Experiment 6

Extraction: Separation of Benzoic Acid and Phenanthrene

Reading: Handbook for Organic Chemistry Lab, sections on Extraction (Chapter 11), Filtration (Chapter 13), Drying Organic Solutions (Chapter 15), and Solvent Removal (Chapter 14).

Distillation and recrystallization are techniques used by the organic chemist to purify compounds. In an organic synthesis or in the isolation of natural products, another purification technique is often used before recrystallization or a distillation is performed. This is the technique of extraction: the removal of a compound from a solid or liquid mixture by a solvent. In liquid-liquid extraction, a solution containing a mixture of compounds is shaken with an immiscible solvent. The compounds in the mixture then distribute between the two liquid layers, or "phases", according to the solubility of the components in each of the two phases.

In chemically active extraction, one of the compounds in the mixture is altered chemically to change its solubility characteristics. Generally, the compound is altered by making the mixture either acidic or basic. This causes certain classes of organic compounds to form salts that are soluble in water, or the "aqueous" phase in a liquid-liquid extraction. Chemically active extraction is explained in detail in the Handbook for Organic Chemistry Lab. The following paragraphs explain some nomenclature terms referred to in the Handbook that you may not have encountered as a first-semester organic chemistry student.

Separation of Benzoic Acid and Phenanthrene

In this experiment, a mixture of benzoic acid and phenanthrene (Figure 6-1) will be separated.

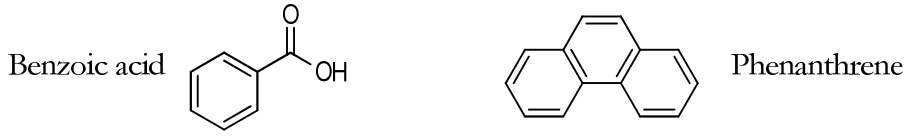


Figure 6-1: You will separate benzoic acid and phenanthrene.

As explained in the *Handbook*, under neutral conditions, both compounds are soluble in an organic solvent, which in this case is dichloromethane (also known as methylene chloride, CH_2Cl_2 or DCM). However, when the mixture is treated with an aqueous base, the benzoic acid is deprotonated and forms a water-soluble salt as shown in Figure 6-2.

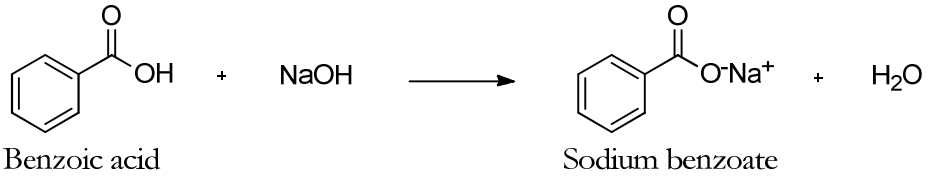


Figure 6-2: Benzoid acid is deprotonated with base.

As a water-soluble salt, the benzoic acid is more soluble in the aqueous layer than it is in the organic layer, while the unchanged phenanthrene remains more soluble in the organic layer than in the aqueous layer.

An efficient way of keeping track of the various steps in an extraction is by means of a flowchart. For example, the separation you will carry out can be summarized in the flowchart shown in Figure 6-3.

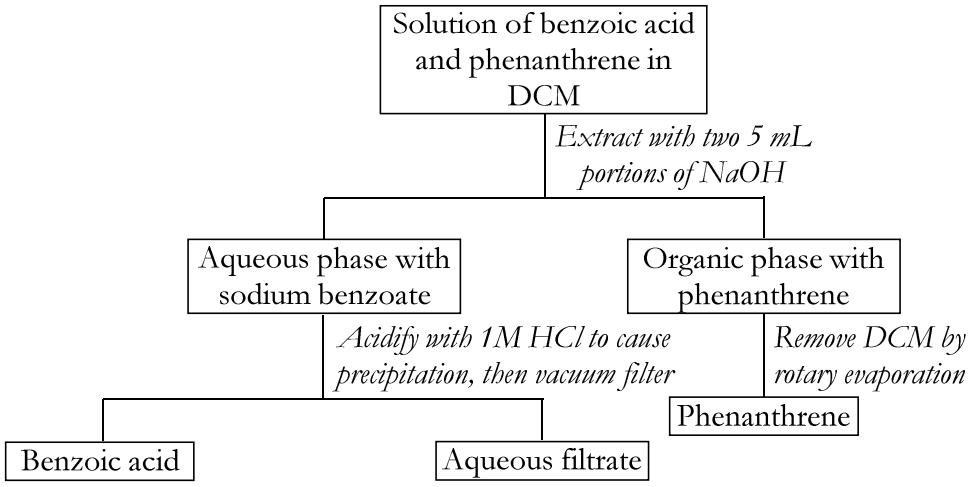
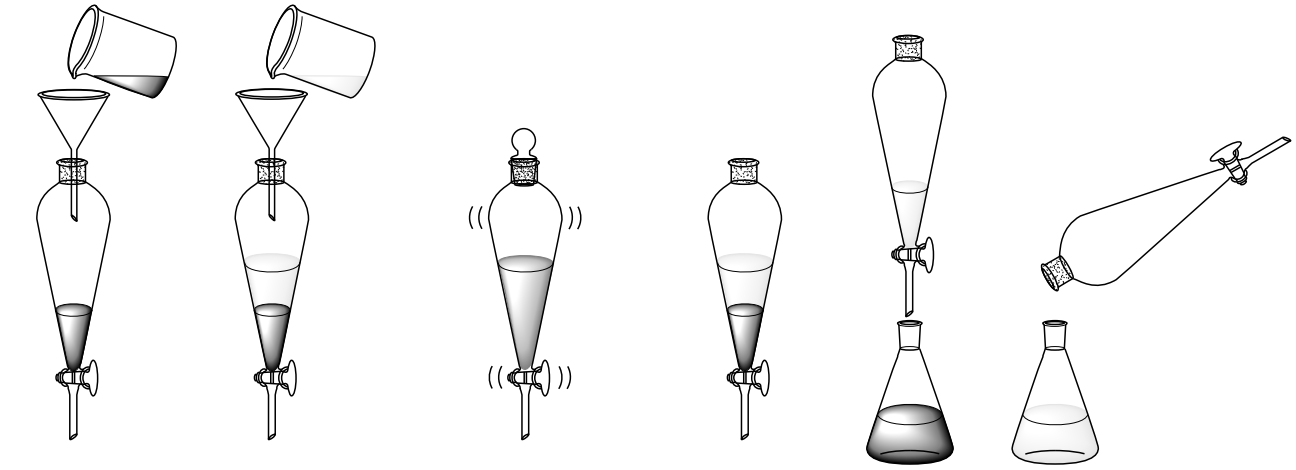


Figure 6-3: A flowchart of the extraction procedure you will use.

Liquid-Liquid Extraction

Your prelab for this experiment will need to be more detailed than just the steps in the flowchart above, since each extraction involves multiple steps. These are shown in Figure 6-4.



1) Add the DCM mixture to the separatory funnel
2) Add the aqueous solution
3) Stopper and shake (to vent, turn upside down and open stopcock)
4) Allow the layers to separate
5) Drain the lower layer into a flask
6) Pour the upper layer into another flask

Figure 6-4: Steps in a liquid-liquid extraction performed with a separatory funnel.

This experiment involves two extractions of the organic layer, each with a 5 mL portion of aqueous NaOH. This means that once you have completed steps in Figure 6-3, you must return the organic layer to the separatory funnel and repeat all these steps with a new 5 mL portion of aqueous NaOH.

To help determine which layer the organic is and which is the aqueous layer, look up the density of the organic solvent in an appropriate set of data tables. If the density is *less* than that of water (d=1), the organic layer will usually be the upper layer, whereas if it is *greater* than that of water it will be the lower layer. However, this can sometimes be misleading – if something very dense is dissolved in one layer, it may actually become the bottom layer regardless of the density of the pure solvent.

For this reason, it is better to use a more empirical method to determine which layer is aqueous and which is organic. This can be done by using a Pasteur pipet to inject a few drops of water into the upper layer. If the droplets disappear and blend into the upper layer, the upper layer is aqueous; if they sink to the layer interface and blend into the lower layer, then the upper layer is organic.

Depending on whether the organic layer is the upper or the lower layer, follow one of the methods below:

- If the organic layer is the upper layer, drain the lower aqueous layer into an Erlenmeyer flask, leave the organic layer in the separatory funnel, and add the fresh aqueous solution specified for the second extraction.
- If the organic layer is the lower layer, drain it into an Erlenmeyer, pour off and save the upper aqueous layer, then replace the organic layer in the dirty, empty separatory funnel, and add the fresh aqueous liquid specified.

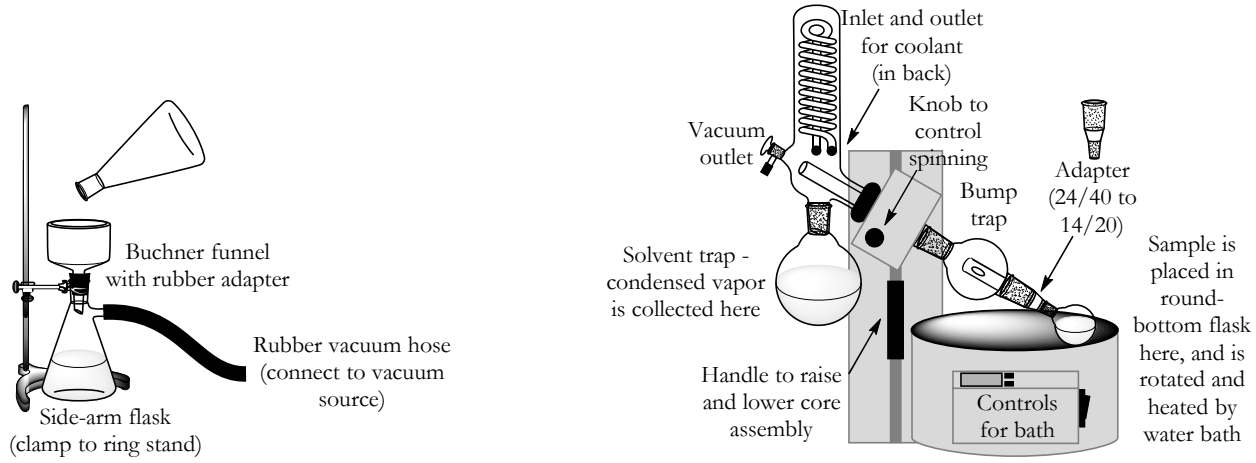
Whatever the case, **save all layers** in labeled Erlenmeyer flasks, so that if you make a mistake, you can still recover your products (this cannot be stressed enough).

Drying Agents

During the extraction lab you will be using drying agents for the first time (see the *Handbook*). A drying agent is an anhydrous, inorganic salt that is insoluble in organic solutions and that can absorb water. These agents are used to remove traces of water from organic solutions. Drying an organic layer is a very common step after performing an extraction, since the organic solvent will usually have some small amount of water dissolved in it (even if it is "immiscible" with water) and this must be removed.

Vacuum Filtration and Vacuum Solvent Removal

Techniques for both vacuum filtration and vacuum solvent removal will also be used for the first time in this experiment; these are covered in the *Handbook*. It is important to distinguish between these two techniques (Figure 6-5). **Vacuum filtration** involves taking a mixture of solid and liquid and using vacuum to pull it through a Buchner funnel, separating the solid from the liquid. **Vacuum solvent removal** involves taking a solution of compound dissolved in solvent and subjecting it to vacuum to force the solvent to evaporate, leaving a solid behind. This is usually done by means of a rotary evaporator (often called a "rotovap").



Vacuum filtration **Vacuum solvent removal ("rotovapping")**

Figure 6-5: The setups for vacuum filtration and vacuum solvent removal.

Safety Precautions

Both hydrochloric acid and sodium hydroxide solutions will cause burns if they remain in contact with your skin for a prolonged period—wear gloves and protective clothing while handling these reagents. While phenanthrene and dichloromethane are rated as only moderate health hazards, you should wear gloves and appropriate clothing while handling these chemicals.

Procedure

You will perform this lab individually. Before you begin, clean two NMR tubes and let them dry so they are ready to use later.

Weigh out 0.5 g of the benzoic acid/phenanthrene mixture (1:1 by weight) and record the weight to the nearest 0.01 g. Place the mixture in a beaker and add 10 mL of dichloromethane. When the solids are completely dissolved, transfer the mixture to your separatory funnel.

Using the steps shown in Figure 6-4, extract the organic layer (the dichloromethane solution) two times with 5 mL (each time) of 1M NaOH (aq.). Remember to make sure the stopcock at the bottom of the funnel is closed before putting anything in the funnel! Before draining the lower layer into a flask, be sure to remove the stopper at the top of the funnel.

Combine the resultant two aqueous layers, or aqueous extracts, and carefully add 1M HCl until the mixture is acidic (pH of 3 or below) according to pH paper. You do not have to use a new strip of pH paper for each measurement – you can lay a strip of paper on a Kimwipe, dip a glass rod in the liquid, and then touch it to a new spot on the pH paper each time. This allows you to make multiple measurements with a minimum of waste.

A white solid should "crash out" or precipitate from the solution as the acidification proceeds. Cool the solution in an ice bath, and then collect the precipitate by vacuum filtration. Be sure to clamp your side-arm flask to a ring stand – otherwise the rubber hose may twist it over, breaking your Buchner funnel. Wash the precipitate on the filter paper with a small amount of cold water. Allow the benzoic acid to dry and then determine the weight and melting point of this compound. Submit a sample for NMR, using $CDCl_3$ as the solvent.

Dry the organic solution over anhydrous sodium sulfate. Decant the solution to remove the drying agent. Remove the solvent (dichloromethane) from this solution by placing it in a round-bottom flask and connecting it to a rotary evaporator. Determine the weight and melting point of the solid phenanthrene that remains when all the dichloromethane has evaporated. Submit a sample for NMR, using $CDCl_3$ as the solvent. Make sure you name the samples differently so the files for the first spectra don't get overwritten.

Save your compounds for use in the recrystallization experiment!

When you are done with your separatory funnel, clean it and store it in your lab drawer with any glass parts removed (the stopper and/or stopcock, if they are made of glass). This is very important, as they may fuse onto the separatory funnel, ruining it and requiring you to purchase a replacement.

Wastes

Aqueous Waste: All aqueous filtrates.

Solid Chemical Waste: Used drying agents, pipets, filter papers and weigh papers.

Lab Report

Your conclusions should include:

- Analysis of the NMR spectra, following the checklist from the Practical NMR lab.
- How pure are the recovered compounds, based on NMR? What impurities are present?
- How pure are the compounds, based on melting point? Is this roughly in agreement with your NMR results?
- What is the percent recovery for each compound?
- Where does product loss occur in an extraction scheme?

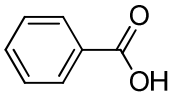
Study Questions

1) The organic layer is "dried" by adding anhydrous sodium sulfate. How do you know when you have added enough drying agent?

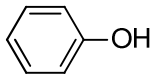
2) The handbook covers both vacuum and gravity filtration techniques. Explain why vacuum filtration is the method of choice for separating the benzoic acid from the neutralized aqueous solution.

3) Problem 8 in the Extraction Study Problem section of the *Handbook for Organic Chemistry Lab*.

4) Carboxylic acids and phenols can be separated by chemically active extraction if the pH of the aqueous layer is properly chosen. Prepare in your notebook a detailed flow chart showing how you would separate a mixture of benzoic acid and phenol:



Benzoic acid



Phenol

5) You have 10 grams of compound A dissolved in 100 mL of solvent X, and want to extract it into solvent Y using 100 mL of solvent Y. You know that the partition coefficient, K, is given by:

$$K = \frac{C_y}{C_x} = 2$$

C_y is the concentration of A in solvent Y (g/mL) and C_x is the concentration of A in solvent X (g/mL).

   a. How much compound A remains in X if you extract with 100 mL of solvent Y?

   b. How much compound A remains in X if you extract with 2 x 50 mL portions of Y?

   c. How much compound A remains in X if you extract with 4 x 25 mL portions of Y?

   d. What rule is suggested by your answers to a, b, and c?