CHEM355
EXPERIMENT 9

Adsorption

Adsorption is the accumulation of a gas or liquid solute (*the adsorbate*) on a surface of a solid or a liquid (*the adsorbent)* forming a molecular or atomic film. It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution.

Adsorption has many applications. Its first application was probably the use of bone ashes to remove colour from syrups or alcohol. Today, adsorbent materials are widely used at water-treatment plants to remove especially organic impurities and chlorine as purification treatment.

Atoms on the surface are not wholly surrounded by other atoms and experience a bond deficiency. Thus it is generally energetically favorable for them to bond to the adsorbate.

Adsorption on solid surfaces may be either as chemisorption where a chemical band forms between the surface and the adsorbate - such as the adsorption of chloride ions on AgCl (ionic bond) or of oxygen gas on metals where oxygen to metal bonds are formed (covalent bond) or physical adsorption results from attractions like nonpolar Vander Waals, dipole - dipole etc. The dependence of the extent of adsorption on concentration in bulk is frequently called as the "**adsorption isotherm**" that is, a relation that describes the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid). There are several types of isotherms describing process of adsorption, namely Freundlich isotherm, Langmuir isotherm, BET isotherm, etc.

Langmuir isotherm is applied when the adsorption occurs as a single layer (monolayer), where the following equilibrium condition is considered

$$S^* + M\ (g\ or\ l) \leftrightarrows S - M$$

Here S* refers to vacant sites on the adsorbent surface, M is the gas phase or solution phase molecules with an assumption that there are fixed number of localized surface sites. Thus the equilibrium relation can be written as

$$K = \frac{[S-M]}{[S^*][M]}$$

Let θ describes the surface coverage where the saturation leads a maximum value of 1 then note that $[S - M]$ is directly proportional to the surface coverage hence, proportional to θ, $[S^*]$ is proportional to the vacant site, (1- θ), and $[M]$ is proportional to the pressure, P or concentration, c of the adsorbate. Then the relation can be simplified as

$$\theta = \frac{Kc}{1 + Kc}$$

To relate the experimental observations one can use the fraction of the surface covered as equal to x/x_{max}, where the x and x_{max} are experimental and maximum amount of adsorbed molecule per gram of adsorbent, respectively. Then the relation becomes;

$$\frac{c}{x} = \frac{1}{K.x_{max}} + \frac{c}{x_{max}}$$

The plot of c/x vs c gives a straight line with a slopeequal to $1/x_{max}$ and an intercept equal to $1/(K.x_{max})$.

Classical adsorption isotherm in the most general sense is the Freundlich isotherm:

$$x = k.c^{\frac{1}{n}}$$

where k and n are constants with no physical significance while c is the same as above. The latter equation can be presented as

$$\log x = \log k + (1/n) \log c$$

and a plot of $\log x$ vs $\log c$ yields a straight line with a slope equal to $1/n$ and an intercept equal to $\log k$.

Freundlich equation usually fails both at low and high concentrations. Freundlich isotherm is somewhat better for the adsorption from liquid solution and Langmuir equation gives better results for adsorption of gases.

Neither Freundlich or Langmuir expressions, however, are adequate for adsorption of vapors on porous solids at high vapor pressures: which is assumed to yield multi-molecular adsorption layers, and the Brauner - Emmett - Teller (B.E.T.) semi - empirical isotherm is applied in such a case, which will not be discussed here.

We will prepare our acetic acid-charcoal isotherm by allowing acetic acid solutions of various concentrations to equilibrate with a given mass of charcoal. The amount of acetic acid (HAc) not adsorbed to the charcoal will be determined by titration with sodium hydroxide ($NaOH$).

$$HAc(aq) + NaOH(aq) \rightarrow NaAc(aq) + H_2O$$

This will allow us to easily determine the amount of acetic acid that has adsorbed to a given mass of the charcoal.

Purpose: In this experiment the adsorption isotherms for the adsorption of acetic acid on activated charcoal will be studied.

Apparatus and Chemicals

Apparatus: Erlenmayer, graduated cylinder, pipette, filter paper, funnel, stirring rod, watch.

Chemicals: charcoal, 0.4M HAc, 0.1M NaOH, phenolphthalein, distilled water.

Procedure

1. Weigh about 1.5g Charcoal into 6 stopper 250 mL Erlenmeyer flasks. This should be recorded to +/- 1 mg.
2. Prepare 100 mL of acetic acid solutions according to:

Sample	Molarity of Acetic Acid	Aliquot for Analysis (mL)
1	0.4	10
2	0.3	10
3	0.2	10
4	0.1	25
5	0.04	25
6	0.02	25

3. For each sample above, add 100 mL of the solution to a charcoal sample. Swirl the flasks vigorously and then place them into the water bath at 25 ˚C for 20 minutes.
4. Mix the mixtures for several times by flasks shaking within this period.
   (***Attention***: *Put charcoal into flasks at the same time as adsorption is a function of time too.)*
5. Filter your charcoal solutions (discard the first 10 ml of filtrate to clean the filter flask of any contaminants and to saturate with acid any adsorption sites which might be on the filter paper)
6. Add 2-3 drops of phenolphthalein and titrate by NaOH.

(Waste container of experiment: acid waste container)

Treatment of Data

1. Using your titration data, for each sample:

   Calculate the number of moles of acetic acid in the solution *before* adsorption.

   Calculate the number of moles of acetic acid in the solution *after* adsorption.

2. Determine x (mmoles of Acetic Acid /1.5 grams of Charchoal) for each sample.
3. Plot the Langmuir isotherm and determine the Langmuir parameters x_{max} and K.
4. Make the suggested plot to determine the Freundlich parameters k and n.

QUESTIONS

1. Why did you use charcoal as an adsorbent?
2. Which isotherm is more suitable? Why?

DATA SHEET **Experiment 9.Adsorption**

Group Number:…………………………Group Members:………………………………………………………

Date:……..Assistant name and Signature:…………………………………………..

HAc(M)	NaOH used for titration