

EXPERIMENT 2 RECRYSTALLIZATION

A. PRELAB ASSIGNMENT

1. Prepare a Table of Physical Constants in your lab notebook listing structures, formulae, molecular weights, and solubilities for each of the following, and boiling points of solvents, and melting point of solute.

Solvents: Toluene, Methanol, Water

Solute: Triphenyl methane

2. Copy the table given on page 23 in the **Observations** section of your notebook, opposite the **Procedure** for the Solubility Tests.

B. THEORETICAL BACKGROUND

Recrystallization is one of the most important purification techniques used in organic chemistry. Recrystallization is used to purify solids contaminated by relatively small amounts of solid impurities. Compounds having different solubilities at different temperatures can generally be recrystallized. For most compounds, the solubility increases as the temperature of the solvent increases. In practice, this means that a suitable solvent for recrystallization is one in which there is a large difference between the solubility of the compound in hot solvent compared with that in cold solvent. A compound which dissolves to form a saturated solution at or near the boiling point of a suitable solvent can be largely recovered since it will come out of the solvent, or recrystallize, when the solution is cooled. If the compound is impure, removal of insoluble impurities (by gravity filtration) is accomplished with the desired product dissolved in the hot solution. Other impurities remain largely dissolved even when the solution is cooled because they are more soluble and/or present in much smaller amounts than the desired product. Recrystallizations are designed, by proper use of solvents, to maximize the yield and purity, although the degree of recovery and quality often vary inversely.

Choice of a suitable solvent:

1. The desired compound should be very soluble in the hot solvent.
2. The desired compound is very insoluble in the cold solvent.
3. The solvent should be easily removable (fairly volatile) from the desired product.

Choice of a solvent pair:

Sometimes no single solvent can fill the requirements of suitability. In such cases, two miscible solvents (solvent pair) can be combined to produce a suitable solvent. Criteria for solvents in a solvent pair are:

1. The desired compound will be relatively soluble in solvent #1 even when the solvent is cold.
2. The compound will be relatively insoluble in solvent #2 even when the solvent is hot.
3. Solvent #1 and solvent #2 must be miscible.

A combination of two miscible solvents as described will often provide a solvent pair in which there is a large difference between the solubility of the compound in hot and cold solvent.

Solubility

The theory of solubility is simplistically described by the phrase "*like dissolves like*," i.e. solutes tend to dissolve in solvents of similar, or like polarity. Some commonly used solvents for recrystallization are pentane, hexane, toluene, ethyl acetate, ethanol, methanol, and water.

In this experiment, we will use the solvents, toluene, methanol, and water. Of these solvents, toluene is the least polar, and water is the most polar.

tube in an ice bath and observe and note the amount of recrystallization, if any.

Refer to the structures of the solvents and solute to give a tentative prediction of the solubilities on the basis of polarity. This will help you develop a sense of lab work as you compare theoretical prediction with actual result.

Remember, as you fill in the table, that the results are a matter of degree, judged more by correct trend than by actual number of '+'s and '-'s. Record your Results in the Solubility Table you copied. When you have found a solvent suitable for the recrystallization of C, report this to your instructor and if you are correct, proceed with the recrystallization.

b. Recrystallization of Compound C

Plan ahead. Obtain about 120 mL of the most suitable solvent found. (Use a 250 mL flask and keep it covered.)

1. Weigh about 4 g impure C (note the exact amount to four decimal places) into a 125 mL Erlenmeyer flask on an analytical balance. Record the weight to four decimal places. Add a boiling chip (boiling chips should never be added to a hot solution). Dissolve this sample of impure C in the minimum volume of suitable hot solvent necessary to dissolve the desired product and soluble impurities. Watch for insoluble impurities, which do not change in amount no matter how much solvent is added. Too much solvent will reduce recovery, unless extra time is spent evaporating the excess. Mark the final solvent level on the outside of your flask with a wax pencil.
2. Add an extra 25 mL of solvent to the Erlenmeyer to avoid premature crystallization of the desired product in the filter funnel during step **4.(c)** below. This extra amount will be evaporated before recrystallization is allowed to take place (in step **5**, below).
3. If colored impurities are present, add an adsorbent such as Norite (finely divided carbon), which adsorbs colored compounds onto its surface. Once again, judgment is required, since too much Norite will adsorb not

only the colored impurity, but the desired product as well, reducing yield.

Do not add Norite to a boiling solution; it will erupt! Cool slightly and add roughly two level scoop tipfuls. Reheat the solution to boiling.

4. To remove the insoluble impurities, Norite, and adsorbed colored impurities, the solution should be filtered hot, according to the following procedure:

The following procedure must be done quickly and efficiently, so that glassware stays hot and the loss of solvent by evaporation is kept to a minimum.

- (a) Stir and boil the recrystallization mixture on the side of the steam bath. At the same time, heat about 30 mL of solvent in a 50 mL flask on the side of the bath.
 - (b) Remove the stemless funnel from the oven, and suspend it on a ring with the funnel tip inside the mouth of a 125 mL receiving flask located on the center of the bath. Use a paper towel to handle the hot funnel; place a few boiling chips in the receiving flask. Insert a fluted filter paper, and wet it with a little hot solvent.
 - (c) Immediately pour the boiling mixture into the filter. Fill it no more than 1 cm from the top. As the filtration proceeds, keep the mixture boiling, and keep the filter nearly full (no more than 1 cm from the top) of hot liquid.
 - (d) When the flask is “emptied,” rinse it with two 5 mL portions of hot solvent. Pour each rinse through the funnel in order to collect as much product as possible.
5. The filtered solution must be concentrated, since excess solvent was used in step 2 above to avoid premature crystallization. Maximum recovery will result if the hot solution is close to saturation at this point. A saturated solution is one that has dissolved all the solute that it can hold at a given temperature. Place a take-off tube over the flask and evaporate solvent on a steam bath until the level reaches the volume that you marked on the

original flask in step 1 (page 24). (See diagram on the last page of this manual.)

6. When the solution is concentrated, remove the take-off tube and reheat the solution to a full boil. Make sure that all solid is dissolved. Then carefully set the solution aside and allow it to recrystallize until it cools to room temperature. Cool the solution in an ice bath for about 10 minutes. (While the solution is cooling, set up the suction filtration apparatus. Also, cool about 10 mL of fresh solvent in a small beaker in an ice bath to be used in steps 7 and 8, below).
7. Scrape the crystals off the walls, swirl the flask and slowly pour the mixture into the Büchner funnel. As soon as the bulk of the liquid has been sucked through, disconnect the suction hose. At this point the crystals are wet with the mother liquor, which contains the dissolved soluble impurities. If suction continues, solvent will evaporate and deposit the impurities on the surface of the recovered crystals. Use a small amount of ice-cold solvent to aid in completing the transfer of recrystallized C to the Büchner funnel. Wash the product. With the suction off, cover the surface of the crystals with a minimum volume of ice-cold fresh solvent. Immediately turn the suction on. Repeat, if necessary, keeping in mind that some C is lost with each wash. Pour all filtrates into the non-halogenated waste container.
8. Cover the Büchner funnel containing the solid with a Kimwipe and secure with a rubber band. Make a few holes in the Kimwipe to permit the crystals to air dry. Store the covered Büchner funnel in a beaker.

Steps 9 and 10 should be done only after C is dry (during next week's laboratory session).

9. Weigh an empty vial (this is called the "tare" weight), add the purified C, and reweigh. Record the weights. Label the vial with your name, the identity of contents, i.e., "Purified Triphenylmethane," lab day, weight of product, and melting point of contents.

10. Determine the melting points of recrystallized C, the original impure C, and pure C (on reagent shelf) side by side and record the values.
11. Calculate the % recovery.
12. Place the vial containing the recrystallized product in the box for your lab day on the front desk.

D. QUESTIONS

1. Given the solubility results shown in the table below, choose the most suitable solvent or solvent pair for each solute. Neither water nor ethanol is miscible with ligroine (mixed hexanes), and water does not mix with toluene.

Solubility Data

| Compound | water | | ethanol | | toluene | | ligroine | |
|----------|-------|-----|---------|-----|---------|-----|----------|-----|
| | cold | hot | cold | hot | cold | hot | cold | hot |
| G | - | + | - | ++ | ++ | +++ | ++ | ++ |
| H | +++ | +++ | +++ | +++ | +++ | +++ | - | - |
| I | - | - | +++ | +++ | ++ | ++ | + | + |
| J | - | - | - | - | + | +++ | +++ | +++ |

Please keep your answers to the following questions brief.

2. If impure "C" had been a white crystalline solid, should Norite have been used in the recrystallization? Explain.
3. Why is some "C" lost each time it is washed with fresh cold solvent while in the Buchner funnel?
4. If the melting point of purified "C" was determined before the sample was completely dry, what errors would most likely result? Explain.
5. Explain why the suction is turned off before the wash liquid is added to the Büchner funnel.

6. Naphthalene is an aromatic hydrocarbon with m.p. = 80°C. Is toluene likely to be a good solvent for recrystallization of naphthalene? (Hint: Find the structure of naphthalene. Then refer to your Table of Physical Constants.)
7. 11.00 g of compound X (solubility 1.0 g/100 mL at 0°C) is contaminated with 1.00 g of compound Y (solubility 1.1 g/100 mL at 0°C) and 1.00 g of compound Z (solubility 1.5 g/100 mL at 0°C). The impure mixture is recrystallized from 70 mL of solvent, cooled to 0°C and filtered. (The collected crystals are called a **crop**.)

Showing your calculations, answer **a-g** below: (for **b** and **d-f**, compare % X in each).

- a. What is the composition (grams of X, Y, and Z) of first crop of crystals?
What is the percentage of X in the first crop?
- b. Has the purity of compound X in the first crop improved over that in the original mixture?

The mother liquor was evaporated to 40 mL, then cooled to 0°C and filtered to obtain a second crop of crystals:

- c. What is the composition of the second crop?
- d. Is the second crop of compound X as pure as the first crop?
- e. Is the second crop of the compound X as pure as the original mixture?

If the original mixture was recrystallized from 90 mL of solvent instead of 70 mL:

- f. Would the purity of the first crop increase or decrease?
- g. Would the yield of compound X in the first crop increase or decrease?

E. DISCUSSION AND CONCLUSIONS

Comment on the purity of the given compound before and after recrystallization. Also comment on the percent recovery. Add your own Discussion.