CHAPTER 4

ADSORPTION MODEL

The adsorption of a gas mixture containing an adsorbable component and inert (weakly adsorbed) component, on a biporous adsorbent can be described by a four-step mechanism (see Fig. 4.1):

a) Diffusion from the main body of the gas phase to the external surface of the adsorbent particle, i.e. external diffusion.

b) Diffusion through the macropores of the solid, i.e. macropore diffusion.

c) Diffusion through the micropores of the solid, i.e. micropore diffusion.

d) Adsorption on the pore surface.

The following model is based on the following assumptions (7):

1) The temperature is uniform throughout the column.

2) There is negligible pressure drop so that the superficial velocity is constant.

3) The amount adsorbed is proportional to the gas phase concentration and independent of the fraction of the surface covered with the adsorbate. That is, the equilibrium relationship between adsorbed molecules and those in the gas phase is linear.

4) Gas flow in the column is plug flow with axial dispersions and concentration gradients in the radial direction in the gas phase are negligible.
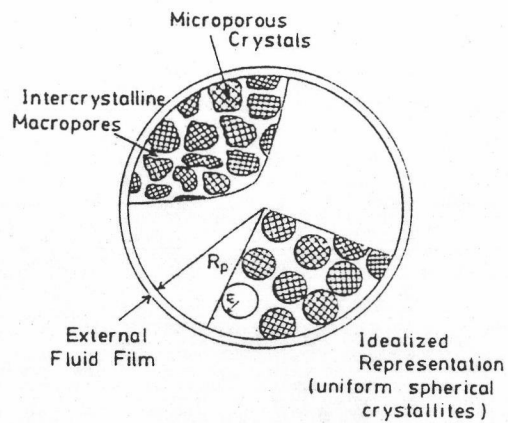
Fig. 4.1 Schematic diagram of composite adsorbent pellet showing the three principal resistances to mass transfer.
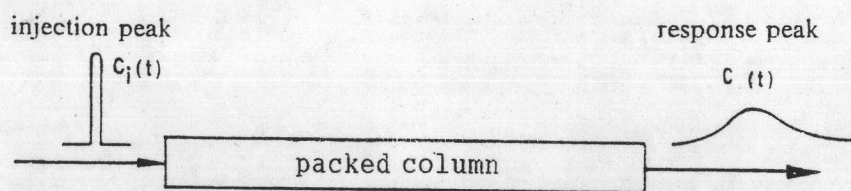

Fig. 4.2 Chromatographic experiment.

5) Adsorption on the walls of the macropores is neglected since the macropore surface is negligibly small compared to that within the zeolite crystallines.

6) The adsorption rate is extremely fast.

Under these conditions, the response of an adsorption column of length L (see Fig. 4.2), subjected to a pulse injection of sorbate at the inlet at time zero, may be described by the following set of equations (7):

Micropore diffusion:

$$D_c \left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial t} \right) = \frac{\partial q}{\partial t} \tag{4.1}$$

$$q(r_c, t) = K_c c(R, t) \tag{4.2}$$

$$\frac{\partial q}{\partial r} (o, t) = o \tag{4.3}$$

$$\overline{q} = \frac{3}{r_c{}^3} \int_o^{r_c} r^2 q \ dr \tag{4.4}$$

Macropore diffusion:

$$\theta D_p \left(\frac{\partial^2 c}{\partial R^2} + \frac{2}{R} \cdot \frac{\partial c}{\partial R} \right) = w(1 - \theta) \frac{\partial \overline{q}}{\partial t} + \theta \frac{\partial c}{\partial t} \tag{4.5}$$

$$\frac{3k_f}{R_p} [C(z, t) - c(R_p, t)] = \frac{\partial \overline{Q}}{\partial t} \tag{4.6}$$

$$\frac{\partial c}{\partial t} (o, t) = o \tag{4.7}$$

$$\overline{Q} = \frac{3w(1 - \theta)}{R_p{}^3} \int_o^{R_p} \overline{q} \ R^2 \cdot dr + \frac{3\theta}{R_p{}^3} \int_o^{R_p} cR^2 dR \tag{4.8}$$

External diffusion:

$$D_L \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \left(\frac{1-\epsilon}{\epsilon} \right) \frac{\partial \overline{Q}}{\partial t} = \frac{\partial C}{\partial t} \qquad (4.9)$$

$$C(z,o) = c(R,o) = q(r,o) = o \qquad (4.10)$$

$$C(o,t) = C_o \cdot \delta(t) \qquad (4.11)$$

$$C(\infty,t) = o \qquad (4.12)$$

The above set of equations were solved by Laplace transformation. To obtain the solution of the model equations in the Laplace domain is straightforward but inversion of the transform to obtain an analytic expression for the breakthrough curve or pulse response may, however, be derived rather easily directly from the solution in Laplace form by the application of van der Laan's theorem (17):

First moment

$$\mu \equiv \bar{t} \equiv \frac{\int_0^\infty ct\,dt}{\int_0^\infty c\,dt} = - \lim_{s \to 0} \frac{\partial \tilde{c}}{\partial s} \frac{1}{c_0} \qquad (4.13)$$

Second moment

$$\sigma^2 = \frac{\int_0^\infty c(t-\mu)^2 dt}{\int_0^\infty c\,dt} = \lim_{s \to 0} \frac{\partial^2 \tilde{c}}{\partial s^2} \left(\frac{1}{c_0} \right) - \mu^2 \qquad (4.14)$$

$$\tilde{c}(s) = \int_0^\infty \exp(-st) \cdot c(t)\,dt \qquad (4.15)$$

The first absolute moment, μ, characterizes the position of the center of gravity of the chromatographic curve, whereas the

second central moment, σ^2, represents the variance of the curve. By this method, the expressions for the first and second moments of the pulse response for the above model were obtained.

$$\mu = \frac{L}{v}\left\{ 1 + \left(\frac{1-\epsilon}{\epsilon}\right)K_p \right\} \tag{4.16}$$

$$\frac{\sigma^2}{2\mu^2} = \frac{D_L}{vL} + \left(\frac{v}{L}\right)\left(\frac{\epsilon}{1-\epsilon}\right)\left(\frac{R_p}{3k_f} + \frac{R_p^2}{15\theta D_p} + \frac{r_c^2}{15D_cK_p}\right) \tag{4.17}$$

$$K_p = \theta + w(1-\theta)K_c \tag{4.18}$$

and we have assumed $K_p \gg 1$.

Since experimental values of the first absolute and second central moments for the bed can be evaluated accurately from the observed effluent chromatographic peaks, Equations (4.16)-(4.18) provide the means for determining several of the rate parameters. The equilibrium adsorption constant, K_c, is calculated directly from the first moment. In order to obtain the time constant for zeolitic diffusion from the second moment, it is necessary to estimate the contributions arising from axial dispersion, external film, and macropore diffusional resistance. In the low Reynolds number regime $Sh = 2k_fR_p/D_m \sim 2.0$, so Equation (4.17) may be written

$$\frac{\sigma^2}{2\mu^2}\frac{L}{v} \approx \frac{D_L}{v^2} + \left(\frac{\epsilon}{1-\epsilon}\right)\left(\frac{R_p^2}{3D_m} + \frac{R_p^2}{15\theta D_p} + \frac{r_c^2}{15K_pD_c}\right) \tag{4.19}$$

It is evident that in this regime both the external mass transfer and macropore resistances are directly proportional to the square of the particle radius. The contribution of these terms may therefore be reduced to an insignificant level by using sufficiently small particles. Furthermore, in the low Reynolds number regime, the

axial dispersion coefficient becomes independent of particle size so variation of the particle size provides a convenient experimental test for the significance of external film and macropore diffusion resistances.

It follows from Equation (4.19) that within the low Reynolds number regime a plot of $(\sigma^2/2\mu^2)(L/v)$ versus $1/v^2$ should be linear with slope D_L and intercept corresponding to the total mass transfer resistance:

$$\frac{\epsilon}{(1-\epsilon)}\left(\frac{R_p^2}{3D_m} + \frac{R_p^2}{15\theta D_p} + \frac{r_c^2}{15K_pD_c}\right)$$

Such a plot provides a convenient way of separating the mass transfer and axial dispersion terms. If the experiments are repeated with two or more different particle sizes the individual values of the intracrystalline and macropore plus film time constants may be found.