Separation Methods Based on Distributions in Discrete Stages (01/21/15)

1. Chemical Separations: The Big Picture

   Classification and comparison of methods

2. Fundamentals of Distribution Separations

3. Separation Methods Based on Distributions in Discrete Stages
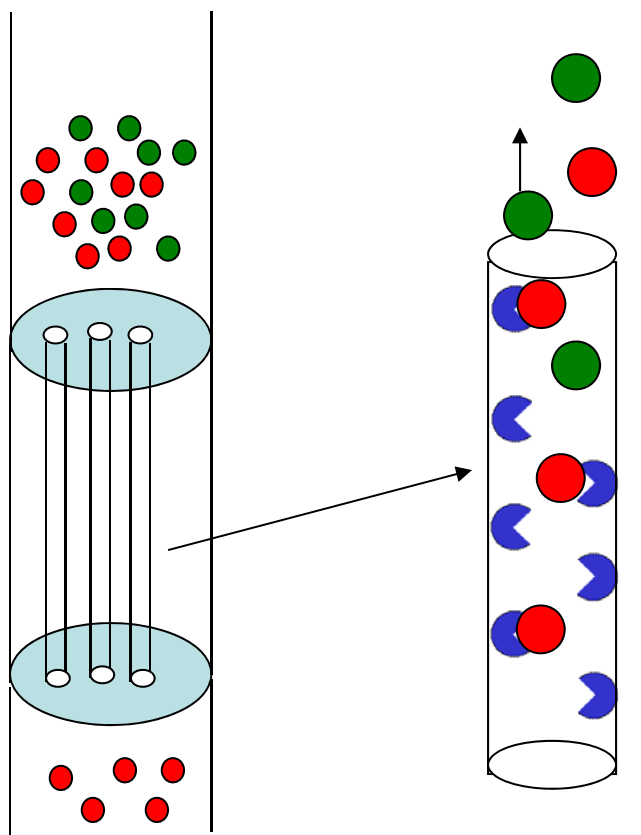
   Such as solvent extraction and distillation

4. Introduction to Distribution Separations in chromatographic

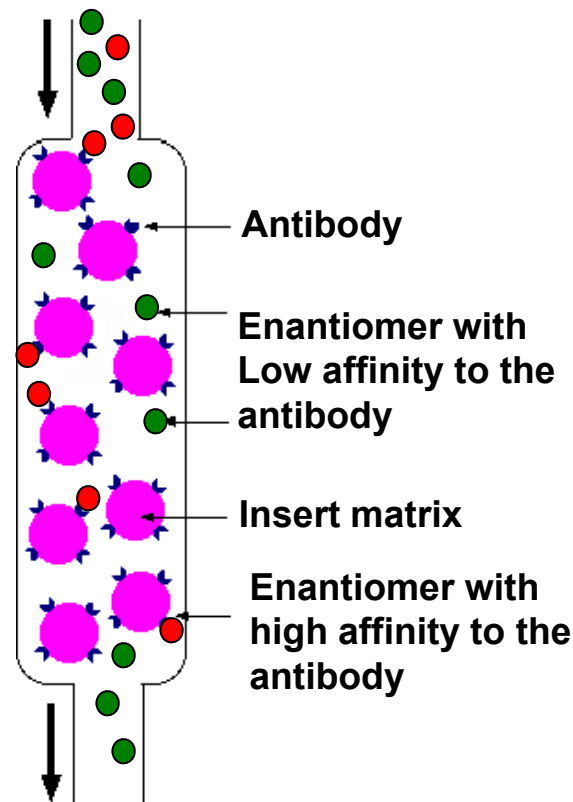   methods. The plate theory, the rate theory; van Deemter's equation.

Question: What Controls the Selectivity of Nanotubes?

Enantiomers

nanotube

Affinity

Antibody

Enantiomer with Low affinity to the antibody

Insert matrix

Enantiomer with high affinity to the antibody

Affinity Chromatography

1. Lakshmi, B.; Martin, C.R. "Enantioseparation Using Apoenzymes Immobilized in a Porous Polymeric Membrane," Nature, 1997, 388, 758-760.

*Why ?*

Entropy Effects in Phase Distribution

$$K = \exp\left(\frac{-\Delta\mu_i^0 - \Delta\mu_i^{ext}}{RT}\right) \quad \textit{distribution coefficient}$$

$$\Delta\mu_i^0 = \Delta\bar{H}_i^0 - T\Delta\bar{S}_i^0$$

(1) **The entropy change (ΔS_i^0)** relates to the way the solute molecule i fits into the liquid structure of two respective phases and the associated reorientation and repositioning of the liquid molecules.

(2) **In most separation cases**, the structural changes accompanying the arrival of a solute molecule are similar in different phases, and thus the entropy term is much smaller than the enthalpy term.

(3) **In the case of hydrophobic interaction**, the presence of non-polar intruder induces a semi-rigid structure in the surrounding water molecules, and leads to a significant reduction in entropy. In such case, the entropy change play a major role in influencing phase distribution.

Hydrophobic Interaction (entropy affects solubility)

Fatty acids have a hydrophilic head
and a hydrophobic tail.
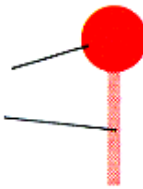
In water they can form a surface film
or form small micelles.
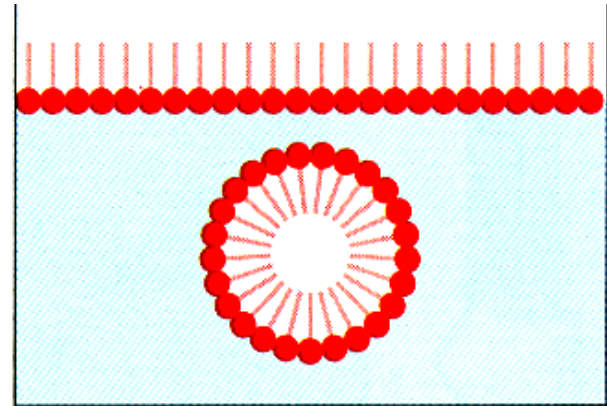
(4) The entropy term plays a significant role whenever one of the phase has ***Porous Media***, providing the mean pore diameter is of the same order of magnitudes as the diameter of the partitioning species.

<u>**Porous media used in separation field**</u> include various polymer gels, membranes, and chromatographic packing used for size exclusion chromatography (stationary phase).
<u>**The partitioning species**</u> involved are of macromolecular or colloidal size: protein, DNA, virus, synthetic polymers, inorganic colloids and may others.

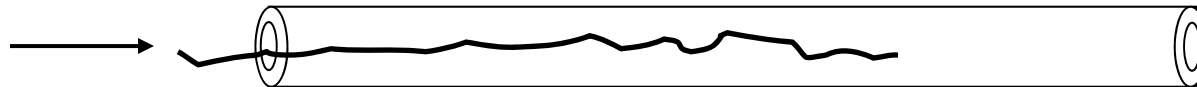# Entropy Effects in Phase Distribution: porous media

In the porous media, the motion of contained molecules are severely Restricted. The loss of freedom in molecular motion is associated with a corresponding loss of entropy.

Example:

Polymer
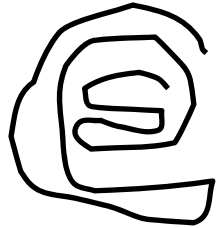
Pore media

When a linear polymer snake its way into a long thin pore,the polymer would lose the normal conformational entropy associated its bends and twists in space. The unfavorable entropy change leads to a rejection of this polymer from the pore.

Distribution coefficient in porous media

$$K = \frac{c_{i,pores}}{c_{i,bulk}}$$

Where, $c_{i,pores}$ is the amount of i per unit volume of pore space (not including the volume of the solid matrix), and $c_{i,bulk}$ is the concentration of bulk solution.

(1) the partitioning specie i is a sphere

Capillary tube   volume

a

d_c

L

$V = \pi\,(1/2*d_c)^2*L$

a

d_c

$V = \pi\,(1/2*d_c-a)^2*L$

i
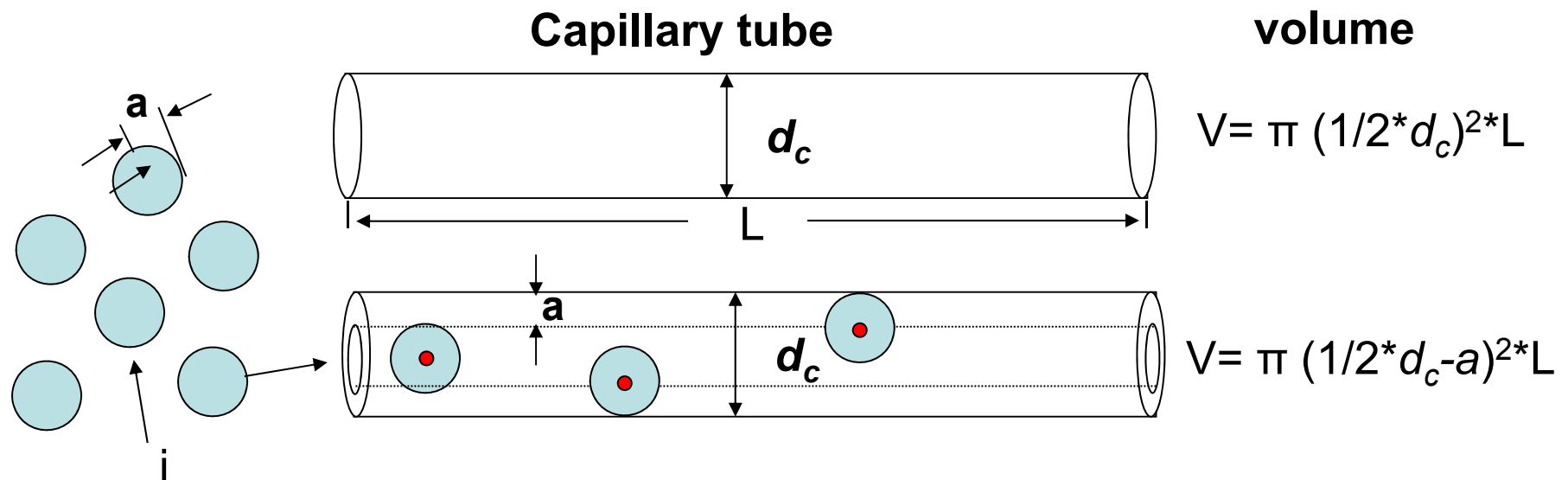
Distribution coefficient in porous media

When the absence of disturbing force, the distribution k is simply the volume ratio (A reduction in entropy naturally accompanies the the shrinkage in effective volume).

$$K = \frac{\text{accessible volume}}{\text{true volume}} = \frac{\pi \, (1/2*d_c - a)^2 * L}{\pi \, (1/2*d_c)^2 * L} = \left(1 - \frac{2a}{d_c}\right)^2$$

(This expression is valid for $2a < d_c$; $K = 0$ for $2a > d_c$)

If d_c is replaced by 4/s, where s is the wall area of the capillary per unit volume of the pore space, we get

$$K = \left(1 - \frac{sa}{2}\right)^2$$

RIGID-ROD MOLECULES   SPHERICAL MOLECULES

FLEXIBLE CHAINS
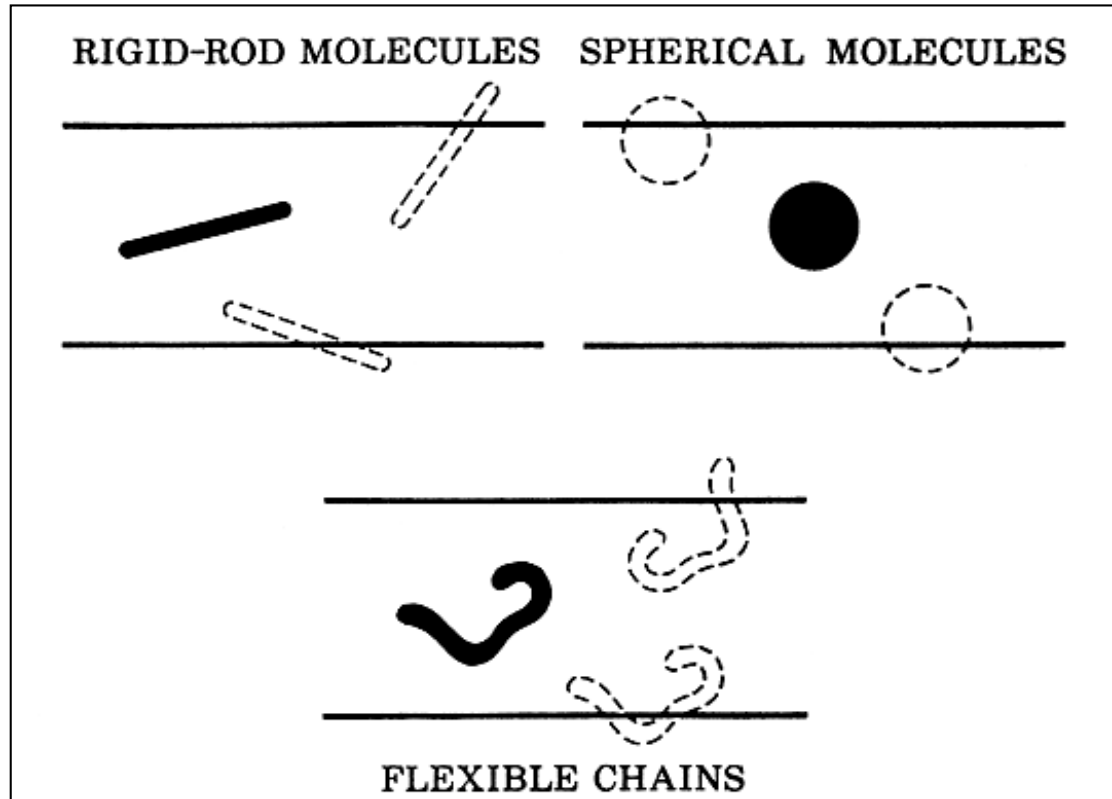
(2) the partitioning specie i with other shapes

The distribution coefficient K for such complex bodies can no longer be considered as a simple volume ratio. Instead, K becomes a ratio of volumes in multidimensional configuration space which all possible positions, orientations, and conformations must be considered. For the random-plane model of pole space,

$$K = \exp\left(-\frac{s\bar{L}}{2}\right)$$

Where, $\bar{L}$ is the mean external length (or mean projection length)

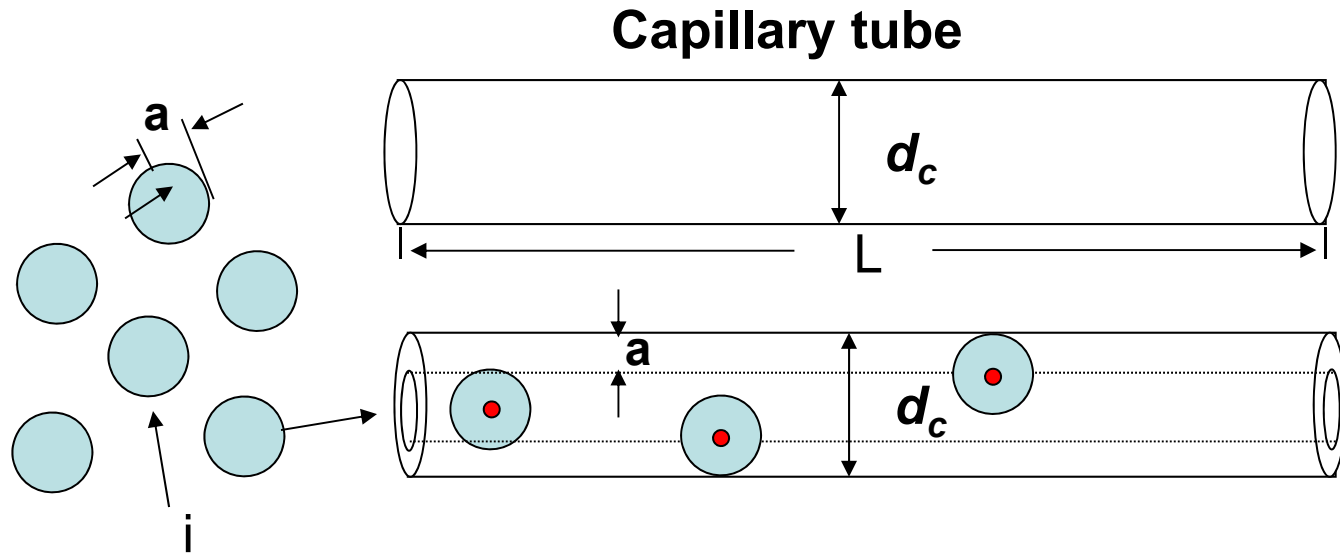$$K = \exp\left(-\frac{s\bar{L}}{2}\right) \qquad K = \frac{C_{i,pores}}{C_{i,bulk}}$$

Where, L is the mean external length (or mean projection length)

For spheres, $\bar{L} = 2\,a$, then we get

$$K = \exp(-sa) = 1 - sa + (sa)^2/2 + \ldots.(-sa)^n/n!$$

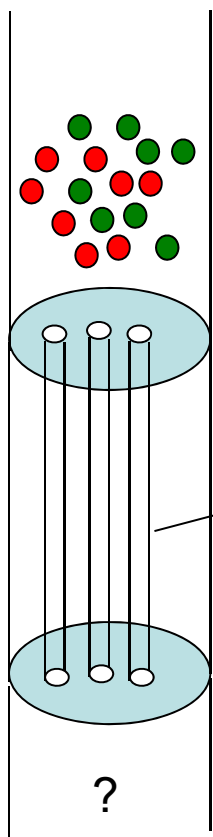$$K = \left(1 - \frac{sa}{2}\right)^2$$

Selectivity of Nanotubes

Capillary tube

$$K = \exp\left(-\frac{s\bar{L}}{2}\right) \qquad K = \frac{C_{i,pores}}{C_{i,bulk}}$$

In the presence of intermolecular interactions, ΔH plays addition role.
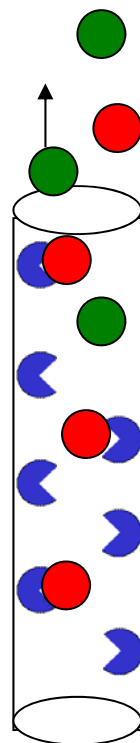
Question: What Controls the Selectivity of Nanotubes?

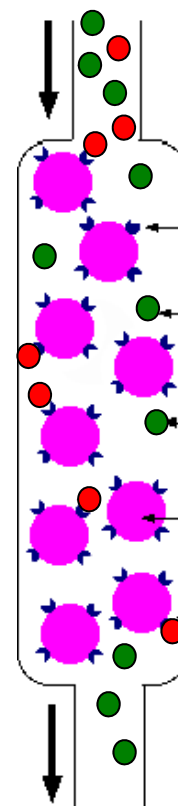$$\Delta G^0 = \Delta \bar{H}_i^0 - T\Delta \bar{S}_i^0$$

Enantiomers

nanotube

Antibody

Enantiomer with
Low affinity to the
antibody

Insert matrix

Enantiomer with
high affinity to the
antibody

?

Non-affinity

$$\Delta \bar{H}_i = 0$$

Affinity

$$\Delta \bar{H}_i < 0$$

Affinity Chromatography

Homework

14. Put a nanotube with uniform pore of square cross section (length of the tube =20μm, side length of the pore=80 nm) in a solution containing 1nM of polystyrene latex pheres (diameter=20 nm). Assuming no interactions between the spheres and the nanotube, calculate the amount of polystyrene latex spheres inside the nanotube. If decrease the diameter of the polystyrene latex spheres, what is the results?

15. For thin rods of length l, it can be shown that L = l/2. Estimate K for fibrinogen, which can be approximated as a thin rod of length 70 nm, partitioning into a porous solid with s= 0.12/nm. What does K change to if all pore dimensions are exactly doubled in size? Assume the applicability of the random-plane of pore space.

S = k. log W

$$K = \frac{\text{accessible volume}}{\text{true volume}} = \left(1 - \frac{2a}{d_c}\right)^2$$