient parameter (eqn. 9)
ε = void fraction
λ = $2k_2/(1+k_1)$, non-linearity parameter.

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