A MATHEMATICAL TREATMENT OF NONEQUILIBRIUM CHROMATOGRAPHY

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INTRODUCTION

A considerable number of papers have been published on nonequilibrium gas chromatographic processes[1-5]. The solutions have been obtained both by the use of Laplace transforms[1] and by the perturbation methods[3,4]. The former method requires fairly complicated procedures involving inverse transforms and the solutions obtained are too complicated to compare directly with the experimental data. The latter method does not provide complete knowledge of the peak shape. A third method, the stochastic approach, is also applicable to this problem[6]. However, so far only the forward processes with definite transition probability have been considered, which corresponds to the omission of the diffusion term from the treatment. In the present paper the Mellin transform is used to obtain the moments of the distribution function[7]. From these the various statistical quantities are evaluated, thus providing information about the peak characteristics which can be easily compared with the experimental data.

THEORY

The basic equations and their transformations

The following equations are obtained from conservation of the species in the mobile and the stationary phase[1].

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - U \frac{\partial C}{\partial x} - \alpha \frac{\partial C^*}{\partial t} \tag{1}$$

$$\frac{\partial C^*}{\partial t} = kC - k^* C^* \tag{2}$$

where $C(x,t)$ is the concentration of the sample in the mobile phase, asterisks refer to the stationary phase**; α is the volume ratio, V^*/V, of the stationary and the mobile phase; k and k^* are rate constants of adsorption and desorption, respectively; and D and U are the diffusion constant and the linear velocity of carrier gas. The Mellin

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** In adsorption chromatography C^* ($= v_m\theta$) is the number of molecules adsorbed per unit volume of solid phase. C is the number of sample molecules in unit volume of gas phase.

transforms[8] of the distribution functions $C(x,t)$ and $C^*(x,t)$ in the two phases are defined for a "semi-infinite" column model as

$$g(s,x) = \int_0^\infty C(x,t)t^{s-1}\mathrm{d}t \tag{3}$$

$$g^*(s,x) = \int_0^\infty C^*(x,t)t^{s-1}\mathrm{d}t \tag{4}$$

When

$$C(x,t) \sim t^{-p} \text{ as } t \to \infty \; (p > s - 1)$$

and

$$C(x,t) \sim t^{-q} \text{ as } t \to 0 \quad (q < s - 1)$$

the transform* of the derivative of the distribution function is given by

$$g(s,x) \; (s,x) = \int_0^\infty \frac{\mathrm{d}C(x,t)}{\mathrm{d}t} t^{s-1}\mathrm{d}t = -(s-1)g(s-1,x) \tag{5}$$

Eqn. (5) is valid for $s = 1$ provided it is assumed that $c(x, 0) = 0$. Therefore, eqns. (1) and (2) are transformed into

$$D\frac{\mathrm{d}^2 g(s,x)}{\mathrm{d}x^2} - U\frac{\mathrm{d}g(s,x)}{\mathrm{d}x} = -(s-1)[g(s-1,x) + \alpha g^*(s-1,x)] \tag{6}$$

$$-(s-1)g^*(s-1,x) = kg(s,x) - k^*g^*(s,x) \tag{7}$$

Eqns. (6) and (7) are the recurrence equations from which $g(s,x)$ and $g^*(s,x)$ can be obtained from $g(s-1,x)$ and $g^*(s-1,x)$. Eqn. (7) is transformed into eqn. (8).

$$g^*(s,x) = \left(\frac{k}{k^*}\right)g(s,x) + \frac{(s-1)}{k^*}\left(\frac{k}{k^*}\right)g(s-1,x) +$$

$$+ \frac{(s-1)}{k^*}\frac{(s-2)}{k^*}\frac{k}{k^*}g(s-2,x) + \cdots \tag{8}$$

It follows from eqn. (7) that

$$g^*(1,x)/g(1,x) = \int_0^\infty C^*(x,t)\mathrm{d}t \Big/ \int_0^\infty C(x,t)\mathrm{d}t = k/k^* \tag{9}$$

The total amount of the sample which passes through any unit column cross-section will be equated to U.

$$U g(1,x) = \int_0^\infty U C(x,t) \, \mathrm{d}t = U \tag{10}$$

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* p and q define strips $q + n < s < p + n$ in which the Mellin transform of the function and its derivatives (of order n) exist.

It is also assumed that sample imput is in the form of a pulse which reaches the steady state concentrations in both phases instantaneously. The condition is given by the following equations.
When $x = 0$,

$$C(0,t) = \delta(t) \tag{11}$$

and

$$C^*(0,t) = \delta(t)\, k/k^* \tag{12}$$

where $\delta(t)$ is delta function defined between zero and infinity.

Solutions

The solution of eqn. (6) is

$$g(s,x) = -(s-1)\int_0^x \exp\left(\frac{Ux}{D}\right)\left[\frac{1}{D}\int_0^x \{g(s-1,x) + \alpha g^*(s-1,x)\} \exp\left(\frac{-Ux}{D}\right) \mathrm{d}x + \right.$$

$$\left. + (C_1)_s\right]\mathrm{d}x + (C_2)_s \tag{13}$$

where $(C_1)_s$ and $(C_2)_s$ are the integration constants. Since the moments $g(s-1,x)$ and $g^*(s-1,x)$ are algebraic functions of x, and tend to zero at $x = 0$, integration by parts is used to obtain the recurrence equation, and thus the higher moments can be obtained successively:

$$g(s,x) = \frac{(s-1)}{U}\left[\sum_{r=0}^{s-1}\left(\frac{D}{U}\right)^r \frac{\mathrm{d}^{r-1}}{\mathrm{d}x^{r-1}}\{A(x)\}\right]_0^x \tag{14}$$

where $(\mathrm{d}/\mathrm{d}x)^{-1}$ means integration and

$$A(x) = \left\{1 + \left(\frac{\alpha k}{k^*}\right)\right\}g(s-1,x) + \frac{(s-2)}{k^*}\left(\frac{\alpha k}{k^*}\right)g(s-2,x) + $$

$$+ \frac{(s-2)}{k^*}\frac{(s-3)}{k^*}\frac{\alpha k}{k^*}g(s-3,x) + \cdots \tag{15}$$

$g(1,x)$ and $g^*(1,x)$ are obtained by use of eqns. (9) and (10).

$$g(1,x) = 1 \tag{16}$$

and

$$g^*(1,x) = k/k^* \tag{17}$$

From eqns. (14) and (8), $g(2)$ and $g^*(2)$ are derived

$$g(2,x) = (x/U)\{1 + \alpha k/k^*\} \tag{18}$$

$$g^*(2,x) = (k/k^*)\{1/k^* + (1 + \alpha k/k^*)x/U\} \tag{19}$$

The retention time, t_r, is equal to the statistical mean value of time, $E\{t\}$,

$$t_r = E\{t\} = (g(2)/g(1))_{x=L} = \frac{\int_0^\infty tC(L,t)\mathrm{d}t}{\int_0^\infty C(L,t)\mathrm{d}t} = L(1 + \alpha k/k^*)/U \tag{20}$$

$$t^*_r = E\{t^*\} = (g^*(2)/g^*(1))_{x=L} = \frac{\int_0^\infty tC^*(L,t)\mathrm{d}t}{\int_0^\infty C^*(L,t)\mathrm{d}t} = L(1 + \alpha k/k^*)/U + 1/k^* \tag{21}$$

where L is the total length of the column. These equations show that t^*_r differs from t_r by the term $1/k^*$, which is the relaxation time of desorption; this term is negligibly small compared with the first term, so that the experimental retention time may be simply equated to $E\{t\}$.

$g(3)$ and $g(4)$ are similarly derived by use of eqns. (14), (20) and (21):

$$g(3,x) = \left(1 + \frac{\alpha k}{k^*}\right)\left(\frac{x^2}{U^2} + \frac{2Dx}{U^3}\right) + \frac{2x}{Uk^*(1 + k^*/\alpha k)} \tag{22}$$

$$g(4,x) = \left(1 + \frac{\alpha k}{k^*}\right)^2 \frac{x^3}{U^3} + \left(1 + \frac{\alpha k}{k^*}\right)^2 \frac{6Dx^2}{U^4} + \frac{6\alpha k}{k^{*2}} \frac{x^2}{U^2} +$$

$$+ \left(1 + \frac{\alpha k}{k^*}\right)^2 \frac{12D^2x}{U^5} + \frac{12Dx}{U^3} \frac{\alpha k}{k^{*2}} + \frac{6}{Uk^{*2}} \frac{\alpha k}{k^*} \frac{x}{(1 + \alpha k/k^*)} \tag{23}$$

The standard deviation of the peak is expressed in terms of $g(1)$, $g(2)$ and $g(3)$, and is given by

$$\sigma^2\{t\} = [g(3,x) - g^2(2,x)]_{x=L}$$

$$= (1 + \alpha k/k^*)^2 \left(\frac{2LD}{U^3}\right) + \frac{2L\alpha k}{k^{*2}U} \tag{24}$$

The first and second term express, respectively, the broadening due to the axial diffusion and to the nonequilibration resulting from the slow adsorption and desorption processes. The height equivalent of a theoretical plate, H, is then

$$H = \sigma^2 L/t_r^2 = 2D/U + 2U/\alpha k(1 + k^*/\alpha k)^2 \tag{25}$$

This expression is similar to the equation derived by VAN DEEMTER et al.[2] and by GIDDINGS[9], both derived using different procedures. If the second term is of an appreciable magnitude, the rates of desorption and adsorption can be evaluated from eqn. (25) either by varying the flow rate or by assuming a value from the diffusion broadening ($2D/U$) by analogy with a suitable standard.

The peak asymmetry is defined by skewness $\gamma_1\{t\}$, and is calculated from $g(1)$, $g(2)$, $g(3)$ and $g(4)$[10].

$$\gamma_1\{t\} = \mu_3/\sigma^3 = \frac{g(4) - 3g(2)g(3) + 2g^3(2)}{[g(3) - g^2(2)]^{3/2}} =$$

$$= \frac{12D^2L(1 + h^*/\alpha h)^2/U^5 + 12DL\alpha h/U^2h^{*2} + 6\alpha hL/Uh^{*3}}{(2DL(1 + h^*/\alpha h)^2/U^3 + 2L\alpha h/Uh^{*2})^{3/2}} \tag{25}$$

where μ_n is the n-th moment about median. $\gamma_1\{t\}$ is positive and proportional to the inverse square root of L, so that the peak shows tailing and this effect becomes smaller for longer columns. It is possible also to evaluate the moments of higher order as for example, excess, which is defined by $\gamma_2\{t\} = \mu_4/\sigma^4 - 3$.

Multiple adsorption sites

The foregoing discussion may be extended to the more complicated reaction mechanism, for example, to the case of multiple adsorption sites:

$$A_1 \rightleftharpoons A^*_1$$
$$A_1 \rightleftharpoons A^*_2$$
$$A_1 \rightleftharpoons A^*_3$$
$$\cdots\cdots\cdots$$
$$A_1 \rightleftharpoons A^*_n$$
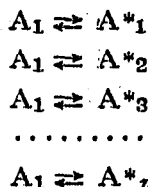
The basic equations for this reaction mechanism are given by

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} - U \frac{\partial C(x,t)}{\partial x} - \sum_{i=1}^{n} \alpha_i \frac{\partial C_i(x,t)}{\partial t}$$

$$\frac{\partial C^*_i(x,t)}{\partial t} = h_i C(x,t) - h^*_i C^*_i(x,t) \ (i = 1,2,3,\ldots n) \tag{27}$$

The transformed equations are as follows:

$$-(s - 1)g(s - 1,x) = D \frac{d^2 g(s,x)}{dx^2} - U \frac{dg(s,x)}{dx} + (s - 1) \sum_{i=1}^{n} \alpha_i g^*_i(s - 1,x)$$

$$-(s - 1)g^*_i(s - 1,x) = h_i g(s,x) - h^*_i g^*_i(s,x) \tag{28}$$

The moments $g(1,x)$, $g(2,x)$ and $g(3,x)$ are derived from the recurrence equation,

$$g(s,x) = \frac{(s - 1)}{U} \left[\sum_{r=0}^{s-1} \left(\frac{D}{U}\right)^r \frac{d^{r-1}}{dx^{r-1}} \{A_n(x)\} \right]_0^x \tag{29}$$

where

$$A_n(x) = \left\{ 1 + \sum_{i=1}^{n} (\alpha_i h_i/h^*_i) \right\} g(s - 1,x) + (s - 2) \sum_{i=1}^{n} (\alpha_i h_i/h_i^{*2}) g(s - 2,x) + \cdots$$

Thus,

$$g(1,x) = 1/(1 + \sum_{i=1}^{n} (\alpha_i h_i/h^*_i)) \tag{30}$$

$$g(2,x) = x/U \tag{31}$$

$$g(3,x) = (1 + \sum (\alpha_i k_i / k^*_i)) \left(\frac{x^2}{U^2} + \frac{2Dx}{U^3} \right) + \frac{2x \sum (\alpha_i k_i / k_i^{*2})}{U(1 + \sum (\alpha_i k_i / k^*_i))} \tag{32}$$

The expressions for the retention time and the height equivalent to a theoretical plate are then

$$t_r = E\{t\} = L(1 + \sum (\alpha_i k_i / k^*_i))/U \tag{33}$$

$$H = \sigma^2 L / t_r^2 = 2D/U + 2U \sum (\alpha_i k_i / k_i^{*2}) / (1 + \sum (\alpha_i k_i / k^*_i))^2 \tag{34}$$

With a slightly different definition of k_i, this equation is reduced to the corresponding GIDDINGS expression[3,4,9].

In recent studies of the electron donor–acceptor complexes of olefins using the gas chromatographic technique, peak broadenings due to nonequilibration have been observed[11,12] and use has been made of eqns. (33) and (34) to interpret the data[13]. The present method is not limited to chromatography, but may be applied to the other zone-separating processes.

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SUMMARY

A nonequilibrium chromatographic process has been analyzed mathematically using Mellin transforms. The peak characteristics, i.e. retention time, peak width, peak asymmetry and deviation from the Gaussian distribution are expressed in terms of the mean, variance, skewness and excess of the distribution function. The rates of the desorption and adsorption processes can be evaluated from the statistical quantities. The theory has also been applied to the adsorption on multiple sites.

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