

**IN-CLASS PROBLEMS – SEPARATION SCIENCE  
CROMATOGRAPHY UNIT**

**Thomas Wenzel, Bates College**

**In-class Problem Set - Extraction**

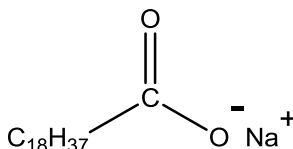
1. Devise a way to separate the materials in the following sample by performing an extraction.

The sample consists of water with a complex mixture of trace levels of organic compounds. The compounds can be grouped into broad categories of organic acids, organic bases and neutral organics. The desire is to have three solutions at the end, each in methylene chloride, one of which contains only the organic acids, the second contains only the organic bases, the third contains only the neutrals.

Remember - Ions are more soluble in water than in organic solvents.

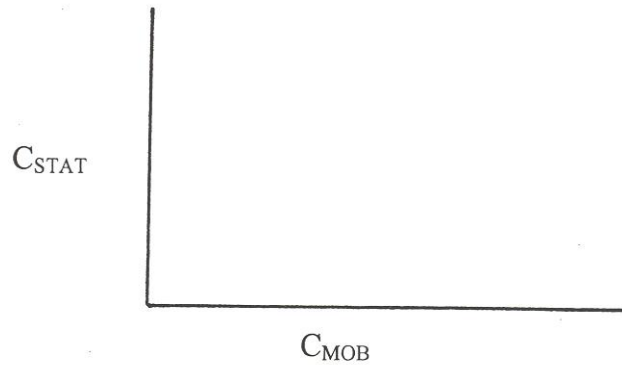
- Neutrals are more soluble in organic solvents than in water.

2. Devise a way to solubilize the organic anion shown below in the organic solvent of a two-phase system in which the second phase is water. As a first step to this problem, show what might happen to this compound when added to such a two-phase system.

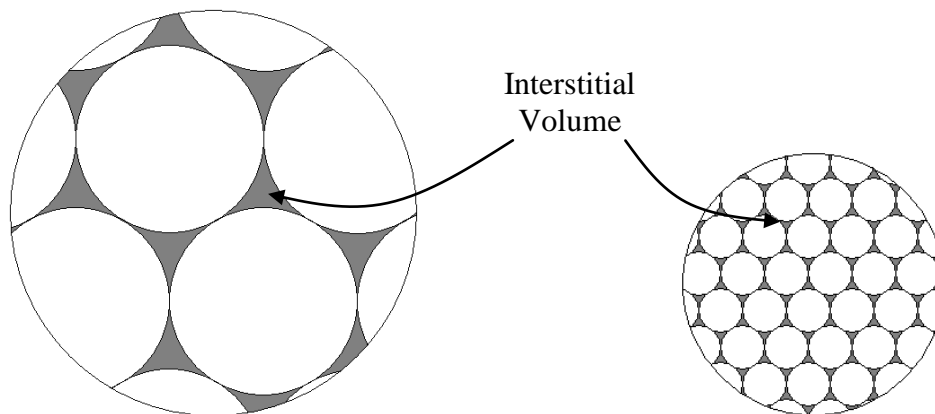


## In-class problems – Chromatography Set #1

1. Consider a plot that has the concentration of analyte in the stationary phase on the Y-axis and the concentration of analyte in the mobile phase on the X-axis.



- a) Draw an idealized plot as greater concentrations of analyte are injected into the chromatographic column.
  - b) Draw what you suspect would really happen.
  - c) What might the peaks look like in the real versus ideal situations?
2. What term would we use to describe the movement of a molecule in a liquid stationary phase?
  3. What processes would account for the movement of a molecule through a region of interstitial volume in a mobile phase?

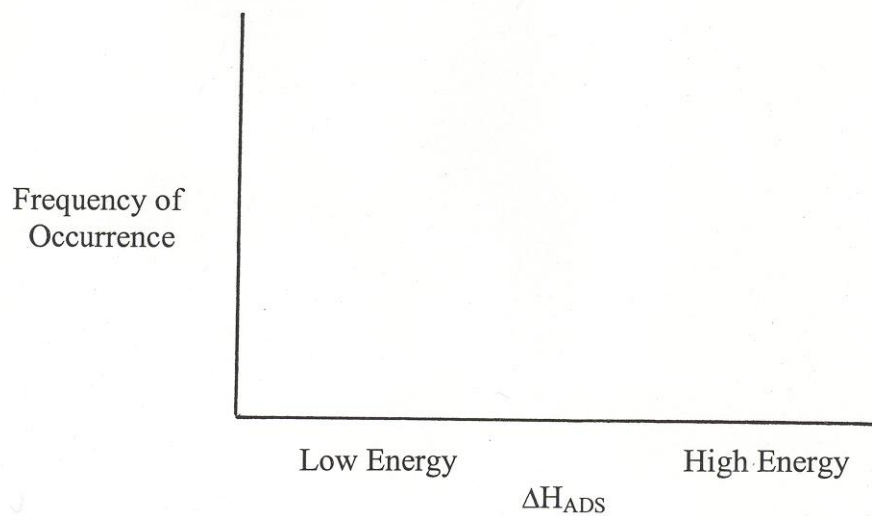


4. Tswett used starch as his stationary phase.

a) What is the dominant surface functionality of starch?

b) The two other common solid stationary phases are silica gel ( $\text{SiO}_2$ ) and alumina ( $\text{Al}_2\text{O}_3$ ). What do you think are the surface functionalities of these materials?

c) Draw a plot of the distribution of enthalpies of adsorption for a molecule on the surface of starch, silica gel, or alumina.



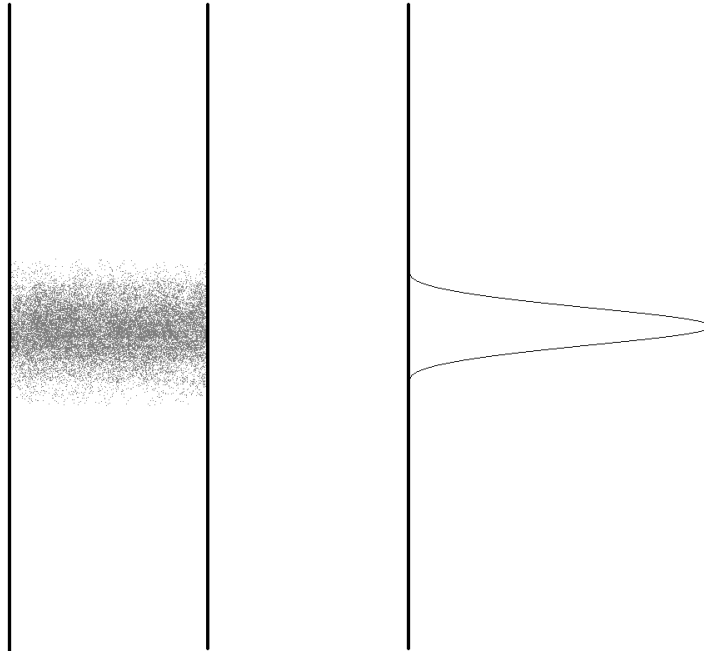
d) What would a chromatographic peak look like on such a phase with such a plot of adsorption enthalpies?

e) What is the problem with your peak?

## In-class problems – Chromatography set #2 – Peak Broadening

Development of **Longitudinal Diffusion Broadening** in Chromatography

Consider a “band” of a compound in a chromatographic column. The band has the following concentration profile.



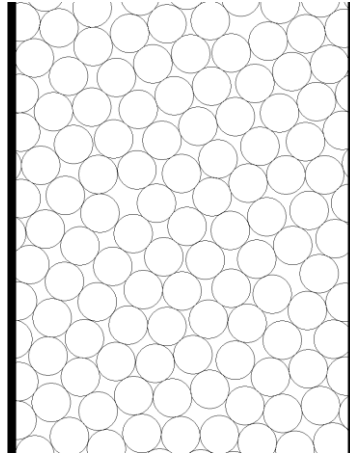
a) What would happen to this profile if the flow of the column were stopped and the column was allowed to sit?

b) Would this phenomena be more significant (i.e., happen faster) in a gas or a liquid?

c) Does this phenomena contribute more to band broadening at higher or lower flow rates?

## Development of **Eddy Diffusion Broadening** in Chromatography

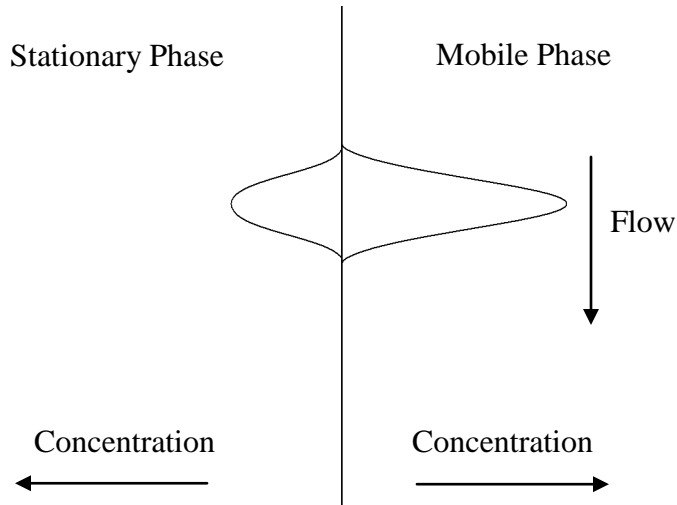
Consider molecules flowing through a packed bed of particles.



- a) Would different molecules have different path lengths as they passed through the bed?
  
- b) Is the difference in length between the shortest and longest path dependent at all on the diameter of the particles? If so, which particles (smaller or larger) would lead to a greater difference?
  
- c) Some packed columns exhibit channeling. What do you think is meant by this term?
  
- d) Would channeling be more likely to occur with smaller or larger particles? In other words, which is more difficult to pack efficiently, larger or smaller particles? A column is packed efficiently when the particles are in a uniform bed with the minimum amount of voids.
  
- e) Do open tubular capillary columns exhibit eddy diffusion?
  
- f) Does this phenomena exhibit any dependence on the flow rate?

## Development of **Stationary Phase Mass Transport Broadening** in Chromatography

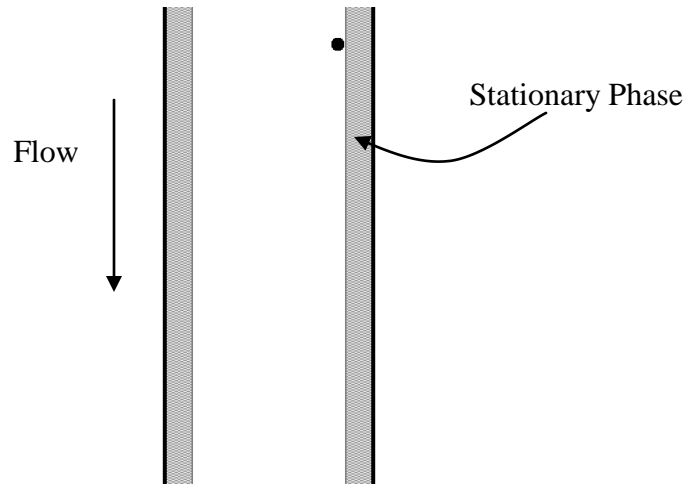
Consider a compound that has distributed between the mobile and stationary phase within a plate in a chromatographic column. The following might represent the concentration distribution profiles in the two phases (note that the compound as depicted has a slight preference for the mobile phase).



- What would happen to these concentration profiles a brief instant of time later?
- Will what happens in (a) contribute to band broadening? Explain.
- Does the contribution of this phenomenon to band broadening exhibit a dependence on flow rate? If so, are there any troublesome aspects to this dependence?
- What happens to this effect as the stationary phase coating is made thicker?
- Capillary GC columns have very thin coatings. Describe one advantage of these columns.
- Compare the effect of this phenomenon on a uniform versus non-uniform stationary phase coating.
- Is this effect of more concern in gas or liquid chromatography?

## Development of **Mobile Phase Mass Transport Broadening** in Chromatography

Consider a capillary column as shown below.



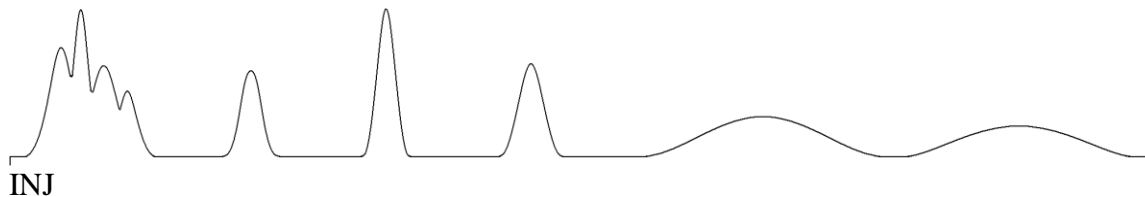
The dot represents a molecule that has just left the stationary phase and is about to diffuse across the mobile phase and re-encounter the stationary phase on the other side of the column.

- Draw a line representing the path of the molecule.
- What would this path look like if the flow rate were doubled?
- Is it important for the molecule to encounter the stationary phase? Think about a situation in which the flow was so fast that the molecule never re-encountered the stationary phase.
- If using capillary columns, what does this suggest about the desirable diameter for such a column?
- Is this phenomenon worse in gas or liquid chromatography?
- How does the contribution to band broadening depend on flow rate?
- Would this effect be observed in a packed column? If so, how?
- How could you reduce this effect in a packed column?
- Say something about the length of column needed if you undertake what you have suggested in (h), assuming that you have maintained a constant thickness of stationary phase.

### In-class problems – Chromatography set #3 – Fundamental Resolution Equation

1. Describe ways in which the number of plates on a chromatographic column can be increased. Are there any tradeoffs associated with these changes?
2. Describe ways in which the separation factor can be increased. Are there limits to the effect that increasing the separation factor has on chromatographic resolution?
3. Describe ways in which the retention or capacity factor can be increased. Are there any tradeoffs associated with these changes? Are there limits to the effect that increasing the retention factor has on chromatographic resolution?

4. Consider the following chromatogram.



The early eluting peaks and later eluting peaks exhibit a problem.

- a) Describe the chromatographic nature (there is a particular term that describes each) of the problem.
- b) Propose a way in gas chromatography to eliminate both problems.
- c) Propose a way in liquid chromatography to eliminate both problems.



## **In-class problems – Chromatography set #4 – Ion-Exchange Chromatography**

1. Describe a scheme using ion exchange chromatography that would enable you to deionize water. Say something about the capacity of the ion exchange resins you would use for this purpose.
2. Would ion exchange resins that are useful for deionizing water be useful for analytical separations?
3. What would be the order of retention for the ions Li(I), Na(I), and K(I) on a cation exchange resin? Justify your answer.
4. Consider the case of separating the alkali ions in (3) on a polystyrene resin using a fairly dilute solution of hydrochloric acid as the mobile phase.
  - a) What is the bound ion and mobile counter ion?
  - b) One problem is how to detect these ions. They do not absorb ultraviolet or visible light in the accessible portion of the spectrum. They do not absorb infrared light. Conductivity might work except that the hydrochloric acid in the mobile phase produces too high a background signal. Devise a way to remove the conductivity of the eluent ions (HCl) but retain the conductivity of the alkali ions you wish to detect.