Fall Organic Chemistry Experiment #2  
(Recrystallization and Melting Point)

Suggested Reading:
"The Student's Lab Companion: Laboratory Techniques for Organic Chemistry”, by John W. Lehman

   OP-7 (Heating using hotplates and hot water baths), p. 59-61
   OP-8 (Cooling), p. 70-71
   OP-15 (Gravity Filtration), p. 84-88
   OP-16 (Vacuum Filtration), p. 88-93
   OP-17 (Centrifugation), p. 93-95
   OP-28 (Recrystallization), p. 161-178

Introduction

Crystallization is the most important tool for the purification of solid organic compounds. In some cases, the crystals can be grown from a molten state. However, the removal of impurities becomes very difficult for crystals grown in this fashion. Therefore, recrystallization techniques involve dissolving the solid material in the minimum amount of hot solvent and enabling the solution to become saturated with respect to the solute, which then crystallizes (precipitates) from the solution. The goal is for a perfectly regular array of crystallizes to form in which foreign materials (impurities) are excluded. The ideal situation involves the complete precipitation of pure crystalline material (of a single substance) while the impurities remained dissolved in solution. In order to achieve this scenario, the impurities must be in a sufficiently low concentration relative to the desired substance. Once crystallized, the solid can be collected by vacuum filtration, washed with cold solvent, and dried (usually air-dried). The crystallization process generally involves the following seven steps.

1. Choosing the crystallization solvent
2. Dissolving the solute.
3. Decolorizing the solution.
4. Removing suspended (undissolved) solids.
5. Crystallizing the solute.
6. Collecting and washing the crystals.
7. Drying the product.

(1) Choosing the crystallization solvent.

The general rule of thumb to follow here is “like dissolves like”. If our solute is relatively nonpolar, then we will likely choose a solvent like hexane or petroleum ether. If our solute is polar, then we will choose something more toward methanol or acetone. At any rate, the best solvent will dissolve all of the solute when the solution is hot and none of the solute when cold. In addition, the solvent should either not dissolve
impurities at all or dissolve them very well (so they remain in solution at all times). The table shown at the end of this experiment has been included to help in your choice of solvent. The solvents are listed in decreasing order of polarity.

(2) Dissolving the solute.

When dissolving the solute, we want to be aware of a few details. The usual procedure involves adding the crystals to some beaker, flask, etc. and slowly (if not dropwise) adding the solvent with stirring. We want to be sure that we are also heating our solution over a hot plate or steam bath. We add just enough boiling solvent to get the crystals to dissolve (the **MINIMUM** amount). We will also like to avoid superheating our solution (a solution that is heated above the boiling point without boiling). These types of solution may all of a sudden boil violently and explosively. To avoid this, we generally insert a wooden applicator stick directly into the solution to promote even boiling. Boiling chips can also work and both devices provide an excellent surface for nucleation (the initial crystals that come out of solution). If you have added too much solvent, you may have to boil it off to a sufficient volume to allow crystallization.

(3) Decolorizing the solution.

To remove colored impurities from the solution, we often add a bit of activated carbon (charcoal) to which impurities can adsorb onto the surface. Pelletized Norit is the most common form and can be easily removed by gravity filtration.

(4) Removing suspended solids.

Any material that does not dissolve can be readily removed by a HOT gravity filtration or by decantation. Vacuum filtration is not a good option because it cools the solution in the process. The two primary gravity filtration options are: (a) filtration through a cotton-plugged Pasteur pipette; and (b) gravity filtration through a glass funnel fitted with fluted filter paper. *A diagram of each apparatus can be found in the suggested reading.*

(5) Crystallizing the solute.

This step is the most time consuming and often the most frustrating. However, keep in mind a few key points and you should be able to readily crystallize your solute. The most important thing is to be sure that you do not have too much of your hot solvent. If this is the case, then boil some of it off until you reach the saturation point. Once you are at this point, then you will want to SLOWLY cool your solution to room temperature on the benchtop. If crystallization does not begin (after a reasonable amount of time), then you can employ a few tricks to aid in the process. Some of the tricks include: (a) adding a seed crystal; (b) scratching the inside of the container with a glass stirring rod; or (c) further cooling the solution in an ice bath. Always remember to be patient. We want to do this step slowly to insure the formation of large, pure crystals.

(6) Collecting and washing the crystals.

Once crystallization is complete, the crystals can be separated from the ice-cold mother liquor (the filtrate) by vacuum filtration. We will also want to remove excess impurities
the may be dissolved in the solvent by washing with pure solvent. Keep in mind that we will want to wash with COLD solvent so that we do not redissolve any of the crystals.

(7) Drying the product.

Normally we let the suction run for a few minutes to pass as much of the solvent through to the filtrate as possible. Afterwards, we let the crystals air-dry for a sufficient period (24 hours) before performing further experiments or analyses (e.g. melting point).

Be aware that you may run into problems. If such is the case and you are unable to acquire crystalline material, do not give up. The process is really more art than it is science. You need to be patient and seek out help if you get stuck or things do not work out as expected.

Techniques:

1. Crystallization
2. Vacuum Filtration
3. Melting Points

Before Lab:

Go the web address shown below and watch Video #9 (Recrystallization) and Video #12 (Melting Point Determination):

http://ocw.mit.edu/ans7870/resources/chemvideo/index.htm

Procedure:

Obtain a sample of a solid unknown (approximately 2.5 g) and record the unknown number and mass in your laboratory notebook. Split the material into five "equal" portions. Record the mass of each sample and place each of the five solid fractions into five different 10 x 75 mm test tubes. Label the tubes according to the type of solvent used to dissolve each sample (you may choose from water, methanol, hexanes, toluene, diethyl ether, ethyl acetate, ethanol, and acetone). I would suggest that you select a wide variety of solvents based upon their polarities. Attempt to dissolve each of the solid samples using approximately 2 mL of the appropriate solvent. Record your results (soluble or insoluble). If the solid is soluble, discard the contents into the appropriate waste container in fume hood #2. For the insoluble ones, add a boiling chip and heat each to the boiling point in a boiling-water bath (boil 35-50 mL of water in a 150 mL beaker) or sand bath. Again record your results (soluble or insoluble). If the solid remains insoluble, discard the contents into the appropriate waste container in fume hood #2.

Select one of the remaining solutions, perform a HOT gravity filtration to remove undissolved impurities. You may want to use a small funnel fitted with filter paper and a 50 mL Erlenmeyer flask to collect the filtrate. Allow these solutions to cool to room temperature and observe whether crystallization occurs or not. If crystals do not appear, try to induce it to occur. Collect the crystals by vacuum filtration on a Hirsch funnel and wash the crystals with 1-2 mL of the COLD recrystallization solvent. Allow the crystals to air dry until later in the week and then
obtain its \textbf{mass} and \textbf{melting point} (See Lehman OP-33, page 222-230 -- you'll be determining melting point by the Mel-Temp method). Determine the identity of your unknown according to the table provided in Appendix VI (pgs. 341-355) of the Lehman text.