

## Taylor Dispersion with adsorption at the ~~wall~~ wall

capillary wall provides the chromatographic effect

Chromatography allows for separation and identification of unknown/poorly known components of a sample. (unknown sample)

In macroscale process, a pulse of mixed solutes is injected into one end of a packed bed of adsorbent with continuation of the flow of solvent only.

The solutes are adsorbed to different degrees, and elute at different times.

In microfluidic device, instead of adsorbent beads forming a porous structure, the inner walls <sup>capillary</sup> are coated with adsorbent. Capillaries may be embedded in a monolith.

For a single capillary, the mass balance equation becomes

$$\frac{\partial q}{\partial t} = D \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial q}{\partial r} \right) + \frac{\partial^2 q}{\partial z^2} \right] - 2V_0 \left[ 1 - \left( \frac{r}{R_0} \right)^2 \right] \frac{\partial q}{\partial z}$$

axial

Axial diffusion is included

Boundary Conditions

$$t=0, \text{ for all } z, \quad C_1 = \frac{M}{\pi R_0^2} \delta(z)$$

$$t > 0, \text{ for } r=0, \quad \frac{\partial q}{\partial r} = 0$$

$$r=R_0, \quad C_1' = H C_1$$

$$D' \frac{\partial C_1'}{\partial r} = D \frac{\partial q}{\partial r}$$

$C_1' \equiv$  conc<sup>n</sup> of the solute in adsorbed layer.

$D' \equiv$  Diffusion coefficient of solute in the adsorbent layer.

$H$  is an equilibrium constant.

## Mass Balance within the adsorbent

The convection and the axial diffusion is not possible in the adsorbent

$\Rightarrow$  the mass balance equation becomes

$$\frac{\partial C_1'}{\partial t} = \frac{D'}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_1'}{\partial r} \right)$$

with corresponding boundary conditions as

$$\left. \begin{array}{l} t=0, \text{ for all } r, \quad C_1' = 0 \\ t > 0, \text{ for } r = R + \delta, \quad \frac{\partial C_1'}{\partial r} = 0 \end{array} \right\} \text{ Here } \delta \text{ is the thickness of the adsorbent layer.}$$

With assumption of thin adsorbed layer,

$$\bar{C}_1 \approx \frac{M / (\pi R_0^2)}{\sqrt{4\pi E_2 t_0}} e^{-\frac{(z - v_0 t_0)^2}{4 E_2 t_0}}$$

where  $t_0 = \frac{L}{v_0} (1 + k') =$  Average residence time of solute

$k' = \frac{H\delta}{R_0} =$  Equilibrium ratio of solute held in the adsorbent to that in the capillary itself.

$$\text{and } E_2 = D(1 + k') + \frac{R_0^2 v_0^2}{48D} \left[ \frac{1 + 6k' + 11(k')^2}{1 + k'} \right] + \frac{\delta^2 v_0^2}{3D'} \left[ \frac{k'}{1 + k'} \right]$$

# The significance of various terms in the expression for $E_2$

First term:  $D(1+k')$  arises from axial diffusion, which was not considered in original Taylor Dispersion.

Second term:  $\frac{R_0^2 v_0^2}{48D} \left[ \frac{1 + 6k' + 11(k')^2}{1+k'} \right]$  shows that smaller the radius and  $v_0$ , the dispersion would be less.

For 10 times smaller radius of capillary with velocity remaining unchanged, the dispersion will be reduced 100 times.

Third term:  $\frac{\delta^2 v_0^2}{3D'} \left[ \frac{k'}{1+k'} \right]$  reflects the retardation by the adsorbent layer.

For very fast diffusion in adsorbent, ( $D' \uparrow \uparrow$ ), or for very thin adsorbent layer ( $\frac{\delta}{R_0} \ll 1$ ), this component

will be least dominant. ~~when~~

$R_0 \downarrow$   $v_0 \downarrow$  for better identification.

When  $E_2 \rightarrow 0$ , each solute will elute as a sharp pulse (desirable).

For non-zero  $E_2$ , the solutes elute as broader pulse, and overlap of pulses will get the separation and identification compromised.