Chem 230, Fall, 2014
Homework Set # 1
Do by Sept. 16

Short Answer Questions

1. Resorcinol (see below) has a hexane - water partition coefficient of 4.0. How could the organic phase be changed to give resorcinol a greater organic – water partition coefficient?

2. It is desired to remove radioactive strontium (in the form Sr^{2+}) from a waste stream containing other metals. List two possible methods which could be used to transfer the radioactive strontium into an organic phase.

3. Hydrogen peroxide is a highly water soluble gas that is an important oxidant in the atmosphere. Suggest a method to trap hydrogen peroxide in water.

4. How can temperature play a role in trapping gases on solid or liquid supports?

5. Explain why glycine ($NH_2CH_2CO_2H$) can not be partitioned at any pH into an organic phase without an ion-paring reagent.

6. List one factor that will determine whether a crown ether can effectively move cations from an aqueous phase to an organic phase.

7. Indicate three factors that can influence the partitioning of metals between the aqueous and organic phases using ligands that form metal-ligand complexes.

8. What is the difference between exhaustive extractions and non-exhaustive extractions?

9. List two simple separation methods that are not based on partitioning?

10. Why is it easier to trap non-polar compounds in an aqueous matrix than polar compounds (assuming both sets of compounds are uncharged) in an aqueous matrix using solid phase extraction?

11. Which type of solid phase extraction cartridge would make the most sense for retaining ethanol (a polar organic compound) in a gasoline (mostly non-polar alkyl and aromatic hydrocarbons) sample.
a) normal phase (or hydrophilic interaction)   b) reversed phase
c) cation-exchange   d) anion-exchange

Longer Problems – to be turned in
1. For the following compounds, indicate the approximate pH range in which the compound can be extracted from an aqueous layer into an organic layer. You may need to look up pK_a values.
a) $CH_3CH_2CH_2CO_2H$ b) $(CH_3)_3CNH_2$ c) o- $HOC_6H_4NH_2$

2. Compound X has an octanol water distribution coefficient of 3.8 (ratio of X in octanol to X in water). X initially exists at a concentration of 1.0×10^{-3} M in 20 mL of water.
a) Calculate the concentration of X in octanol if 60 mL of octanol is used in a liquid-liquid extraction with the aqueous solution (assume the extraction goes to equilibrium).
b) Calculate the concentration in octanol if the aqueous solution is extract twice with 20 mL of octanol in each extraction? Assume that the two octanol fractions will be combined.

3. Aniline, in the $-NH_3^+$ form, has a pK_a of 4.62.
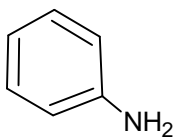
a) If the octanol-water K_p value is 4.0 (again, assuming that octanol is the raffinate), calculate the value for K_D at a pH of 3.00.
b) If an amide, which was formed from aniline, has no acidic or basic groups and a similar K_p value, describe how you would separate aniline from the amide. Indicate which pH you would use and which phase aniline and the amide would end up in.

4. It is desired to transfer Zn^{2+} from an aqueous phase to organic phase using 8-hydroxyquinoline (with NH^+ $pK_a = 4.91$ and OH $pK_a = 9.81$).
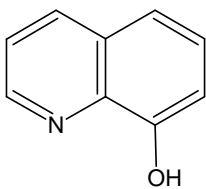
a) Draw a diagram showing two cross phase reactions and all of the reactions which can occur in the aqueous phase.
b) If no Zn^{2+} is present, over which pH range do you think 8-hydroxyquinoline will be most readily extracted to the organic phase (e.g. ether)? Indicate if you think very little 8-hydroxyquinoline will be extracted.
c) What might limit the extraction of Zn^{2+} at low pH and at high pH?

5. Acetic acid in the atmosphere is measured by trapping the gas using a bubbler and analyzing the liquid by ion chromatography. 200 L of air is passed into a bubbler containing 4 mL of water and the acetic acid is trapped with 100% efficiency (with no evaporation of water). If the liquid concentration is found to be 2.7×10^{-6} M, calculate the air concentration in mol m^{-3}.

6. Acetic acid is to be separated from other polar compounds in water by extraction using benzene (see p. 393 of text).
a) Is the distribution constant affected by the aqueous acetic acid concentration if the aqueous phase is buffered? and if the aqueous is unbuffered?
b) Explain why it is beneficial for this extraction to keep solvent volumes small (concentrations high).

7. Several important fragrant compounds, that are present at moderately high concentrations, are to be analyzed in wine by high resolution GC. However, sugars and other compounds will decompose following injection on the column, reducing the column lifetime. Describe what the primary purpose of a simple separation will be.

8. Pyruvic acid (CHC(O)COH) is a polar compound. It is desired to analyze its concentration in biological samples. Suggest an advanced separations method to separate it from other major constituents in biological fluids (aqueous solutions with inorganic salts, such as NaCl, and uncharged sugars present). Describe the steps by which you would remove pyruvic acid from the inorganic salts and uncharged sugars.