

THEORY OF PARTITION CHROMATOGRAPHY. III.

HANS VINK

Institute of Physical Chemistry, University of Uppsala (Sweden)

(Received April 16th, 1965)

As a supplement to earlier work on the theory of partition chromatography^{1,2} the direct solution of the differential equations for steady state conditions is considered. Use is made of the method of moments, which has proved to be a powerful tool in the study of transport processes³⁻⁶.

Using the model in refs. 1, 2 for the chromatographic column and making minor changes in the notations, the differential equations for column operation are written in the form:

$$\frac{\partial f}{\partial t} = D_1 \frac{\partial^2 f}{\partial x^2} - v \frac{\partial f}{\partial x} + \frac{2D_2}{V_1 V_2} (g - \gamma f) \quad (1)$$

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

In this model the partition process is represented by the formula:

$$g - \gamma f = (g_0 - \gamma f_0) e^{-mt} \quad (3)$$

where:

$$m = \frac{2D_2}{V_2} \left(\frac{\gamma}{V_1} + \frac{1}{V_2} \right) \quad (4)$$

The symbols have the following meaning:

- f = concentration of solute in the mobile phase;
- g = concentration of solute in the stationary phase;
- v = translational velocity of the mobile phase;
- V_1, V_2 = volumes per interphase area of mobile and stationary phase, respectively;
- D_1, D_2 = diffusion coefficients in mobile and stationary phase, respectively;
- γ = partition coefficient.

DEFINITION OF MOMENTS

The problem is specified by considering a column of indefinite length containing a concentration peak of arbitrary form. The peak is localized in the sense that there are regions in the column on both sides of the peak where the concentration is zero. Taking two points a and b in these regions, on either side of the peak, the moments of the concentration distribution are defined as follows:

$$F_i = \int_a^b x^i f dx; \quad G_i = \int_a^b x^i g dx \quad (5)$$

The time derivatives of the moments take the form:

$$\dot{F}_i = \int_a^b x^i \frac{\partial f}{\partial t} dx, \quad \dot{G}_i = \int_a^b x^i \frac{\partial g}{\partial t} dx \quad (6)$$

To evaluate these derivatives eqns. (1) and (2) are substituted into (6). Restricting the treatment to the first three moments, we have to consider integrals of the following type:

$$\int_a^b x^i \frac{\partial f}{\partial x} dx = \int_a^b x^i f - i \int_a^b x^{i-1} f dx = \begin{cases} 0 & \text{for } i = 0 \\ -iF_{i-1} & \text{for } i = 1, 2 \end{cases} \quad (7)$$

$$\int_a^b x^i \frac{\partial^2 f}{\partial x^2} dx = \int_a^b x^i \frac{\partial f}{\partial x} - i \int_a^b x^{i-1} \frac{\partial f}{\partial x} dx = \begin{cases} 0 & \text{for } i = 0, 1 \\ i(i-1)F_{i-2} & \text{for } i = 2 \end{cases} \quad (8)$$

Zeroth moment

For the zeroth moment the following equations are obtained:

$$\dot{F}_0 = \frac{2D_2}{V_1 V_2} (G_0 - \gamma F_0) \quad (9)$$

$$\dot{G}_0 = -\frac{2D_2}{V_2^2} (G_0 - \gamma F_0) \quad (10)$$

These equations have a solution of the type of eqn. (3).

$$G_0 - \gamma F_0 = (G_0 - \gamma F_0)_0 e^{-mt} \quad (11)$$

Substituting (11) into (9) and (10), the latter equations may be integrated and we get:

$$F_0 = K_0 + a e^{-mt} \quad (12)$$

$$G_0 = L_0 + b e^{-mt} \quad (13)$$

Here a and b are constants and K_0 and L_0 designate the moments for steady state conditions. They obviously satisfy the relation:

$$L_0 - \gamma K_0 = 0 \quad (14)$$

First moment

For the first moment we get the equations:

$$\dot{F}_1 = vF_0 + \frac{2D_2}{V_1 V_2} (G_1 - \gamma F_1) \quad (15)$$

$$\dot{G}_1 = -\frac{2D_2}{V_2^2} (G_1 - \gamma F_1) \quad (16)$$

These equations may be combined to:

$$\dot{G}_1 - \gamma \dot{F}_1 + m(G_1 - \gamma F_1) = -\gamma v F_0 \quad (17)$$

where m is defined by eqn. (4).

Substituting for F_0 from (12) and integrating we get:

$$G_1 - \gamma F_1 = -\frac{\gamma v K_0}{m} + (c_1 + c_2 t) e^{-mt} \quad (18)$$

Substitution into (15) and (16) and integration yields:

$$F_1 = K_1 + (d_1 + d_2 t) e^{-mt} \quad (19)$$

$$G_1 = L_1 + (e_1 + e_2 t) e^{-mt} \quad (20)$$

where d_1 , d_2 and e_1 , e_2 are constants and K_1 and L_1 are the steady state moments. We have:

$$L_1 - \gamma K_1 = -\frac{\gamma v K_0}{m} \quad (21)$$

and:

$$K_1 = \frac{2vD_0K_0}{mV_2^2} t + C' \quad (22)$$

where C' is the constant of integration.

Second moment

For the second moment we get:

$$\dot{F}_2 = 2D_1F_0 + 2vF_1 + \frac{2D_2}{V_1V_2} (G_2 - \gamma F_2) \quad (23)$$

$$\dot{G}_2 = 2D_2G_0 - \frac{2D_2}{V_2^2} (G_2 - \gamma F_2) \quad (24)$$

These equations may be combined to:

$$\dot{G}_2 - \gamma \dot{F}_2 + m(G_2 - \gamma F_2) = 2D_2G_0 - 2D_1\gamma F_0 - 2v\gamma F_1 \quad (25)$$

Substituting for F_0 , G_0 and F_1 from (12), (13) and (19), respectively, and integrating we get:

$$G_2 - \gamma F_2 = f_1 + f_2 t + (f_3 + f_4 t + f_5 t^2) e^{-mt} \quad (26)$$

where:

$$f_1 = \frac{4v^2\gamma D_2 K_0}{m^3 V_2^2} - \frac{2\gamma K_0}{m} (D_1 - D_2) - \frac{2v\gamma}{m} C' \quad (27)$$

$$f_2 = -\frac{4v^2\gamma D_2 K_0}{m^2 V_2^2} \quad (28)$$

and f_3 , f_4 and f_5 are constants.

Substituting (26) into (23) and (24) and integrating we get:

$$F_2 = K_2 + (g_1 + g_2t + g_3t^2) e^{-mt} \quad (29)$$

$$G_2 = L_2 + (h_1 + h_2t + h_3t^2) e^{-mt} \quad (30)$$

with g and h representing constants and K_2 and L_2 the steady state moments.

We have:

$$L_2 - \gamma K_2 = f_1 + f_2t \quad (31)$$

and:

$$K_2 = \frac{4v^2D_2^2K_0}{m^2V_2^4} t^2 + \left\{ 2D_1K_0 + \frac{4vD_2C'}{mV_2^2} + \frac{8v^2\gamma D_2^2K_0}{m^3V_1V_2^3} - \frac{4\gamma D_2(D_1 - D_2)K_0}{mV_1V_2} \right\} t + C'' \quad (32)$$

Denoting the variance corresponding to K_2 by μ_2 , we have:

$$\mu_2 = \frac{K_2}{K_0} - \frac{K_1^2}{K_0^2} \quad (33)$$

From (22), (32), (33) and (4) we get finally:

$$\mu_2 = \left\{ 2D_1 + \frac{v^2\gamma}{D_2V_1 \left(\frac{\gamma}{V_1} + \frac{1}{V_2} \right)^3} - \frac{2\gamma(D_1 - D_2)}{\gamma + \frac{V_1}{V_2}} \right\} t + C''' \quad (34)$$

A similar relation may be derived for the variance in the stationary phase.

CONCLUSIONS

The following conclusions may be drawn from the above solutions of the differential equations for steady state conditions.

The zeroth moment of concentration distribution represents the total solute concentration in a phase and is constant. Steady state conditions are attained exponentially according to:

$$e^{-mt} \quad (35)$$

The first moment determines the location of a peak and increases linearly with time. The relative peak velocity v has the value:

$$v = \frac{\dot{K}_1}{vK_0} = \frac{2D_2}{mV_2^2} = \frac{1}{1 + \frac{\gamma V_2}{V_1}} \quad (36)$$

The steady state conditions are established quasi-exponentially according to:

$$(d_1 + d_2t) e^{-mt} \quad (37)$$

The variance determines the peak spreading and increases linearly with time. It may be expressed in terms of a spreading coefficient D in the following way:

$$\mu_2 = 2Dt + \text{const.} \quad (38)$$

D can be expressed as:

$$D = D_1 + \frac{v^2\gamma}{2D_2V_1 \left(\frac{\gamma}{V_1} + \frac{1}{V_2}\right)^3} - \frac{\gamma(D_1 - D_2)}{\gamma + \frac{V_1}{V_2}} \quad (39)$$

Steady state is established quasi-exponentially according to:

$$(g_1 + g_2t + g_3t^2) e^{-mt} \quad (40)$$

SUMMARY

Steady state solutions of the differential equations for a partition chromatography column are derived for the first three moments of concentration distribution. Expressions for the peak velocity and spreading coefficient are obtained in terms of the characteristic parameters of column operation.

REFERENCES

- 1 H. VINK, *J. Chromatog.*, 15 (1964) 488.
- 2 H. VINK, *J. Chromatog.*, 18 (1965) 25.
- 3 S. LJUNGGREN, *Trans. Roy. Inst. Technol., Stockholm*, No. 142 (1959).
- 4 T. THEDÉN, *Trans. Roy. Inst. Technol., Stockholm*, No. 165 (1960).
- 5 H. VINK, *Nature*, 205 (1965) 73.
- 6 B. NAGEL, *Arkiv Matematik*, 5 (1965) 363.