BACKGROUND

The adsorption of molecules on the surfaces of solids is a very interesting and useful phenomenon. Surface adsorption is at the heart of such things as chromatography and ion-exchange resins to name just two examples. To some degree virtually all solids are capable of adsorbing material on their surfaces. Solids can show significant selectivity in their adsorbing abilities that can be taken advantage of in chromatography applications to successfully perform separations. The degree to which a solid will adsorb material depends on a number of things including: temperature, nature of molecule being adsorbed, degree of surface pore structure, and, in the case of adsorption from solution, solute concentration and solvent. Other factors such as pressure may play roles as well but these are the important factors for this discussion that deals with the process of adsorption of solutes from aqueous solution by highly porous solids. As a point of information it should be emphasized that the process of adsorption from solution is best viewed as an equilibrium process in which the molecules being adsorbed from solution reach equilibrium with molecules on the surface of the solid. When performing the procedure portion of this experiment the equilibrium nature of the process should be remembered and sufficient time allowed for equilibrium to be established in order to obtain accurate results.

There are two traditional approaches to quantitatively understand the adsorption from solution process. Equation 1 illustrates what is commonly referred to as the ”Freundlich isotherm" technique.

\[
\frac{x}{m} = k \cdot c^{(1/n)}
\]  

where:

- \(x\) = grams of solute adsorbed by \(m\) grams of dry solid
- \(c\) = concentration of solute in grams per liter
- \(n\) = a constant (typically between 0.1 and 0.5)
- \(k\) = a constant (varies with temperature and chemical nature of the adsorbing solid as well as the solute molecule)

It will be useful to refer to the ratio \(x / m\) as the "relative adsorptivity" for discussion here. A convenient form of Equation 1, the Freundlich isotherm, is obtained by taking the logarithm of both sides of Equation 1 to obtain Equation 2.

\[
\log \left( \frac{x}{m} \right) = \frac{1}{n} \cdot \log c + \log k
\]  

Since Equation 2 is in the form of a straight line it is possible to evaluate the two constants based on the values of the slope and intercept of a suitable plot.

A second common approach to data analysis is based on the work of Langmuir. Equation 3 illustrates the "Langmuir isotherm"
\[
x/m = \frac{a \cdot c}{1 + b \cdot c}
\]

Equation 3 can be rearranged to a straight-line form by simple algebra to obtain Equation 4.

\[
c/(x/m) = 1/a + (1/b) \cdot c
\]

Plotting data according to Equation 4 permits the Langmuir constants, \(a\) & \(b\), to be evaluated from the intercept and slope, respectively.

It is worth noticing a significant difference between the predicted concentration dependence of the relative absorptivity for the Freundlich, Equation 2, as opposed to the Langmuir isotherms, Equation 3. Equation 2 predicts that the relative absorptivity will increase indefinitely in a logarithmic fashion with the concentration. Equation 3 predicts that the relative absorptivity will approach a finite limit as the concentration increases. This finite limit is clearly seen when Equation 3 is rearranged to the form seen in Equation 5.

\[
x/m = \frac{a}{b + 1/c}
\]

One can see from Equation 5 that as the concentration, \(c\), becomes high the ratio \(x/m\) approaches the limit of \((a/b)\), a constant. One might guess, based on the differences in prediction of concentration dependence, that the Langmuir treatment comes closer to accurately modeling the real world. This seems reasonable since there are actually a finite number of adsorption sites per gram of solid. Once these sites are fully occupied, corresponding to the maximum value of \(x/m\), further increasing the solute concentration will have no affect on the amount of solute adsorbed. A convenient graphical test of Equation 5 is possible as shown in Equation 6, which results from taking the reciprocal of each side of Equation 5.

\[
1/[x/m] = [1/a] \cdot [1/c] + b/a
\]

A plot of \(1/[x/m]\) versus \(1/c\) should generate a straight line.

Since the adsorption process is an equilibrium process it is desirable to investigate the thermodynamic parameters. Equations 7 and 8 conveniently represent the equilibrium.

\[
S_f + C_u \Leftrightarrow S_{occ}
\]

\[
S_f + C_u \Leftrightarrow C_b
\]

Where:

- \(S_f\) = "free" or unoccupied adsorption sites
- \(C_u\) = "free" unbound solute concentration in solution
- \(S_{occ}\) = "occupied" adsorption sites
- \(C_b\) = concentration of "bound" solute

Note: \(S_{occ} = C_b\) if each adsorption site is occupied by one solute molecule.)
St as depicted in Equation 9 can represent the total number of adsorption sites.

\[ S_t = S_f + S_{occ} = S_f + C_b \]  

An experimental determination of \( S_t \) would be particularly interesting and useful since it represents a fundamentally meaningful characteristic of the adsorbing solid. A determination of \( S_t \) starts with the equilibrium constant expression for Equation 8 as shown in Equation 10.

\[ K = \frac{|C_b|}{|S_f||C_u|} \]  

From Equation 10 it is clear that

\[ C_b = K \cdot C_u \cdot [S_t - C_b] \]  

Equation 11 can be rearranged to Equation 12, which has the same formal mathematical appearance of the Langmuir isotherm in Equation 3.

\[ \frac{C_b}{S_t} = \frac{K \cdot C_u}{1 + K \cdot C_u} \]  

Equation 12 may be rearranged into a convenient straight-line form as shown in Equation 13.

\[ \frac{1}{C_b} = \left[ \frac{1}{(K \cdot S_t)} \right] \cdot \left[ \frac{1}{C_u} \right] + \frac{1}{S_t} \]  

Based on Equation 13 a plot of \( \frac{1}{C_b} \) versus \( \frac{1}{C_u} \) permits a determination of both \( K \) and \( S_t \) from the slope and intercept, respectively.

The \( C_b \) in Equation 13 can easily be identified with the ratio \( \frac{x}{m} \). Since the total solute concentration is \( c \), in grams per liter of solution, then \( C_u \), in grams per liter of solution, can be evaluated based on \( c \) and \( \frac{x}{m} \). When this is done, \( S_t \) will have units of moles of adsorption sites per gram of dry solid.

As a final comment, one should appreciate the utility of performing a measurement of \( K \) at several temperatures. It was seen in basic thermodynamics that Equation 14 is true.

\[ \Delta G^o = -RT \ln K = \Delta H^o - T \cdot \Delta S^o \]  

Equation 14 can be rearranged into two convenient forms for data analysis, Equation 15 and Equation 16.

\[ \ln K = -\frac{\Delta H^o}{R} \cdot \frac{1}{T} + \frac{\Delta S^o}{R} \]  

\[ T \ln K = \frac{\Delta S^o}{R} \cdot T - \frac{\Delta H^o}{R} \]
The advantage to using both Equations 15 and 16 is that by doing so it is possible to evaluate both the enthalpy change and the entropy change from graphical slopes rather than depending on graphical intercepts. This is desirable since graphical intercepts are potentially more subject to systematic errors than are graphical slopes – Can you explain why this is true?

PROCEDURE

Apparatus and Materials Needed:

The following major pieces of equipment and supplies are necessary.

1. Twelve 250-ml Erlenmeyer flasks
2. Two volumetric burets, 25 ml or 50 ml capacity
3. One 100-ml volumetric flask
4. A weighing bottle
5. Volumetric pipets; 5, 10, and 25 ml volume
6. Analytical balance
7. Activated charcoal; or other suitable porous solid as directed by instructor
8. A 1 M acetic acid solution, standardized
9. A 0.1 M sodium hydroxide solution, standardized
10. Phenolphthalein indicator solution
11. Temperature control equipment; if measurements are to be made at different temperatures

Adsorption Measurements

A sample of activated charcoal weighing between 0.9 and 1.1 grams is placed into each of the Erlenmeyer flasks. These samples must be accurately weighed to a tenth of a milligram. The twelve Erlenmeyer flasks are divided into six pairs so that the experiment may be run in duplicate. The six pairs of flasks will be filled with differing concentrations of acetic acid solution. Each individual flask of a given pair will have identical acetic acid concentration. Fill a 50 ml volumetric buret with the standardized acetic acid solution. Deliver exactly 50.00 ml of the acetic acid solution to the 100-ml volumetric flask and dilute to the mark with distilled water then mix thoroughly. Pour all of this acetic acid solution into one of the Erlenmeyer flasks. Repeat this process for a second Erlenmeyer flask. The remaining pairs of flasks are treated similarly using volumes of 25.00 ml, 10.00 ml, 5.00 ml, 2.50 ml, and 1.00 ml of the standard acetic acid solution, each having been properly diluted in the 100-ml volumetric flask. The flasks with their charcoal and acetic acid contents are agitated thoroughly and set aside overnight, or until an equilibrium has been reached.

After equilibrium has been reached an aliquot of clear supernatant solution is removed from each flask using a suitable volumetric pipet. This aliquot is then titrated, using phenolphthalein indicator, to the pink end-point using the standardized sodium hydroxide solution. It may be necessary to use some trial and error in determining the proper size of aliquot for titration.

The aliquot size should be such that a minimum of 15.00 ml of sodium hydroxide are used for titration – Can you explain why we want an aliquot size this magnitude for the endpoint volume.
and not an aliquot with an end point that is reached with say 7.00 ml of sodium hydroxide. The aliquot should not be so large, however, that the buret must be refilled in order to reach the end-point. Aliquots from each of the twelve Erlenmeyer flasks should be carefully titrated.

CALCULATIONS

The total concentration of acetic acid in each of the original solutions, $c$, is easily calculated based on the dilution data. The titration data gives the concentration of acetic acid remaining in solution after the adsorption equilibrium has been reached, $C_u$. The amount of acetic acid adsorbed by the solid is determined by difference. This difference, together with the weight of solid, gives directly the relative adsorptivity, $x/m$. Prepare plots based on Equations 2, 6, and 13. Evaluate the values for $K$ and $S_t$. If measurements were performed at different temperatures, prepare plots based on Equations 15 and 16. Evaluate the free energy, enthalpy, and entropy changes for your equilibrium conditions.