Chromatography theory

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Adsorption Equilibrium

The adsorption of a chemical species can be represented by the equilibrium reaction

$$C + S \xleftrightarrow{K_{eq}} CS \tag{1}$$

C : the dissolved chemical species

S : an adsorption site

CS : the chemical bound to the site

K_{eq} : the equilibrium constant governing the reaction

The equilibrium constant for this adsorption is

$$K_{eq} = \frac{[CS]}{[C][S]} \tag{2}$$

In many case, the concentration of adsorption sites is very much larger than the concentration of dissolved chemical species ($[S] \gg [C]$), and the equilibrium expression becomes

$$K_{eq} = \frac{[CS]}{[C]} \quad or \quad [CS] = K_{eq}[C] \tag{3}$$

This representation is particularly common in analytical liquid chromatography, where sample volumes are very small and solutes typically dilute.

This is known as *linear equilibrium.*

The linear isotherm approximation is less useful for preparative or industry scale adsorption and chromatography.

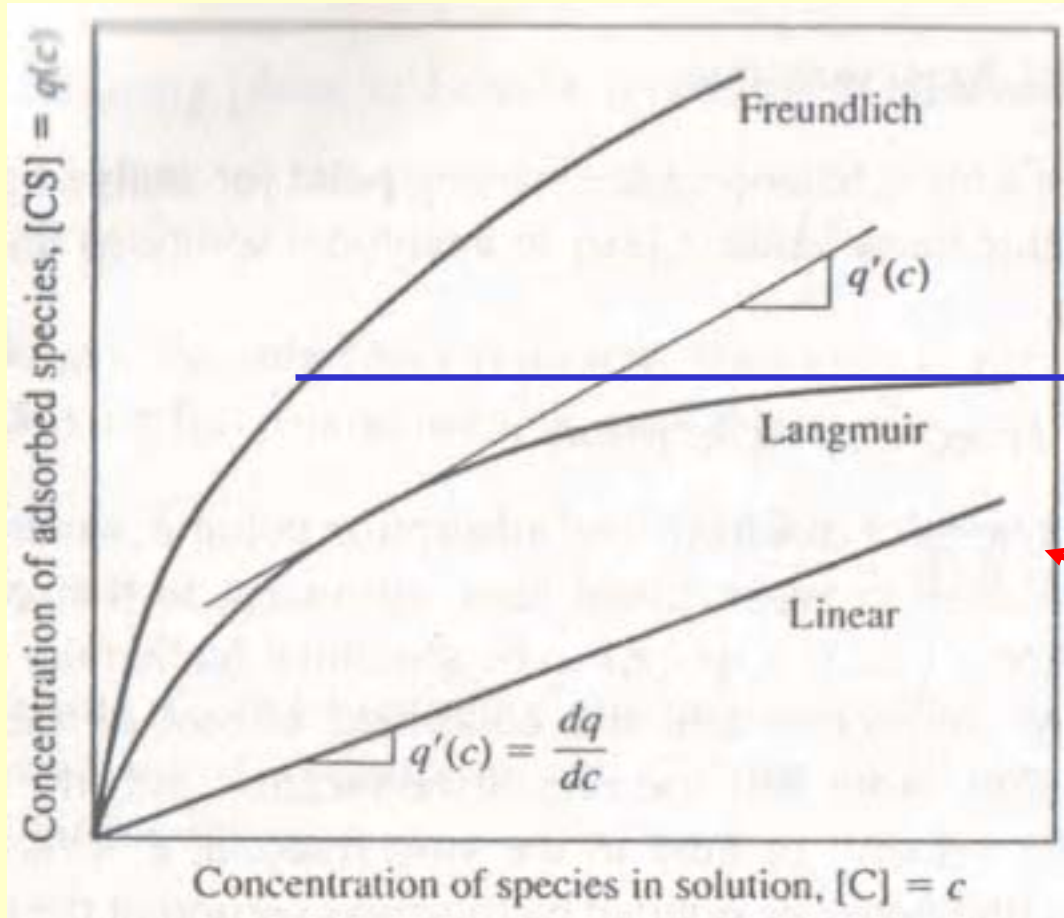The most efficient operation uses all the adsorption sites available.

In this case, the concentration of the empty adsorption sites available cannot be ignored.

$$S_{tot} = [CS] + [S] \qquad (4)$$

Combining eqs.(2) and (4), we can obtain equation(5).

$$[CS] = \frac{K_{eq} S_{tot} [C]}{1 + K_{eq} [C]} \tag{5}$$

This expression is the well-known *Langmuir isotherm.*

Figure 1. Shapes of different equilibrium adsorption isotherms.

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Adsorption Column Dynamics

Fixed-Bed Adsorption

Mass Balance

convection   diff./disp.   flow

C_0

Disk 1

Disk 2

Δx

Disk 3

Disk 4

Disk 5
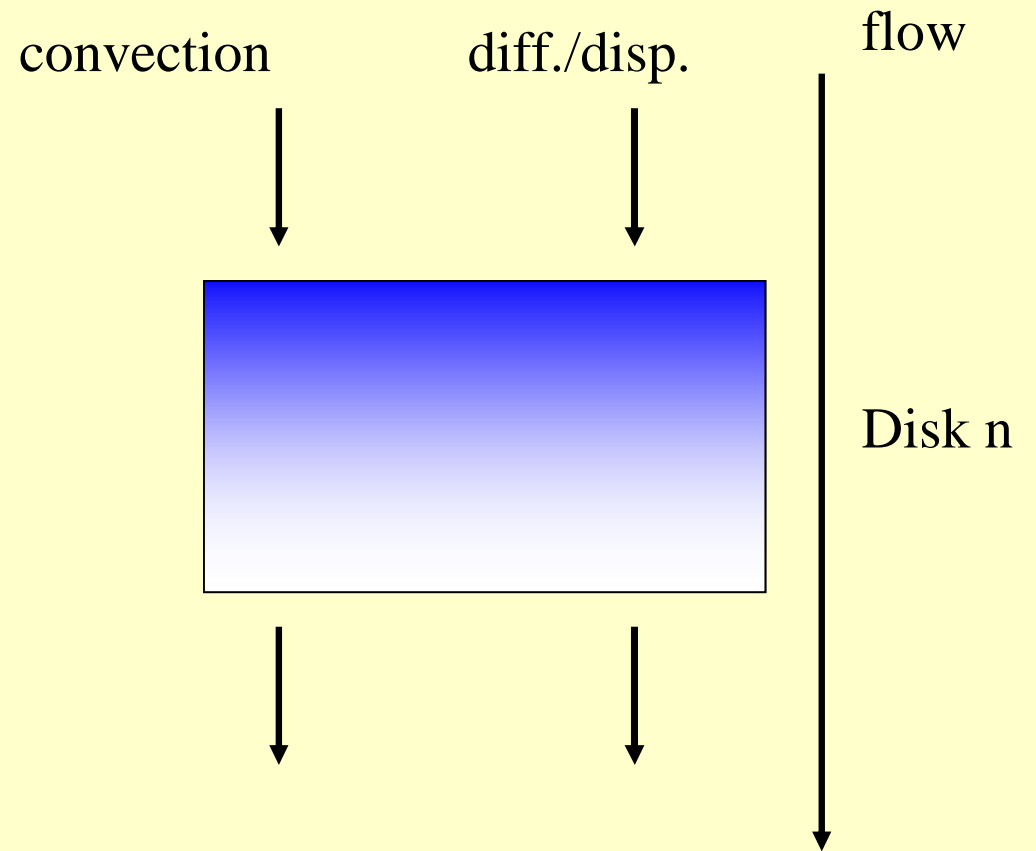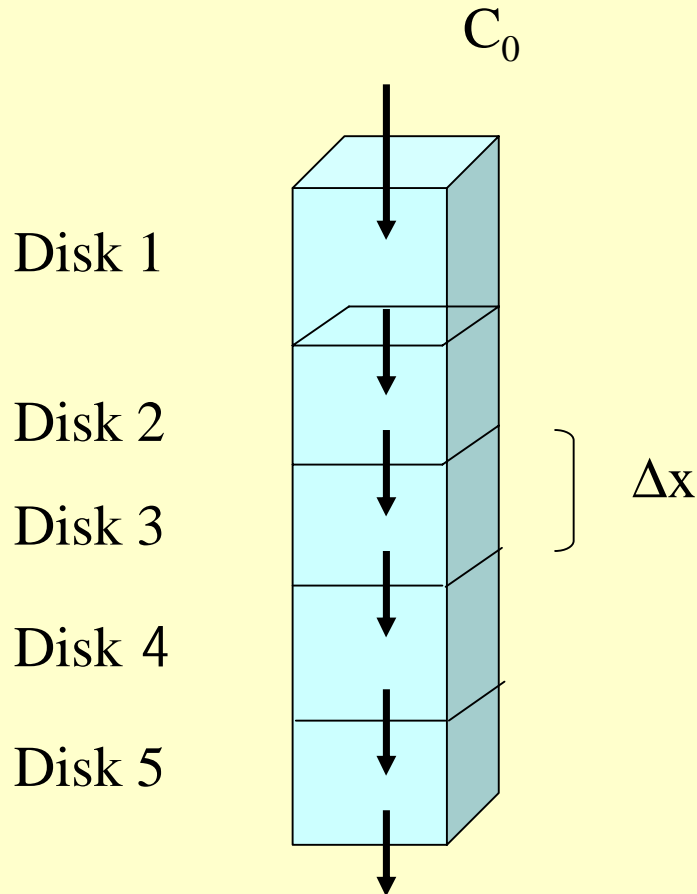
Disk n

(rate of disk n in) - (rate of disk n out)

= (rate of accumulation of disk n)

$$A\varepsilon\Delta t\left(\frac{v}{\varepsilon}c_i - D_{eff}\frac{\partial c_i}{\partial x}\right)\bigg|_{x,t} - A\varepsilon\Delta t\left(\frac{v}{\varepsilon}c_i - D_{eff}\frac{\partial c_i}{\partial x}\right)\bigg|_{x+\Delta x,t}$$

$$= A\varepsilon\Delta x\left(c_i\big|_{t+\Delta t} - c_i\big|_t\right) + A(1-\varepsilon)\Delta x\left(q_i\big|_{t+\Delta t} - q_i\big|_t\right) \qquad (6)$$

c_i = concentration of a species to be separated in the mobile phase=$[C]_i$

q_i = concentration of a species to be separated in the stationary phase

   averaged over an adsorption particle =$[CS]_i$

ε = void fraction

v = mobile phase superficial velocity (Q/A)

D_{eff} = effective dispersivity of a species to be separated in column

t = time

x = longitudinal distance in the column

Dividing by $A \varepsilon \triangle t \triangle x$, and $\triangle t \rightarrow 0$, $\triangle x \rightarrow 0$

This mass balance becomes

$$D_{eff} \frac{\partial^2 c_i}{\partial x^2} - \frac{v}{\varepsilon} \frac{\partial c_i}{\partial x} = \frac{\partial c_i}{\partial t} + \frac{1 - \varepsilon}{\varepsilon} \frac{\partial q_i}{\partial t} \tag{7}$$

The term $\partial q_i / \partial t$ can be represented in general as

$$\frac{\partial q_i}{\partial t} = f\left(c_i, c_j, \ldots\ldots, q_i, q_j, \ldots\ldots\right) \qquad (8)$$

This rate expression may be a linear driving force expression of the form

$$\frac{\partial q_i}{\partial t} = K_a\left(c_i - c_i^*\right) \qquad (9)$$

K_a : the mass transfer coefficient

c_i^* : the liquid phase concentration at equilibrium with q_i

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Assumption of Local Equilibrium and Negligible Dispersion

$$D_{eff} \frac{\partial^2 c_i}{\partial x^2} - \frac{v}{\varepsilon} \frac{\partial c_i}{\partial x} = \frac{\partial c_i}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \frac{\partial q_i}{\partial t} \qquad (10)$$

$$- \frac{v}{\varepsilon} \frac{\partial c_i}{\partial x} = \frac{\partial c_i}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \frac{\partial q_i}{\partial c_i} \frac{\partial c_i}{\partial t} \qquad (11)$$

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$$-\frac{v}{\varepsilon}\frac{\partial c_i}{\partial x} = \frac{\partial c_i}{\partial t} + \frac{(1-\varepsilon)q_i{'}}{\varepsilon}\frac{\partial c}{\partial t} \qquad (12)$$

$$-\frac{v}{\varepsilon}\frac{\partial c_i}{\partial x} = \left(1 + \frac{(1-\varepsilon)q_i{'}}{\varepsilon}\right)\frac{\partial c}{\partial t} \qquad (13)$$

$$-v\frac{\partial c_i}{\partial x} = \left(\varepsilon + (1-\varepsilon)q_i{'}\right)\frac{\partial c}{\partial t} \qquad (14)$$

$$\frac{\partial c}{\partial t} + \frac{v}{\varepsilon + (1-\varepsilon)q_i{'}}\frac{\partial c_i}{\partial x} = 0 \qquad (15)$$

$$u_i = \frac{v}{\varepsilon + (1-\varepsilon)q_i{'}} \qquad : \text{shock wave velocity}$$

$$(16)$$

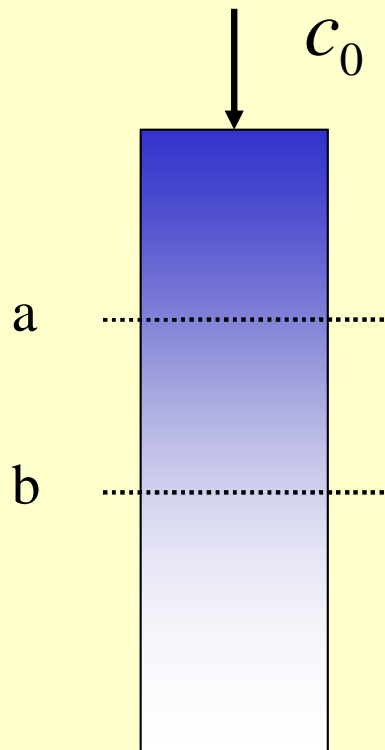$$\frac{\partial c}{\partial t} + u_i\frac{\partial c_i}{\partial x} = 0 \qquad (17)$$

u_i is a velocity of moving solute i .

The expression for u_i given by equation() is the *effective velocity* of component i through the packed bed.

Ex) shock wave

c_0

$$c_a > c_b$$

$$q_a^{'} < q_b^{'}$$

$$u_a > u_b$$

a

b

$\rightarrow$ Back concentration profile can't overtake forward concentration profile physically.