3.9.1 Theory of GPC

GPC separates based on MW and MWD.

HPLC separates based on functional groups such as protein and pharmaceutical polymers containing special active groups.

Various volumes on GPC columns

Void Volume (**V_o**) (Also called interstitial volume, exclusion volume); The volume of solvent (mobile phase) that is located between the packing particles.

Pore Volume (**V_i**) = Pore volume of all particles (Most critical).

Mobile Phase Volume (V_t): **V_t = V_o + V_i**

Gel Volume (**V_g**): Volume occupied by the solid support (gel)

Column volume (**V_c**): **V_c = V_o + V_i + V_g**

Retention Volume (Elution volume) (**V_R**):   **V_R = V_o + (K_d x V_i)**

K_d = **Distribution coefficient** = Ratio of average concentration of solute in the pore volume to that in the interstitial volume. **K_d** = $<c>_i$ /$<c>_o$

This is true if only size interactions are involved (no enthalpic interaction).

Tipically **V_o** ~ 35% of **V_c , V_g** ~ 20-30% of **V_c**

GPC and HPLC depend on the selective distribution of analyte in stationary and mobile phases characterized by distribution coefficient (K_d) defined by

$$K_d = \frac{V_R - V_i}{V} \quad (3.104)$$

V_R=Retention volume of solute

V_i=Interstitial volume of the column

V =Volume of the stationary phase

K_d is related to the Gibbs energy as

$$-RT\ln K_d = \Delta H - T\Delta S = \Delta G \qquad (3.105)$$

Rearranging yields

$$K_d = \exp\left(\frac{\Delta S}{R} - \frac{\Delta H}{RT}\right) \qquad (3.106)$$

Physically

$\Delta S<0$ due to the confinement of polymer chains in pores.

Limited dimension of pore relative to the polymer chain decreases ΔS.

$\Delta H<0$ (>0) if the wall and polymer chains are attractive (repulsive).

Interactions between the pore wall and polymer chain are given by ΔH.

In general K_d is expressed as

$$K_d = K_{GPC}K_{HPLC} \qquad (3.107)$$

K_{GPC}=Entropic interaction, K_{HPLC}=Enthalphic interaction

In the ideal GPC, K_{HPLC}=1, and K_d=K_{GPC} and then

$$K_d = \exp\left(\frac{\Delta S}{R}\right) \qquad (3.108)$$

The opposite is true for ideal HPLC.

Calibration of GPC is left for the students.

End of Ch 3.

Students are encouraged to drill the chapter end problems.