LABORATORY 3

Crystallization

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

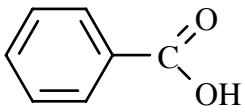
Operational goal: Develop the skill to perform a recrystallization effectively, including the use of minimal solvent, use of charcoal if needed, filtering a hot solution, washing and drying crystals.

Introduction

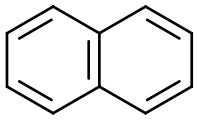
Organic compounds synthesized in the laboratory or isolated from natural sources are often contaminated with impurities. Recrystallization is a method for removing impurities from organic compounds that are solid at room temperature. This method relies on the observation that the solubility of a compound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

Recrystallization can produce very pure compounds. When a warm solution of a compound cools and reaches the saturation point, small seed crystals of the compound form in the solution. Slowly, additional molecules of the compound attach to the seed crystal and the crystals grow. Since molecules in the crystals 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.

In this laboratory you will have the opportunity to carry out the recrystallization of two organic compounds: benzoic acid and naphthalene. The first experiment will give you practice in the technique as you recrystallize benzoic acid from water. In the second experiment, your goal will be to purify an impure sample of naphthalene by recrystallization. You will then assess its purity by taking a melting point.



Benzoic Acid



Naphthalene

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", "Activated Charcoal," 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 keep it a boiling. Continue to add water in 0.5 mL portions until the benzoic acid just dissolves.

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.

Collect the crystals of benzoic acid by vacuum filtration using a small Hirsh funnel. Let the crystals air dry. Weigh it and calculate your percent recovery. If you pre-weigh your filter paper, calculation of percent recovery will be easier. (% 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

Obtain a small sample of impure naphthalene and take its melting point. Observe its physical appearance and record this melting point range as an assessment of its purity.

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

Prepare your small funnel for the filtering step by placing a small piece of glass wool loosely into the bottom of the funnel. Weigh 1.0 g of impure naphthalene and place it in a 50 mL Erlenmeyer flask along with 12 mL of methanol and a boiling stick. Heat the mixture to boiling on a hot plate. Remove the flask from the hot plate and allow for it to cool slightly. Filter the solution through the glass wool into a clean 50 mL Erlenmeyer flask. Add 2 mL of methanol to the used flask, warm it on a hot plate. With a pipette, use this liquid to wash the glass wool. When the filtration is complete, the total volume should be approximately 8-10 mL. If not, evaporate the excess carefully on the hot plate.

Add a boiling stick, heat the solution to the boiling point and 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.

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 to assess the purity of your crystals.

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. Crystallization is a purification technique in which an impure solid is dissolved in a hot (usually boiling) solvent and the solution is filtered and cooled to room temperature or below, in order to crystallize the pure solid. The impurities will remain insoluble even in the hot solvent and hence would be gotten rid of during filtration of the hot solution.
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.^{o}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^{o}C (g/10 mL)	Solubility at 100^{o}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 will crystallize after cooling to 20^{o}C (show calculations)
c) Will any salicylic acid crystals form? Why or why not? (show calculations/ reason for answer)
d) What is the maximum amount 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?