THE ADDITIVITY OF RATE AND DIFFUSION PHENOMENA IN CONTINUOUS CHROMATOGRAPHY

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In a recent analysis[1] it has been possible to treat the fairly general problem of pulse-input chromatography with instantaneous equilibrium for linear and nonlinear isotherms, with and without axial dispersion; it had already been demonstrated[2,3] that the partial differential equations of continuous chromatography were very difficult to solve for the case of a finite rate of exchange and that even when analytical solutions are found they are much too complicated for use in correlating experimental data from actual chromatographic columns. While such analytical solutions are of mathematical interest they do not resolve the major problem of the experimental chromatographer who would much rather have a fundamental picture of the way in which finite rate phenomena and axial dispersion can influence elution time and band broadening. To quote GOLDSTEIN[4], who discusses equilibrium theory as a limiting case of kinetic theory, "what is needed, in addition to experimental work to determine the exchange equations, is a method for obtaining a closer approximation to the kinetic theory than is provided by the equilibrium theory without solving the kinetic theory equations in full. It will clearly be useful to do this first for a single solute." It is the purpose of the present communication to develop an approximate model for finite rate phenomena as a perturbation on equilibrium theory such that a useful working knowledge can be evolved of the way in which finite rate phenomena and axial dispersion can influence chromatography. In effect, the present analysis clearly defines the conditions under which dispersion and rate phenomena can be additive such that the final partial differential equation is the continuous rate theory analog of the plate approximation of VAN DEEMTER, ZUIDERWEG AND KLINKENBERG[5].

In the discussion that follows $C(t,z)$ denotes the moles of solute per unit volume of mobile phase, $n(t,z)$ the moles of solute taken up by unit volume of stationary phase, u the constant mobile phase velocity through the interstices, ε the void fraction, D the effective molecular diffusivity of the solute in the mobile phase accounting for the effect of the packing and K is the corresponding virtual coefficient of axial dispersion in the TAYLOR[6,7] sense. The concentration of solute in the mobile phase as a function of time t and axial position z is then given by[1,2]:

$$\frac{\partial C}{\partial t} + u\,\frac{\partial C}{\partial z} = (D + K)\,\frac{\partial^2 C}{\partial z^2} - \frac{1}{\varepsilon}\,\frac{\partial n}{\partial t} \tag{1}$$

In effect the use of equation (1) presumes that there are no radial concentration gradients within the interstices of the stationary phase so that in the TAYLOR[7,8]

sense this means that dispersion terms of order $(K^2/u)\partial^3 C/\partial z^3$ and higher have been neglected. The derivative $(1/\varepsilon)\partial n/\partial t$ represents the exchange of solute between the mobile and stationary phases, so that by assuming a finite rate with a linear isotherm:

$$\frac{\partial n}{\partial t} = k_A C - k_D n \tag{2}$$

where k_A and k_D are the rate constants for absorption and desorption respectively. Equation (2) can then be rearranged into the more convenient form:

$$\frac{1}{k_D} \frac{\partial n}{\partial t} = kC - n \tag{3}$$

where $k = k_A/k_D$ is the equilibrium constant for the linear isotherm. It is clear from eqn. (2) that if $k_D \to \infty$ and $\partial n/\partial t$ is finite as required by eqn. (1), then $n = kC$ and $\partial n/\partial t = k\partial C/\partial t$, corresponding to instantaneous equilibrium at each point in the column. However, small departures from equilibrium can be considered by permitting k_D to have a large, but finite, value when $\partial n/\partial t = k\partial C/\partial t$ may be considered to be the zeroth approximation to $\partial n/\partial t$ in eqn. (3), so that the next higher approximation for n becomes:

$$n = kC - \frac{k}{k_D} \frac{\partial C}{\partial t} \tag{4}$$

By repeating the above perturbation method, it is possible to generate the following infinite series for n:

$$n = k\left(C - \frac{1}{k_D} \frac{\partial C}{\partial t} - \frac{1}{k_D^2} \frac{\partial^2 C}{\partial t^2} - \cdots\right) \tag{5}$$

The most useful approximation for n is that obtained by truncating series (5) at the term of order $1/k_D$, corresponding to expression (4), Thus, substituting eqn. (4) for n into partial differential equation (1) and redefining the coefficients, we obtain

$$\frac{\partial C}{\partial t} + U \frac{\partial C}{\partial z} = (D_c + K_c) \frac{\partial^2 C}{\partial z^2} + R_c \frac{\partial^2 C}{\partial t^2} \tag{6}$$

where:

$$U = u/(1 + k/\varepsilon)$$
$$D_c = D/(1 + k/\varepsilon)$$
$$K_c = K/(1 + k/\varepsilon)$$
$$R_c = k/k_D \, \varepsilon(1 + k/\varepsilon)$$

It is clear from eqn. (6) that the effects of diffusion and a finite rate can be made additive if

$$\frac{\partial^2}{\partial t^2} = U^2 \frac{\partial^2}{\partial z^2} \tag{7}$$

when eqn. (6) reduces to the following simple form:

$$\frac{\partial C}{\partial t} + U \frac{\partial C}{\partial z} = (D_c + K_c + U^2 R_c) \frac{\partial^2 C}{\partial z^2} \tag{8}$$

Differential eqn. (8) can be further reduced to the form of the parabolic diffusion law by the change of variable $\xi = z - Ut$, when

$$\frac{\partial C}{\partial t} = E_c \frac{\partial^2 C}{\partial \xi^2} \tag{9}$$

where $E_c = D_c + K_c + U^2 R_c$. Equation (9) may now be used to analyze experimental chromatography data in the manner discussed by HOUGHTON[1]. The solution to eqn. (9) for an initial pulse of length L_0 centered around $z = 0$ and containing a solute of concentration C_0 is

$$\frac{C}{C_0} = \tfrac{1}{2} \operatorname{erf}\left(\frac{\xi + \tfrac{1}{2} L_0}{2\sqrt{E_c t}}\right) - \tfrac{1}{2} \operatorname{erf}\left(\frac{\xi - \tfrac{1}{2} L_0}{2\sqrt{E_c t}}\right) \tag{10}$$

It is now appropriate to discuss the conditions under which rate and diffusion phenomena are additive, as in eqns. (8) and (9):

(1) Necessary but not sufficient conditions for an additive law are (a) a linear equilibrium isotherm, (b) the absence of appreciable radial gradients of concentration in the interstices so that dispersion terms of order $(K^2/u)\partial^3 C/\partial z^3$ or higher may be neglected, and (c) the existence of only small deviations from instantaneous equilibrium, corresponding to the neglect of rate terms of order $(1/k_D^2)\partial^3 C/\partial t^3$ and higher. In addition to the above three requirements, the experimental conditions must be such that at least one of the following three conditions is satisfied:

(2) As discussed above, small deviations from equilibrium require R_c to be small, so that if it is also presumed that D_c and K_c are small then the terms on the right of eqn. (6) can be considered negligible compared with those on the left, leading to the Lagrangian subsidiary equation

$$\left(\frac{\partial}{\partial t} + U \frac{\partial}{\partial z}\right) C = 0 \tag{11}$$

Relationship (7) between the distance and time operators follows immediately from degenerate eqn. (11). The assumption of small values of D_c, K_c and R_c corresponds to the case treated by VAN DEEMTER et al.[5], who demonstrated additivity for the plate theory using the solution of LAPIDUS AND AMUNDSON[2].

(3) It is not necessary, however, to assume that D_c and K_c are small if the initial pulse width L_0 is small enough, since the solutions for small R_c will still be of the form (10), when it is readily observed that values of $[\xi]$ leading to appreciable ratios C/C_0 must be of order $L_0/2$; thus as $L_0 \to 0$ then $z \to Ut$, leading again to relationship (7) and solution (10).

(4) Since solutions for small R_c will be of the form (10), it is clear that the first time derivative, $\partial C/\partial t$, will decrease as $t^{-\frac{1}{2}}$ while $\partial^2 C/\partial t^2$ will decay as $t^{-\frac{3}{2}}$; similarly $\partial C/\partial z$ will decrease as $t^{-\frac{1}{2}}$ and $\partial^2 C/\partial z^2$ as t^{-1}. Thus as $t \to \infty$ the terms on the right of eqn. (6) will again become negligible in comparison with first derivatives on the left, because the second derivatives decay to zero faster than the first derivatives. Thus the additive eqns. (8) and (9) will become asymptotically valid at large times approaching infinity.

Under the above restrictions the effects of diffusion and rate phenomena are additive in that, to a first approximation, they both cause band broadening without affecting the elution time.

SUMMARY

By considering a finite rate of exchange between the mobile and stationary phases as a perturbation on equilibrium theory, it has been possible to arrive at conditions for the additivity of rate and diffusion phenomena in continuous chromatography. The resulting diffusion equation and its solution for a pulse input provide an alternative method to the plate theory for the treatment of experimental chromatography data.

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