# Chem 230, Fall, 2014
## Homework Set # 1 Long Problem Solutions

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.

c) o- $HOC_6H_4NH_2$

a) $CH_3CH_2CH_2CO_2H$

*This is an acid with $pK_a = 4.82$. At $pH < pK_a$, most of compound is un-ionized. So appropriate range would be at pH values less than about 4.*

b) $(CH_3)_3CNH_2$ [need to look up Ka value]

*This is a base with a conjugate acid with a $pK_a$ of 10.68. At $pH > pK_a$, most of compound is un-ionized. Appropriate pH would be above about 12.*

c) o- $HOC_6H_4NH_2$

*This compound has an acidic group (-OH) and a basic group ($-NH_2$). The $pK_a$ ($pK_{a1}$ since it is the lower $pK_a$) of the conjugate acid of the $-NH_2$ group is 4.70. The $pK_a$ ($pK_{a2}$) of the -OH group is 9.97. At $pH > pK_{a1}$, the basic group is un-ionized and at $pH < pK_{a2}$, the acidic group is un-ionized. Appropriate pH would be between around 5.5 and 9.*

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 $1.0 \times 10^{-3}$ 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).

$K_{ow} = [X]_{octanol}/[X]_{water} = 3.8$

$K_p = [X]_{water}/[X]_{octanol} = 1/3.8$

$k = K(V_{water}/V_{octanol}) = (1/3.8)*(20\text{ mL}/60\text{ mL}) = 0.088$

$Q = 1/(1 + k) = 1/(1 + 0.088) = 0.92$ = fraction in octanol phase

$[X]_{octanol} = Q*n_{octanol}/V = (0.92)*(1.0 \times 10^{-3}\text{ M})*(20\text{ mL})/60\text{ mL} = \mathbf{3.1 \times 10^{-4}\ M}$

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.

$K_p = [X]_{water}/[X]_{octanol} = 1/3.8$

$k = K(V_{water}/V_{octanol}) = (1/3.8)*(20\text{ mL}/20\text{ mL}) = 0.263$

*Fraction in octanol (1st extraction)* $= Q = 1/(1 + 0.263) = 0.792$

*So fraction in water (1st extraction)* $= 1 – Q = 0.208$

*2nd extraction, fraction of original in octanol* $= Q(1 – Q) = 0.792*0.208 = 0.165$

*The combined fraction* $= 0.792 + 0.165 = 0.957$

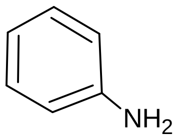
$[X]_{octanol} = Q*n_{octanol}/V = (0.957)* (1.0 \times 10^{-3}\text{ M})*(20\text{ mL})/40\text{ mL} = \mathbf{4.8 \times 10^{-4}\ M}$

*(40 mL = combined volume)*

*This problem also can be solved (easier) by calculating the amount of X left in the water after the 2nd extraction* $= (1 – Q)^2 = 0.0434$

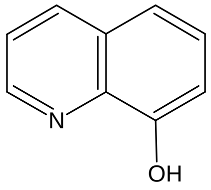
*Everything not in the water is in the octanol (so fraction in octanol =* $1 - (1 - Q)^2 = 0.957$*)*

3. Aniline, in the $-NH_3^+$ form, has a $pK_a$ of 4.62.



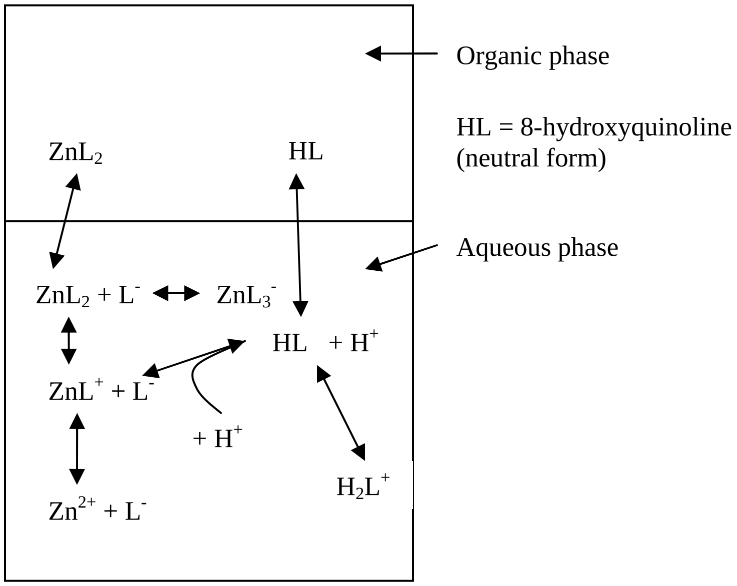
a) If the octanol-water $K_p$ value is 4.0 (again, assuming that octanol is the raffinate), calculate the value for $K_D$ at a pH of 3.00.
$K_D = [RNH_2]_{octanol}/[RNH_2]_{aq\ total} = [RNH_2]_{octanol}/([RNH_2]_{aq} + [RNH_3^+]_{aq})$
$K_D = K_p[1/(1 + [H^+]/K_a)] = 4.0[1/(1 + 1.00 \times 10^{-3}/2.40 \times 10^{-5})]$
**$K_D = 9.4 \times 10^{-2}$**
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.
*You can separate the two compounds by using a low pH (such as 3 or lower) to move the aniline to the aqueous phase while the amide should preferentially move to the octanol phase.*

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.
*To simplify the system, let's make the assumption that only neutral molecules or complexes will exist in the organic phase.*
*The two cross phase reactions will be:*
*1)* $C_9H_7NO(aq) \leftrightarrow C_9H_7NO(org)$
*2)* $Zn(C_9H_6NO)_2(aq) \leftrightarrow Zn(C_9H_6NO)_2(org)$
*Reactions in the aqueous phase are:*
*Those related to charge of 8-hydroxyquninoline:*
*1)* $C_9H_7NO(aq) \leftrightarrow C_9H_6NO^- + H^+$ *(loss of phenol H)*
*2)* $C_9H_7NO(aq) + H_2O(l) \leftrightarrow C_9H_8NO^+ + OH^-$ *(protonation of N)*
*Complexation reactions:*
*1)* $Zn^{2+} + C_9H_6NO^- \leftrightarrow ZnC_9H_6NO^+$ *(1st complexation rxn)*
*2)* $ZnC_9H_6NO^+ + C_9H_6NO^- \leftrightarrow Zn(C_9H_6NO)_2(aq)$ *(2nd complexation reaction)*
*3)* $Zn(C_9H_6NO)_2(aq) + C_9H_6NO^- \leftrightarrow Zn(C_9H_6NO)_3^-$ *(3rd complexation reaction – this is assuming a maximum of 3 ligands per* $Zn^{2+}$ *ion)*

***Full Diagram***



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.
*At* $pK_{a1} < pH < pK_{a2}$*,*$(4.9 < pH < 9.8)$ *8-hydroxyquinoline will mostly be in the organic phase.*

c) What might limit the extraction of $Zn^{2+}$ at low pH and at high pH?
*At low pH, not enough 8-hydroxyquinoline will be in the anionic form needed to form the Zn complex. At high pH,* $Zn^{2+}$ *is not very soluble (as* $Zn(OH)_2$ *forms).*

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 $2.7 \times 10^{-6}$ M, calculate the air concentration in mol $m^{-3}$.
$n(CH_3CO_2H) = (2.7 \times 10^{-6}\ mol/L\ aq)(4\ mL\ aq)(1\ L\ aq/1000\ mL\ aq) = 1.08 \times 10^{-8}\ mol$
*(n = moles)*
*Air conc.* $= n/V = 1.08 \times 10^{-8}\ mol(1/200\ L)(1000\ L/1\ m^3) = \mathbf{5.4 \times 10^{-8}\ mol\ m^{-3}}$.

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?
*The concentration of acetic acid affects the distribution coefficient in both cases because of the dimer formation in benzene is dependent upon the concentration of acetic acid. If it wasn't for the dimer formation, the distribution coefficient would be unaffected by the*

*acetic acid concentration for buffered aqueous phases. In unbuffered solutions, pH is affected by the acetic acid concentration, and this in turn affects the distribution coefficient.*

b) Explain why it is beneficial for this extraction to keep solvent volumes small (concentrations high).
*At higher concentrations, more dimer forms (this is a consequence of Le Châtelier's principle). This draws more acetic acid into the benzene phase.*

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.
*The main purpose of a simple separation will be to remove impurities affecting GC performance.*

8. Pyruvic acid (~~CHC(O)COH~~ $CH_3C(O)CO_2H$) 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.
*[Since we didn't cover the advance separations methods, this question will be graded for bonus points].*
*Pyruvic acid is fairly polar ($K_{OW}$ = 0.42 from site in class resources), so it likely will not be possible to trap it efficiently on non-polar substrates such as C18 SPE cartridges. However, it does have an acidic group which allows it to be trapped on SPE cartridges with an anion exchange functional group. It could be separated from NaCl and uncharged sugars by passing the sample through an anionic exchange SPE cartridge (with the sample buffered above pyruvic acid $pK_a$). Other salts would also be trapped, but uncharged sugars mostly would pass through the SPE cartridge. Then, pyruvic acid can be removed by passing a buffer with a low pH (below pyruvic acid $pK_a$) through the SPE cartridge to remove pyruvic acid. Permanent anions like $Cl^-$ would remain on the SPE cartridge.*