EXPERIMENT 1

ORGANIC CHEMISTRY BOOT CAMP: USE OF ORGANIC TECHNIQUES TO SEPARATE A MIXTURE (A TWO WEEK EXPERIMENT)

WEEK 1: RECRYSTALLIZATION AND EXTRACTION

Part 1: Purification of Crude Biphenyl or Naphthalene using Recrystallization
Part 2: Purification of Crude Biphenyl or Naphthalene using Extraction

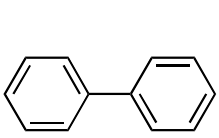
Reading Assignment: Pavia, Sections 1.1 - 1.4; 2.1 - 2.4; 3.1 – 3.9, 8.3, 8.5; 10.1 - 10.3, 11.1 - 11.3, 11.5 - 11.6, 11.8A, 12.1.

Viewing assignment: Watch the following video, which explains how to use a rotary evaporator:
http://mirandamusic.com/mpnorganic/rotovap.html
Extraction video:
http://www.youtube.com/watch?v=CyIA8NhMUl4

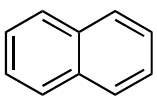
Pre-lab Questions:

1) Comparing biphenyl, naphthalene and methyl orange, which compounds are polar, and which are non-polar? Would you expect methyl orange to be soluble in hexane? What about biphenyl and naphthalene? What solvent would you use to dissolve methyl orange?
2) Pavia, page 161 - 162, problems 1, 2, 7a.
3) Explain how the rate of crystal growth can affect the purity of a sample.

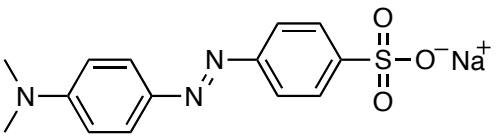
This two-part experiment is designed to introduce you to some of the main organic techniques that are used to separate and purify organic compounds: recrystallization, extraction, and column chromatography.



biphenyl



naphthalene



methyl orange

You will be given a crude sample of biphenyl contaminated with methyl orange, *or* a crude sample of naphthalene contaminated with methyl orange. Your job is to purify this sample three different ways over a period of two lab sessions. In the second lab section your will determine

purity using melting point. You will then compare and contrast the three methods based on time required, purity, and yield to see which technique works best for your compound. Keep in mind that different techniques may be best for biphenyl *vs*. naphthalene.

Part 1: Recrystallization of Crude Biphenyl or Naphthalene

You will be provided with a sample vial containing approximately 1.2 g either biphenyl ***or*** naphthalene contaminated with methyl orange, a polar organic dye. Label this vial as crude and set it aside.

Part 1A: Solubility Tests

The object of Part A is to find a suitable recrystallizing solvent that can be used to purify the biphenyl or naphthalene. A good recrystallizing solvent will dissolve biphenyl or naphthalene when it is warm, but will dissolve a minimal amount when it is cold. If a poor recrystallizing solvent is chosen, yields of the recovered biphenyl or naphthalene will be very low.

1) You will be using **pure biphenyl** or **pure naphthalene** for the solubility trials. Place 5 labeled medium test tubes (1.3 X 10cm) in a test tube holder. Place about 10 mg pure biphenyl or pure naphthalene into each tube. Using the same solvents as you did in Part 1, add a ½ to 1 mL methanol to the first tube, and the same amount of acetone to second tube, dichloromethane to the third tube, toluene to the fourth tube, and hexane to the last tube. Mix each tube by holding it between your fingers at the top, and tapping the bottom, while watching to see if any solid goes into solution. A solid tends to dissolve more readily in a solvent whose polarity is similar to its own. Record the solubility of each solid at room temperature. *Are the solubilities what you expect based on the polarities of the solvents and the polarity of biphenyl or naphthalene?*

2) Observe which tubes still contain undissolved biphenyl/naphthalene. Add a boiling stick to each of these and, using a test tube holder, heat these samples gently by passing back and forth into the sand bath. *MAKE SURE THE SANDBATH IS NOT TOO HOT. The volatile liquids can easily* ***pop*** *out of the test tube and burn your skin.*

3) If the phenacetin goes into solution when heated in a particular solvent, cool to room temperature, then plunge the test tube into ice water and see if a precipitate or crystals form. If you see a precipitate or crystals form in more than one tube, compare the amount of solid in each tube.

4) Based on your observations, identify the most suitable recrystallizing solvent.

Part 1B: Macroscale Recrystallization of Crude Biphenyl or Naphthalene

1) Weigh and transfer approximately 0.5 g of your crude sample into an Erlenmeyer flask. Keep the rest of the crude for later experiments.

2) ***Perform a hot filtration:*** Slowly add hot hexane to your sample until no more solid dissolves (the methyl orange dye is very insoluble in hexanes.) Filter off the insoluble dye by vacuum filtration (using a Buchner funnel) into a *pre-weighed* 125 mL side arm test tube.

Rinse with a small amount of hexane, then transfer to a medium *pre-weighed* round-bottom flask, again rinsing with a small amount of hexane.

3) Remove the solvent using rotary evaporation. Notice that the flask gets cold as the solvent is evaporating on the rotary evaporator. *Why does it get cold?* Hexane should collect in the large round- bottom reservoir attached to the rotary evaporator – be sure to empty the hexane that is in this reservoir into the organic waste container after completion of this step.

4) Record the weight and appearance of the crude biphenyl/naphthalene.

5) In an Erlenmeyer flask, preheat about 15 mL of the solvent you will be using in the recrystallization, and keep this warm until step 8 is completed.

6) Add about 2 mL of the warm solvent to the round bottom flask containing the crude biphenyl/naphthalene. Using a boiling stick, swirl and heat the mixture in the sand bath, allowing time for the solid to dissolve. Transfer additional solvent, about 1 mL at a time, until all of the solid has dissolved.

7) Remove the flask from the sand bath. Cool the solution to room temperature, then place the flask in an ice bath to allow crystals to form. Collect the crystals by vacuum filtration using a Buchner funnel. Break the vacuum, wash the crystals with a minimum amount of ice-cold solvent, then restore vacuum to remove the solvent. Allow crystals to dry in the Buchner funnel. Make a note of the crystal form (needles, flakes, etc.) and color. Save the supernatant solution (mother liquor) in a scintillation vial for Experiment 2.

8) Determine the weight and percent recovery. If the amount of product is exceptionally low (less that 30%), you either chose the wrong solvent, or you did not allow sufficient time for the solid to dissolve, and as a result did not form a supersaturated solution. You may wish to take a second crop if this is the case. This simply means recovering additional crystals from the supernatant solution. If you did not have a supersaturated solution, heat the solution; adjust the volume of solvent (add or evaporate as necessary), then cool so that crystals form and collect as before. If you chose the wrong solvent, remove the solvent by rotary evaporator, then perform the recrystallization using the correct solvent (repeat steps 5-7).

9) Save your recrystallized product in a small, labeled scintillation vial for next week's experiment.

Part 2: Purification of Crude Biphenyl or Naphthalene Using Extraction

1) Place 30 mL hexane in a 125 mL separatory funnel. Weigh and transfer approximately 0.5 g of your crude sample into the separatory funnel. Keep the rest of the crude for later experiments.

2) Add 20 mL water to the separatory funnel, then swirl, venting frequently. Mix well, then allow the two layers to separate. If an emulsion forms, add about 10 mL of saturated NaCl solution (brine) gently swirl, then allow the layers to separate. Record what you see in your lab notebook. *Is hexane on the top or bottom – If you're not sure, how can you check?*

Where is the aqueous layer? Where is the methyl orange? Where you would expect to find the biphenyl or naphthalene?

3) Drain the aqueous layer into a medium beaker. Wash the organic layer with 10 mL water, then allow the layers to separate, then drain the aqueous layer into the beaker containing the aqueous layer from step 2.

4) Wash the organic layer with 10 mL saturated NaCl (brine), drain the aqueous layer into the beaker with the combined aqueous layers, then pour the organic layer into an Erlenmeyer flask, dry with $MgSO_4$ (anhydrous), vacuum filter using a Buchner funnel to remove the drying agent, then transfer the solution into a *pre-weighed* medium round bottom flask and remove the solvent using a rotary evaporator. *What is the reason for the brine wash at the beginning of this step?*

5) Determine the weight and percent recovery of the purified biphenyl/naphthalene. Make note of the solid form (powder, crystals, etc.) and color. Save this in a small, labeled scintillation vial for next week's experiment.

Post-lab Questions:

1) One of the most common causes of inaccurate melting points is heating of the melting-point apparatus too rapidly. Under these circumstances, how will the observed melting point compare with the true melting point?
2) The solubilities for compound X, in grams of compound per 100 g of solvent, are:

Solvent:	Water	Chloroform	Hexane
at 5 °C	0.1 g	1.5 g	7.0 g
at reflux	2.3 g	3.5 g	7.5 g

Which solvent will give the maximum recovery upon crystallization of 1.0 g of X? Briefly explain how you arrived at this conclusion.
What is the maximum amount of X that you could recover?