

THEORY OF SORPTION CHROMATOGRAPHY

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In previous articles¹⁻³ the theory of partition chromatography was developed, based on a diffusion model⁴. In the present article the treatment is extended to sorption chromatography by including sorption of solute in the stationary phase in the mechanism of the chromatographic process.

Symbols

A	= solute
B	= sorbent
k_1	= rate constant for sorption
k_2	= rate constant for desorption
f	= concentration of A in mobile phase
g	= concentration of A in stationary phase
h	= concentration of AB
c	= total concentration of B
D_1, D_2	= diffusion coefficients in mobile and stationary phase respectively
V_1, V_2	= volumes per interphase area of mobile and stationary phase respectively
γ	= partition coefficient (sorption excluded)
v	= translational velocity of the mobile phase
$f^{m_{ij}}$	= matrix element representing concentration of A
$h^{m_{ij}}$	= matrix element representing concentration of AB
τ	= duration of equilibration step
α	= $2 D_1 / \tau v^2$
β	= $1 / V_1$

The sorption process will be represented by the reaction formula



For the rate of this reaction we have

$$\frac{\partial h}{\partial t} = k_1(c - h)g - k_2h \quad (2)$$

The corresponding sorption isotherm, representing the situation at equilibrium, has the form

$$h = \frac{cg}{k_2/k_1 + g} \quad (3)$$

i.e. it is essentially the Langmuir sorption isotherm.

Introducing Eqn. (2) into the differential equations for partition chromatography (Eqns. (1) and (2) in ref. 3), the equations for sorption chromatography may be written down

$$\frac{\partial f}{\partial t} = D_1 \frac{\partial^2 f}{\partial x^2} - v \frac{\partial f}{\partial x} + \frac{2D_2}{V_1 V_2} (g - \gamma f) \quad (4)$$

$$\frac{\partial g}{\partial t} = D_2 \frac{\partial^2 g}{\partial x^2} - \frac{2D_2}{V_2^2} (g - \gamma f) - \frac{\partial h}{\partial t} \quad (5)$$

$$\frac{\partial h}{\partial t} = k_1(c - h)g - k_2 h \quad (6)$$

Here the sorbent B is considered to be distributed uniformly throughout the stationary phase. This case is perhaps best applicable to sorption in gels, *e.g.*, ion exchange resins. Then c may be considered to be the total volume concentration of the sorbing sites B in V_2 .

We may also consider the case of adsorption on a surface, as in conventional adsorption chromatography. Then the partition volume V_2 may be looked upon as an immobilized solvent film covering the adsorbing surface. In this case c refers to the surface concentration of adsorbing sites B. The mechanism of the chromatographic process is in this case governed by diffusion of solute into the immobile solvent film and the adsorption reaction at the underlying surface. Eqns. (4)–(6) are applicable to this case with a slight modification. In Eqn. (5) we must replace $\partial h/\partial t$ by $(1/V_2)(\partial h/\partial t)$ owing to the fact that h is a surface concentration.

If the film represented by V_2 is very thin, Eqns. (4)–(6) may be approximated by eliminating the variables associated with the partition phase V_2 . To perform this in a rigorous way we consider the material balance equation, derived from Eqns. (4)–(6)

$$\frac{\partial}{\partial t} (V_1 f + V_2 g + h) = V_1 D_1 \frac{\partial^2 f}{\partial x^2} - V_1 v \frac{\partial f}{\partial x} + V_2 D_2 \frac{\partial^2 g}{\partial x^2} \quad (7)$$

We observe that in the limit $V_2 = 0$ we have $g = \gamma f$, which follows from the nature of the diffusion model (Eqn. (1) in ref. 1). Hence, in the limit $V_2 = 0$ the balance equation becomes

$$\frac{\partial (V_1 f + h)}{\partial t} = V_1 D_1 \frac{\partial^2 f}{\partial x^2} - V_1 v \frac{\partial f}{\partial x} \quad (8)$$

and Eqn. (6) takes the form

$$\frac{\partial h}{\partial t} = k_1(c - h)\gamma f - k_2 h \quad (9)$$

From Eqn. (9) it follows that it is no longer necessary to retain the parameter γ , as it may be incorporated in k_1 . Hence we put $\gamma = 1$ and rewrite Eqns. (8) and (9) in the form

$$\frac{\partial f}{\partial t} + \frac{1}{V_1} \frac{\partial h}{\partial t} = D_1 \frac{\partial^2 f}{\partial x^2} - v \frac{\partial f}{\partial x} \quad (10)$$

$$\frac{\partial h}{\partial t} = k_1 (c - h) f - k_2 h \quad (11)$$

These are the equations for adsorption chromatography without lateral diffusion. However, the neglect of lateral diffusion seems not to be an essential limitation, as it may at least partially be compensated by adjusting the values of the rate constants k_1 and k_2 .

A direct analytical solution of the partial differential Eqns. (4)–(6) or (10) and (11) seems at present impossible. The moment method, which was successfully applied to partition chromatography³, is not directly applicable because the equations are nonlinear. However, a numerical treatment along the lines of the approach in ref. 2 for partition chromatography is possible. We will here give the details of the procedure in the case of Eqns. (10) and (11).

As before, the chromatographic column is divided into cells of equal width and the operation of the column is assumed to take place in discontinuous steps. The duration of a step is τ and during that time the solution in the mobile phase of a cell is allowed to exchange solute with the stationary phase of that cell (adsorption) and with solutions of the mobile phase in neighbouring cells (longitudinal diffusion). At the end of the step the solutions in each cell are instantaneously shifted one step to the adjacent cells and the equilibration process is repeated. The problem may be formulated as a simultaneous computation of two matrixes of order n , ($f^{m_{ij}}$) and ($h^{m_{ij}}$), where index i refers to the cell number and index j to the time (τ being taken as the time unit). The elements of the matrixes have to be computed from the following recursion formulae.

$$\begin{cases} f^0_{i+1,j+1} = f^{m_{ij}} + 1/2\alpha(f^{m_{i-1,j}} - 2f^{m_{ij}} + f^{m_{i+1,j}}) & i, j = 1, \dots \\ h^0_{i+1,j+1} = h^{m_{i+1,j}} & i, j = 0, \dots \end{cases} \quad (12)$$

$$\begin{cases} f^k_{i+1,j+1} = f^{k-1}_{i+1,j+1} - \beta \delta^k_{i+1,j+1} & i, j = 0, \dots \\ h^k_{i+1,j+1} = h^{k-1}_{i+1,j+1} + \delta^k_{i+1,j+1} & i, j = 0, \dots \end{cases} \quad (14)$$

$$\delta^k_{i+1,j+1} = \frac{\tau}{m} [k_1 f^{k-1}_{i+1,j+1} (c - h^{k-1}_{i+1,j+1}) - k_2 h^{k-1}_{i+1,j+1}] \quad (16)$$

In Eqns. (14)–(16) the index k may have the values $k = 1, \dots, m$.

Initial conditions are given by specifying the following elements in Eqns. (12)–(16)

$$f^0_{i1} \quad \text{for } i = 1, \dots, n$$

$$f^0_{1j} \quad j = 1, \dots, n$$

$$f^{m_{0j}} \quad j = 1, \dots, n - 1$$

$$h^{m_{i0}} \quad i = 1, \dots, n$$

The recursion formulae (12)–(16) may be understood in the following way. Eqns. (12) and (13) give the effect of longitudinal diffusion and translation. In Eqns. (14) and (15) the effect of adsorption has been incorporated and Eqn. (16) gives the concentration change resulting from adsorption. Owing to the nonlinearity of the rate equation a stepwise approach was adopted. The use of m steps in these equations means that the time interval τ is divided into m subintervals, during which the rate is constant. In order to preclude the appearance of negative concentrations and indeterminacy in the equations the following conditions must be satisfied

$$\beta k_1 \frac{\tau}{m} < \frac{1}{c}; \quad k_2 \frac{\tau}{m} < 1 \quad (17)$$

These relations impose upper limits on k_1 and k_2 for given values of τ and m . However, it is easy to verify from Eqns. (14)–(16) that even for values of k_1 and k_2 well below the admissible values in formulae (17), equilibrium is practically established in rather few steps. The value $m = 5$ is found to be sufficient for all practical purposes.

It is obvious that the more general formulae (4)–(6), and also cases with several solutes in competing sorption reactions may be handled by the same techniques. However, then rather extensive computational resources are required.

At present computations according to Eqns. (12)–(16) are in progress and will be presented in a later article.

SUMMARY

The earlier theory of partition chromatography by the author has been extended to sorption chromatography by incorporating a sorption term for solute interaction with the stationary phase of a chromatographic column. A procedure for the numerical solution of the problem is indicated.

REFERENCES

- 1 H. VINK, *J. Chromatog.*, 15 (1964) 488.
- 2 H. VINK, *J. Chromatog.*, 18 (1965) 25.
- 3 H. VINK, *J. Chromatog.*, 20 (1965) 305.
- 4 H. VINK, *Acta Chem. Scand.*, 18 (1964) 409.