Chem 267. Recrystallization - Part 2. (revised 06/30/2014)

If necessary, finish Recrystallization - Part 1. In this experiment, you will also recrystallize an unknown. Review the necessary techniques such as vacuum (suction) and pipet filtration.

Lab Clean-up. For reasons of safety and effectiveness, an essential part of lab work is keeping the lab in a clean and orderly state. Please keep bottles capped. Many chemicals will lose their effectiveness or evaporate if left open to the atmosphere. If caps are not in place, the potential also exists for toxic chemicals to enter the lab atmosphere. Please clean up spills immediately so others do not become contaminated. Most of you will soon join a research group. You will quickly find that sloppy and unsafe behavior is not tolerated one bit by your advisor or coworkers. Learning good lab habits now will help greatly later on.

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

(1.) Purification of an Unknown. Using two different solvents you will recrystallize two 60 mg samples of an unknown that is contaminated with soluble impurities. Your TA will assign the unknown to you. You must first determine suitable recrystallization solvents by doing solubility tests and preparing a table as before. Several solvents are available to you in this experiment. These are water, methanol, ethanol, ligroin, and toluene. Try as many of these solvents as necessary to find at least two that work well. The ideal solvent is one that produces the highest recovery of the purest most well-formed crystals. One of the two that you choose will probably work better in terms of purification or yield. You will assess the effectiveness of a particular recrystallization by comparing the results of the two recrystallizations. After you decide upon a solvent, weigh about 60 mg of unknown into a reaction tube. It does not have to be exactly 60 mg but it must be weighed exactly so that a % recovery can be calculated. Recrystallize the unknown from the two solvents of your choice. Note that water is a good solvent because it is non-toxic and non-flammable but that it does not evaporate readily. A sample recrystallized from water or any high-boiling solvent must be allowed to dry at least overnight. The solid will be filtered either by the pipet method or by suction filtration. If it seems that the crystals are large enough, try the pipet method. If crystals are sucked up into the pipet, you will need to do a suction filtration instead. Once both recrystallized samples have dried to constant weight, weigh them, determine a % recovery and determine the MPs of both samples. To save some time the MP of the impure material may be taken beforehand, while samples are drying. CAUTION: always turn off the Mel-Temp and the digital thermometer after use (turn the voltage to zero AND turn the switches to off). If the Mel-Temp is left on, the apparatus may become overheated and damaged. Using the MP, zero in on the identity of your unknown by checking the list of possible compounds at the end of this handout. Note that if the crystals are not completely dry, the solvent which remains will behave as an impurity and cause a MP depression. On the list you will notice that your MP matches the MP of two possible compounds. From MP alone then you will not be able to distinguish between the two. To help you make an unequivocal determination, a sample of one of the two possible compounds will be available so that you may carry out a mixed MP determination (p. 50 just above "Apparatus". In a mixed MP determination the solids should be powdered and mixed well. Note that a very small sample is all that is needed.

(2) TLC Analysis of Recrystallization Unknown. Run the two samples of purified unknown alongside the impure unknown. You will need to determine an appropriate development solvent by trial and error. Use a different development chamber for each solvent. Use the tables on pp. 170, 171 as a guide. Remember that the solvent used for spotting has no effect on the separation. It is used simply as a vehicle to transport a sample onto the plate. Once a spot has been made, this solvent evaporates. Its only requirements are that it dissolves the sample and that it evaporates readily.

A note on TLC development solvent: the dielectric constant of a solvent is a measure of the solvent's polarity. For example, ethyl acetate, with a dielectric constant of about 6 is more polar than hexane with a dielectric constant of about 2. Mixing the two in varying proportions results in a mixed solvent system that can have a dielectric constant of between 2 and 6. For example a 50:50 mixture would have a dielectric constant of about 4. Thus using a solvent mixture in this way can provide a solvent system with a finely-tuned polarity, which might be required for a particular TLC separation, when any single solvent is too polar or not sufficiently polar. *Tert*-butyl methyl ether and hexane can also be used as a solvent system for TLC

Try also to use other evidence to confirm the identity of your unknown. Draw the structures of the two possibilities. Consider other physical properties such as solubility behavior, crystal structure, or color or if one of the possibilities is an acid or base check the acidity of an aqueous solution using pH paper. Do some detective work. In your report discuss structure and properties of the two compounds. Physical properties of many compounds are given in the Table of Physical Constants of Organic Compounds found in the "CRC Handbook of Chemistry and Physics", which is in the reference section of the Physical Sciences Library (a copy is also available in the lab). Also check chemfinder.com or just google the name of the compound and see what you find. In some cases though these physical properties alone will not be sufficiently different to enable you to make a distinction. The mixed MP however will be definitive.

Postlab Questions.

1.) What solubility behavior is desired in a recrystallization solvent?

2.) What would be the effect of using too much rinse solvent in a recrystallization?

3.) In a recrystallization, what would be the effect of using rinse solvent that has not been cooled in ice?

4.) How can you be certain that a sample is completely dry?

5.) In lecture it was stated that "structure determines properties". Draw the structure of your unknown and comment on two characteristics that define its overall structure as described in lecture.

6.) Based on what was discussed in lecture, list one specific example of each of the following general types of properties - chemical, physical, biological.

7.) In the recrystallizations done so far, insoluble impurities have not been present. If insoluble impurities had been present in your unknown, what additional step or steps would need to be taken. Outline the procedure that you would follow.

Table 1. List of possible unknowns.

Compound	Melting Point (°C)
p-Anisidine	57
cis-Cinnamic acid	58
Benzhydro	69
Biphenyl	71
Vanillin	80-81
Naphthalene	81
Benzil	95-96
Acenaphthene	96
Acetanilide	115-116
Isovanillin	116-117
Benzoic Acid	122
trans-Stilbene	124-125
Benzoin	133-134
trans-Cinnamic Acid	135-136
4-Nitroaniline	149
1-Phenylurea	149
Salicylic Acid	159
Benzanilide	163
Hydroquinine	171
Malonic acid diamide	171-172

Values here differ from those on the Melting Point Known list because you have purified the compounds. Melting point values here are from the CRC Handbook, 54th edition.