Chem 267. Recrystallization – Part 1. (revised 7/10)

Recrystallization is the most common method for purifying solid compounds. It will be used throughout this course so it is vital that you understand the principles behind it and learn to do it correctly from the start. In later experiments you will not be given detailed instructions for recrystallizations. You will simply be told to recrystallize a compound. A good recrystallization solvent is one in which the solid has a very high solubility at high temperatures and a very low solubility at low temperatures. Refer to the flow chart shown below. Note the distinction between melting and dissolving. Melting is the process in which a solid is converted to a liquid by supplying heat. Dissolving is the process that homogeneously disperses a solid into a solvent.

Do the Prelab Exercise on p. 61 as part of your prelab outline. Look over the photos on the course website to help understand the handout.

(1.) Solubility tests. Remember: sand baths take time to heat up so whenever a procedure calls for the use of a sand bath, the first thing to do upon entering the lab is to turn the controller on to a setting of about 35-40 % (NEVER HIGHER). Always turn the heater off before you leave for the day. You will test the solubility of four compounds - resorcinol, anthracene, benzoic acid, and 4-amino-1-naphthalenesulfonic acid, sodium salt (structures in lab text) - using water, toluene, and ligroin as the solvents. Use about 10 mg of each compound for the tests. It is not necessary to use a balance to measure out the solids accurately. A 10 mg sample of each solid in a reaction tube will be on display in the lab. Simply use an amount which approximates that. Use your plastic funnel to help transfer the solid to the tube. The solvent does not have to be measured exactly either. Use a disposable pipet and the calibration markings on p. 15 of your text or the calibrations on the reaction tube. This level of accuracy is enough for qualitative tests such as these and will be done often in certain microscale experiments, in cases where greater accuracy is not required. To heat solutions in a reaction tube, use the sand bath as the heat source and a boiling stick in the tube to promote smooth boiling. Failure to use a boiling stick will result in superheating of the solution followed by bumping of the solution out of the tube. In heating a tube with a sand bath, the temperature of the tube is controlled by adjusting the depth to which it is immersed in the sand. Use care in heating low-boiling solvents such as ligroin on the sand bath. Such solvents evaporate and bump easily. Note that ligroin and toluene are flammable. Never point the tube at yourself or at anyone else while heating.

Test solubilities as follows: First see if 10 mg of the compound is soluble in 0.25 mL of the solvent at room temperature (RT). After adding solvent always flick the tube with a finger to swirl the contents and to help ensure complete mixing, and give it a minute to dissolve. If the solid completely dissolves, it is considered to be very soluble at RT, in which case nothing more has to be done with that solid/solvent combination. If the compound is insoluble at RT, heat the tube to the BP of the solution. If the compound is still insoluble at the BP (give it a minute), it is considered to have very low solubility at all temperatures, in which case nothing more has to be done with that solid/solvent combination. If it seems that some of it has dissolved in 0.25 mL of boiling solvent, add another 0.25 mL and reheat it to see if it will all dissolve. If the compound has dissolved in boiling solvent (either 0.25 or 0.5 mL), cool the tube in cold water to see if crystallization occurs. Scratching the reaction tube with a glass stirring rod at the air-liquid interface may be necessary to induce crystallization (this produces a nucleation site). If crystals form, redissolve the solid by heating and allow the tube to cool more slowly, without cooling in cold water. Slow cooling may allow larger crystals to form. If the crystals are large enough, record the crystal form (needles, plates, prisms). The relative amount of the crystals, compared to the starting amount, should be noted.

In the same way, test all four solid compounds in each of the three solvents. The most efficient strategy is to test one compound with the three solvents before going on to the next compound. Prepare a table, as shown below, to summarize the results. In the write-up include a discussion of any structure-solubility correlations that you observe.

Sample solubility table:

sol of ~ 10 mg of compound A

	in ~0.25 mL solvent			in ~ 0.5 mL solvent		
	cold	hot	observations	cold	hot	observations
HOH	insol	sol	needles on cooling/good yield	-	-	-
toluene	insol	sl sol	plates on cooling/good yield	insol	sol	plates on cooling/gd yield
ligroin	insol	insol	-	-	-	-

sol of ~ 10 mg compound B (prepare a table as for compound A)

Dispose of all solutions in the Nonhalogenated Liquid Waste container in the hood. Minimize the number of Pasteur pipets being used. It is usually not necessary to dispose of a pipet after each use. For example, if you have just transferred an aqueous solution with a pipet and you are going to transfer another aqueous solution, simply rinse the pipet with water, if necessary, and use it again.

(2.) Recrystallization of Phthalic Acid. Microscale. Into a reaction tube, using a plastic funnel to make a clean transfer, weigh about 60 mg of phthalic acid accurately (it can be 55 mg or 65 mg but measure the amount exactly). The approximate amount of HOH needed can be calculated from the table on p. 79. The exact amount will be determined as the experiment is done. Add about half of the water to the phthalic acid and bring the solution to boiling (boiling stick). Continue adding the HOH dropwise at the boiling point (BP), allowing some time for the solid to dissolve after each addition, until the last drop of HOH dissolves the last amount of solid (at the BP). Clamp the tube to a ring stand and observe the solution as it cools to RT, undisturbed. Cool the tube further in ice to obtain a maximum yield.

Filtration using the pipet method. This is described on pp. 71, 72, Procedure A. This will be done many times over the course of the semester. This method of separating crystals from a solution can be done only if the crystals are large enough so that they do not get sucked up into the pipet. If the crystals are too small, another method, suction filtration, must be used. This will be described later on. With the pipet method, to prevent crystals from going into the pipet, it is essential to make a tight seal between the pipet and the bottom of the reaction tube. This can be done by stirring the crystals with the pipet to loosen them, and while expelling some air from the pipet beneath the solution to suspend the crystals above the bottom of the tube, push the pipet down onto the bottom of the reaction tube. With the pipet in place, draw solution up into the pipet. If this method is done correctly, very little solid will be drawn up into the pipet and a clean filtration will be accomplished. Use this method to separate the solution from the phthalic acid crystals. Generally the filtrate should be saved in another tube until it is certain that it is no longer needed. To remove further amounts of solution that may be left behind, tap the tube on a soft surface (such as a notebook) and repeat the pipet filtration. Using several drops of ice-cold water, rinse the crystals while keeping the tube cold in an ice bath, and remove the rinse water with the pipet as before. Rinsing with fresh solvent removes impurities clinging to the surface of the crystals. After removing as much water as possible with the pipet, use the curved end of the spatula to scrape as much of the solid as possible out onto a tared (pre-weighed)

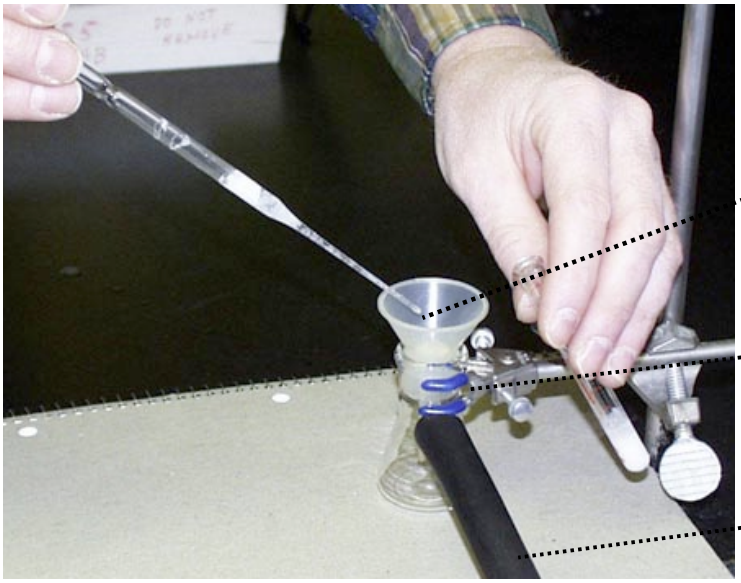
piece of filter paper. Because water evaporates slowly, the crystals must be left to dry at least overnight before weighing. Leave the crystals open in a safe place (e.g., place the filter paper at the bottom of a large beaker) in your drawer so that the crystals can dry completely by the next day or so, at which time they can be weighed, and a % recovery determined. The tube can also be left to dry and any product remaining in it can be scraped out and combined with the material on the filter paper. Do not try to determine the MP of the crystals – phthalic acid decomposes upon heating to the MP. Before you dispose of any sample, have your instructor examine it. Waste: dispose of the water filtrates in the Nonhalogenated Liquid Waste container. When finished with the phthalic acid, place it into the Solid Waste container.

Drying to constant weight. To be certain that a solid is dry, it must be weighed, left to dry for some period of time (at least 15 min), then weighed again. If the sample does not lose weight, it can be considered to be dry. Because water evaporates very slowly, solids recrystallized from water must be left at least overnight to dry. Solids recrystallized from most common organic solvents dry more quickly and are often dry within an hour. Note that solvent remaining in the solid will affect not only the weight of the solid but its MP range as well.

At this point if there is at least one hour left in the lab period, continue. If not, stop work and clean up. There will be time to finish it next week.

(3) Recrystallization of Benzoin. The amount of solvent to use is not given so must be determined by you. This is generally the case in a recrystallization. The solvent used here is a mixture of ethanol and water (70:30). Weigh about 60 mg (weighed exactly) of benzoin into a reaction tube. Remember that using your plastic powder funnel makes the addition of solids to a reaction tube much easier and neater. To add the correct amount of solvent, first add about 10 drops to the solid and allow the solution to boil gently for at least 15 - 30 seconds (use a boiling stick). Add a few drops more and allow it to boil gently for another 15 - 30 seconds. Repeat this until the final addition of solvent results in complete dissolution of the solid at the boiling point (BP). This is like doing a titration. NOTE: a common mistake is to not give the solid enough time to dissolve between additions of solvent. In such a case, too much solvent will be added and a poor or no yield of crystals will result. Another common mistake is to heat the solution too vigorously and/or for too long. This allows low-boiling solvents to evaporate between additions- if you add five drops of solvent and then allow five drops to evaporate you will make no progress - always note the approximate volume in the tube. Once the solid has dissolved completely at the BP of solution, place the tube into an insulated container (beaker with a paper towel stuffed into it) and allow it to cool slowly, undisturbed to RT, and then in an ice-HOH bath for a few minutes for maximum crystallization.

Suction filtration. It is usually advantageous to use the pipet method of filtration. In that method, the number of transfers from one container to another is kept to a minimum, thereby minimizing loss of material. In cases where the crystals are too small however, the pipet method cannot be used. In such cases suction filtration is required. An advantage of suction filtration is that the solution is more completely separated from the solid, so drying time is often shorter. The procedure for doing a suction filtration is described below and in Chapter 4. The set-up is shown in the following photo:



Transferring crystals with a pipet onto the filter paper on the Hirsch funnel.

Three-pronged clamp holding the filter flask securely.

Thick-walled vacuum tubing going from the filter flask to a trap, which then goes to a vacuum outlet.

Using a small three-pronged clamp, clamp the 25 mL filter flask securely to a ring stand and place the plastic Hirsch funnel into it. The funnel should have a small, white polyethylene disk pressed into it. (If the disk is contaminated rinse water then acetone through the funnel. If that does not clean the disk, remove it and insert another. This should be done only in cases of obvious contamination - certainly no more than once per semester.) A small piece of filter paper is added to the top of the disk - it should lie flat on top of the disk. With vacuum (thick-walled) tubing connect the side-arm of the flask to the vacuum trap that is in place at your workspace. The trap (a large filter flask) is connected to the vacuum source in the fume hood. So that the filter paper sits properly in the funnel, it is good practice to add a few drops of fresh solvent to the filter paper just before pouring the crystals onto the filter paper as described next. With the vacuum turned on to full (a few turns of the valve), remove the reaction tube from the ice bath, wipe the water off of the outside of the tube with a paper towel, stir the crystals to loosen them and suspend them in the solution, and in one concerted movement, pour the solution and crystals onto the top of the Hirsch funnel (as shown in the photo, the crystals may also be transferred with a pipet). The vacuum will quickly pull the solvent down into the filter flask, leaving the crystals in the funnel. Sometimes it is necessary to push down gently on the funnel to create a seal. Using the spatula, scrape as many remaining crystals as possible from the tube onto the funnel. As always in a recrystallization, the crystals must be rinsed with fresh solvent (same as that used in the recrystallization) to remove impurities that cling to the surface of the crystals. To minimize redissolving and thus losing product, the rinse solvent must be ice cold, a minimum amount must be used, and it must be left in contact with the crystals for as short a time as possible. Break (interrupt) the vacuum briefly by lifting the Hirsch funnel up away from the filter flask slightly, and using about 10 drops of ice cold ethanol-water mixture, rinse out any crystals remaining in the reaction tube onto the Hirsch funnel, while at the same time covering the crystals in the funnel with rinse solvent. Immediately reestablish the vacuum by pressing the funnel back down onto the filter flask to remove the rinse solvent. If the vacuum is not broken first, the rinse solvent will quickly pass right down into the filter flask without rinsing off all the crystals. This technique is tricky and requires practice. It is important to go through the motions in a concerted fashion, without too much hesitation. It is well worth your while to do a dry run and go through the procedure before doing the actual filtration and rinse. At all steps along the way, try to keep the solutions cold by keeping the tubes immersed in the ice-water bath as much as possible. Using too much rinse solvent and allowing solvent to warm up before separating it from the crystals will result in the product redissolving and thereby being lost. It is also important to dry water from the ice bath off of the outside of the tubes so that the water does not dribble down onto the crystals. Note that often it will appear that crystals have gotten through the filter

into the filter flask. Most often this has not actually happened. Instead, under vacuum, solvent evaporates, causing further crystallization. These crystals will be of lower purity than those collected so should not be combined with them.

Because water is one of the solvents in this recrystallization, the crystals will need to dry at least overnight. When the crystals have dried to constant weight (overnight), weigh them and determine the % recovery and MP. After the crystals are dry store them in a capped labeled vial. Before you dispose of the sample, have your instructor examine it (this is true for all samples.)

Use of the vacuum outlet. Centralized vacuum pumps provide house vacuum in this lab. To prevent solutions from being sucked up into the vacuum outlet, always use a trap between your sample and the vacuum outlet. A trap, which is made from a 500 mL filter flask connected to the vacuum outlet with a piece of vacuum tubing, is available at each work space. To use the trap, simply attach a second piece of vacuum tubing to the filter flask side arm and connect this to the vacuum filtration set-up for filtering. Be sure to clamp the tube or filter flask securely so that it does not fall over. With the trap between the vacuum outlet and your product, if solution gets sucked up into the tubing, it will be trapped in the filter flask. In using the vacuum, turn the valve fully open and check to see that the vacuum is working by placing a finger on the vacuum connection.

Note: slow cooling of a saturated solution, without disturbance, usually produces larger, purer crystals. Removing solvent from larger crystals is easier than removing it from smaller crystals. Allowing the reaction tube to cool slowly in an insulated container is therefore advantageous. A crude insulated container can be fashioned by stuffing a piece of paper towel into a small beaker. The reaction tube can then be pushed into the wad of paper and allowed to cool slowly, without disturbance. Once the tube has cooled to RT, it may be further cooled in an ice-water bath to promote further crystallization.

Minimizing waste - cleaning reaction tubes: once the contents of a tube is disposed of in the correct waste container in the hood, the tube should be washed using soap, water, and a brush. If the tube must be used immediately, and if it must be free of water, rinse it with a SMALL amount of acetone (several drops a few separate times), drain the acetone into the Nonhalogenated Liquid Waste container in the hood, and turn the tube upside down to drip dry. DO NOT FILL the tubes with acetone - this creates excessive waste and is unnecessary- use just a little to rinse the tube. If the glassware must be dried quickly, use a gentle stream of compressed air in the hood. Remember to be environmentally responsible and always minimize the chemical waste generated in the lab.

Conserve pipets. Do not throw away a pipet after each use unless it cannot be easily cleaned. If a pipet is used to measure a volatile (low-boiling) solvent, let the pipet dry after use and use it again. If an aqueous solution is measured, rinse with water and allow it to dry for future use. Minimize waste.

Waste Disposal: place all liquid wastes from these experiments into the Nonhalogenated Liquid Waste container. In your prelab outlines ALWAYS include procedures for the proper disposal of wastes as described in the handouts for that experiment.

BEFORE YOU LEAVE THE LAB: turn off the sand bath and all other utilities (vacuum, water, air), put away your equipment and lock your drawer, clean up your work areas, close the fume hood sash completely and ask your TA for her or his signature. In general, please try to keep the lab is as good condition as you found it. If you see caps off of bottles, replace the caps. If you see spilled chemicals, clean them up or at least report it to your TA.

Postlab Questions

1.) Draw a solubility (y) vs temperature (x) plot showing the three common solubility behaviors and indicate which one is that of a good crystallization solvent.

2.) Briefly describe how soluble impurities are separated from the desired compound, at the molecular level.

3.) Using the information in Chapter 4 of Williamson, how many mL of boiling water are required to dissolve 2.5 g of phthalic acid?

4.) If the resulting solution in Problem 3.) were cooled to 14° C, how many g of phthalic acid would crystallize out?

5.) What structural property of 4-amino-1-naphthalenesulfonic acid, sodium salt makes it very soluble in water?

FLOW CHART FOR RECRYSTALLIZATION