

LABORATORY 3

Recrystallization

Concept goals: Relationship between structure, polarity and solubility, role of temperature on solubility, characteristics of a good recrystallization solvent.

Operational goal: Develop the skill to perform a recrystallization effectively, including the use of minimal solvent, washing and drying crystals.

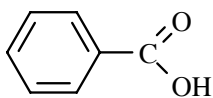
Introduction

Organic compounds synthesized in the laboratory or isolated from natural sources are often contaminated with impurities. **Recrystallization** is a widely used purification technique for removing impurities from organic compounds that are solid at room temperature. This method relies on the observation that the solubility of a compound in a solvent generally increases with temperature. Conversely, as a solution cools the solubility of a compound will decrease until the solution becomes saturated and crystals form.

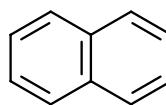
Recrystallization can produce very pure compounds. The choice of recrystallization solvent is critical. A good recrystallization solvent will not dissolve the solid compound at low temperatures, but will dissolve it at high temperatures. The cold solvent also needs to dissolve the impurities. A typical recrystallization procedure involves dissolving the impure solid in a minimal amount of boiling solvent, followed by a cooling period. If insoluble impurities are found in the sample during heating, additional steps (hot-gravity filtration) are taken to remove them before cooling. After the hot solution cools and reaches the saturation point, small seed crystals of the compound will form in the solution. Slowly, additional molecules of the compound attach to the seed crystal and the crystals grow. Since molecules in the crystals typically have a greater affinity for other molecules of the same type than they do for any impurities, the process of crystal formation gives rise to relatively pure crystals. The impurities originally present in the compound are left in solution. The solution containing impurities is then removed from the pure crystals via vacuum filtration.

Typically, a single recrystallization solvent is chosen for purification; however, some solids are not easily purified from a single solvent and require a 'mixed' solvent. A mixed recrystallization solvent contains two miscible solvents. The solid compound must be very soluble in one (solvent A) and nearly insoluble in the other (solvent B). Typically, the impure solid is dissolved in a hot solvent A, followed by addition of solvent B to reach saturation. At this point, seed crystals will form and grow.

In this laboratory you will carry out the recrystallization of two organic compounds: benzoic acid and naphthalene. The first experiment gives you the opportunity to practice the technique by recrystallizing benzoic acid from a single solvent (water). In the second experiment, your goal will be to purify an impure sample of naphthalene by



Benzoic Acid



Naphthalene

recrystallization using a mixed solvent (methanol-water). You will then assess its purity by taking a melting point.

Reading and Pre-Lab Assignments

Read the following sections in *The Organic Chem Lab Survival Manual: A Student's Guide to Techniques* by James W. Zubrick, John Wiley & Sons, Inc.

- Interpreting a Handbook. You will need to use these resources to look up data for benzoic acid, naphthalene, and methanol.
- Recrystallization. See especially "General Guidelines for Recrystallization", and "Working with a Mixed-Solvent System".

Before you come to the laboratory, do the Pre-Lab assignments for this laboratory as assigned by your instructor.

Prepare your laboratory notebook as required by your instructor.

Procedure

Experiment 1 – Recrystallization of Benzoic Acid

Weigh 1.0 g of benzoic acid, recording the exact amount, and place it into a 50 mL Erlenmeyer flask. Place 20 mL of distilled water into a second 50 mL Erlenmeyer flask. Add a boiling stick and, using a hot plate, heat the water to boiling.

CAUTION! *Handle the hot flasks with a towel or tongs to prevent burning your fingers!*

Using a Pasteur pipette, add 0.5-1 mL of the boiling solvent to the flask containing the benzoic acid. Swirl the flask with each addition and place it on the hot plate to maintain boiling. Continue to add water in 0.5 mL portions until the benzoic acid just dissolves.

Why is it important to use a minimal amount of solvent? What would happen if excess solvent were used? If too little solvent were used?

Remove the flasks from the hot plate and allow the benzoic solution to cool to room temperature. When the solution has reached room temperature, place the flask in an ice-water bath for 5 minutes to further cool the solution and complete crystallization.

Is placing the hot flask directly in an ice-bath a good idea?

Collect the crystals of benzoic acid by vacuum filtration using a small Hirsh funnel, rinsing the flask with a minimal amount of cold water. Let the crystals air dry. After the crystals have dried, weigh it and calculate your percent recovery. If you pre-weigh your filter paper, calculation of percent recovery will be easier. Note: % yield is a term reserved for synthesis experiments, % recovery is a more accurate description of what you are doing in this experiment. Use melting point to assess the purity of your crystals.

Experiment 2 – Recrystallization of an Impure Sample of Naphthalene

CAUTION! *Methanol boils at a much lower temperature than water. You will need to turn the temperature of your hot plate down to prevent it from boiling-over. This step should be done in the hood to minimize exposure to fumes.*

Weigh 1.0 g of impure naphthalene and place it in a 50 mL Erlenmeyer flask along with 8-10 mL of methanol and a stir bar. Heat the mixture to boiling on a hot plate with stirring.

Add distilled water dropwise from a pipette while swirling the flask. As each drop of water is added to the solution, it will turn cloudy for an instant and then it will clear. Continue to swirl and add water dropwise until the cloudiness persists while the solution is boiling. At this point add a few drops of methanol to make the solution clear again. Remove the flask from the hot plate and allow to cool to room temperature. When the solution has reached room temperature, place the flask in an ice-water bath along with another flask containing a couple of milliliters of methanol and water in the ratio of 5:1.

Why is the water causing the solution to become cloudy? What is the cloudy substance?

Collect the crystals of naphthalene by vacuum filtration using a small Hirsh funnel. Use the cooled methanol and water mixture to rinse the flask and wash the crystals free of the crystallization solvent. Press the crystals into the Hirsh funnel with a spatula and pull air through the filter cake for a few minutes to promote drying. Transfer the crystals to a piece of filter paper to dry. Determine the weight of the dry naphthalene and calculate your percent recovery. Take a melting point of both your purified sample and of the original impure naphthalene to assess the purity of your crystals.

How is vacuum filtration completing the purification of your sample? Where are the impurities at this point?

Results, Discussion and Conclusion

Write your results, discussion of results and your conclusion. Complete any post-lab questions.

Abstract

This part should be filled in after the completion of the experiment and analysis of all data. When submitting the report, the abstract should appear at the beginning of the report.

Report

Adhere to the format required by your instructor and submit the report on time.

Summary

1. Recrystallization is a purification technique in which an impure solid is dissolved in a hot (usually boiling) solvent and cooled to room temperature or below, in order to crystallize the pure solid. The impurities will remain in solution and can then be separated via vacuum filtration.
2. Given an impure sample and the solubility properties of each component in the mixture, you should be able to figure out how to remove the impurities using crystallization techniques.
3. You should be able to assess the effectiveness of the purification using melting points.

Questions

Your instructor may assign these questions as pre- or post-Laboratory assignments.

1. What is the purpose of crystallization in an organic chemistry procedure?
2. Using the solubility data you found for benzoic acid, calculate the volume of water required to dissolve 1.0 g of benzoic acid at room temperature. Calculate the volume of boiling water needed to dissolve 1.0 g of benzoic acid.
3. Explain why a Büchner or Hirsh funnel is used to isolate the final crystallized product instead of stem funnel.
4. Explain when a mixture of solvents would be used to carry out a recrystallization instead of a single solvent.
5. Assume that you are given 1 g of an unknown compound, which could be acetanilide or phenacetin. The solubility of the two organic compounds, acetanilide and phenacetin are given below. You used to enough water to recrystallize phenacetin but later on you found out that the unknown given to you was acetanilide. Comment on whether or not this would have affected your percent recovery of the unknown after recrystallization and if so, how.

Substance	Formula Wt.	m.p.°C	Solubility, cold water	Solubility,boiling water
Acetanilide	135.2	114	0.54 g/100 mL	5.0 g/100 mL
Phenacetin	179.2	135	0.076 g/100 mL	1.22 g/100 mL

6. Give three criteria for a good recrystallization solvent.
7. You want to purify 10 grams of benzoic acid that has been contaminated with 0.2 g of salicylic acid. You have found the following data by looking at the Merck Index:

Compound	Solubility in water at 20°C (g/10 mL)	Solubility at 100°C (g/10 mL)
Benzoic Acid	0.029	0.680
Salicylic Acid	0.22	6.67

- a) What volume of Boiling water is needed to dissolve the 10 g of benzoic acid? (show calculations)
- b) How much benzoic acid (in grams) will crystallize after cooling to 20°C (show calculations)
- c) Will any salicylic acid crystals form? Why or why not? (show calculations/ reason for answer)
- d) What is the maximum percent recovery of benzoic acid that could be recovered in the first crop of this recrystallization? (Show calculations)
- e) Will the benzoic acid be pure? Why or why not?