From: Intro to Org. Lab. Tech.: a microscale approach, 4/e (PLKE)

3 EXPERIMENT 3

Crystallization

Crystallization
Vacuum filtration
Melting point
Finding a crystallization solvent
Mixture melting point
Critical thinking application

The purpose of this experiment is to introduce the technique of crystallization, the most common procedure used to purify crude solids in the organic laboratory. For a thorough discussion of crystallization, read the chapter on this technique (pp. 647–668) before proceeding because an understanding of this material is assumed in this experiment.

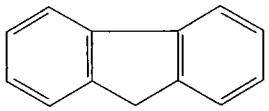
In Experiments 3A and 3B, you will carry out a crystallization of impure sulfanilamide using 95% ethyl alcohol as the solvent. The impurity is acetanilide, which is often used as a starting material for synthesizing sulfanilamide (see Experiment 48, p. 392). Sulfanilamide is one of the sulfa drugs, the first generation of antibiotics to be used in successfully treating many major diseases, such as malaria, tuberculosis, and leprosy (see the essay "Sulfa Drugs," p. 388).

In Experiments 3A and 3B, and in most of the experiments in this textbook, you are told what solvent to use for the crystallization procedure. Some of the factors involved in selecting a crystallization solvent for sulfanilamide are discussed in Section 11.5 on page 660. The most important consideration is the shape of the solubility curve for the solubility vs. temperature data. As can be seen in Figure 11.2 on page 648, the solubility curve for sulfanilamide in 95% ethyl alcohol indicates that ethyl alcohol is an ideal solvent for crystallizing sulfanilamide.

The purity of the final material after crystallization will be determined by performing a melting point on your sample. You will also weigh your sample and calculate the percentage recovery. It is impossible to obtain a 100% recovery. This is true for several reasons: There will be some experimental loss, the original sample is not 100% sulfanilamide, and some sulfanilamide is soluble in the solvent even at 0°C. Because of this last fact, some sulfanilamide will remain dissolved in the **mother liquor** (the liquid remaining after crystallization has taken place). Sometimes it is worth isolating a second crop of crystals from the mother liquor, especially if you have performed a synthesis requiring many hours of work and the amount of product is relatively small. This can be accomplished by heating the mother liquor to evaporate some of the solvent and then cooling the resultant solution to induce a second crystallization. The purity of the second crop will not be as good as the first crop, however, because the concentration of the impurities will be greater in the mother liquor after some of the solvent has been evaporated.

Two procedures are given here for crystallizing sulfanilamide: a semimicroscale procedure using an Erlenmeyer flask and a Hirsch funnel (Experiment 3A) and a microscale procedure with a Craig tube (Experiment 3B). Your instructor may assign both or just one of these procedures.

In Experiment 3C you will be given an impure sample of the organic compound fluorene (see structure that follows). You will use an experimental procedure for determining which one of three possible solvents is the most appropriate. The three solvents will illustrate three very different solubility behaviors: One of the solvents will be an appropriate solvent for crystallizing fluorene. In a second solvent, fluorene will be highly soluble, even at room temperature. Fluorene will be relatively insoluble in the third solvent, even at the boiling point of the solvent. Your task will be to find the appropriate solvent for crystallization and then perform a crystallization on this sample.



Fluorene

You should be aware that not all crystallizations will look the same. Crystals have many different shapes and sizes, and the amount of mother liquor visible at the end of the crystallization may vary significantly. The crystallizations of sulfanilamide and fluorene will appear significantly different even though the purity of the crystals in each case should be very good.

In Experiment 3D of this experiment, you will determine the identity of an unknown using the melting point technique. The **mixture melting point** technique is introduced in this part.

REQUIRED READING

Review:	Technique 10	Solubility
New:	Technique 8	Filtration, Sections 8.3 and 8.5
	Technique 9	Physical Constants of Solids: The Melting Point
	Technique 11	Crystallization: Purification of Solids

SUGGESTED WASTE DISPOSAL

Dispose of all organic wastes into the nonhalogenated organic waste container.

3A EXPERIMENT 3A

Semimicroscale Crystallization— Erlenmeyer Flask and Hirsch Funnel

This experiment assumes a familiarity with the general semimicroscale crystallization procedure (Technique 11, Section 11.3, p. 650). In this experiment, Step 2 in Figure 11.3 (removal of insoluble impurities) will not be required. Although the impure sample may have a slight color, it will also not be necessary to use a decolorizing agent (Section 11.7, p. 663). Leaving out

these steps makes the crystallization easier to perform. Furthermore, very few experiments in this textbook require either of these techniques. If a filtration or decolorizing step is ever required, Technique 11 describes these procedures in detail.

Pre-Lab Calculations

1. Calculate how much 95% ethyl alcohol will be required to dissolve 0.3 g of sulfanilamide at 78°C. Use the data from the introduction to this experiment to make this calculation. The reason for making this calculation is so that you will know ahead of time the approximate amount of hot solvent you will be adding.
2. Using the volume of solvent calculated in Step 1, calculate how much sulfanilamide will remain dissolved in the mother liquor after the mixture is cooled to 0°C.

To dissolve the sulfanilamide in the minimum of hot (boiling or almost boiling) solvent, you must keep the mixture at (or near) the boiling point of 95% ethyl alcohol during the entire procedure. You will likely add more solvent than the amount you calculated because some solvent will evaporate. The amount of solvent is calculated only to indicate the approximate amount of solvent required. You should follow the procedure to determine the correct amount of solvent needed.

PROCEDURE

Preparations

Weigh 0.30 g of impure sulfanilamide[1] and transfer this solid to a 10-mL Erlenmeyer flask. To a second Erlenmeyer flask, add about 6 mL of 95% ethyl alcohol and a boiling stone. Heat the solvent on a *warm* hot plate until it is boiling.[2] Because 95% ethyl alcohol boils at a relatively low temperature (78°C), it evaporates rapidly. Setting the temperature of the hot plate too high will result in too much loss of solvent through evaporation.

Dissolving the Sulfanilamide

Before heating the flask containing the sulfanilamide, add enough hot solvent with a Pasteur pipet to barely cover the crystals. Then heat the flask containing the sulfanilamide until the solvent is boiling. At first, this may be difficult to see because so little solvent is present. Add another small portion of solvent (several drops, or about 0.25 mL), continue to heat the flask, and swirl the flask frequently. You may swirl the flask while it is on the hot plate or, for more vigorous swirling, remove it from the hot plate for a few seconds while you swirl it. When you have swirled the flask for 10–15 seconds, check to see if the solid has dissolved. If it has not, add another portion of solvent. Heat the flask again with swirling until the solvent boils. Then swirl the flask for 10–15 seconds, frequently returning the flask to the hot plate so that the temperature of the mixture does not drop. Continue repeating the process of adding solvent, heating, and swirling until all the solid has

[1] The impure sulfanilamide contains 5% acetanilide as the impurity.

[2] To prevent bumping in the boiling solvent, you may want to place a Pasteur pipet in the flask. Use a 25-mL flask so that the Pasteur pipet does not tip the flask over. This is a convenient method because a Pasteur pipet will also be used to transfer the solvent.

dissolved completely. Note that it is essential to add just enough solvent to dissolve the solid—neither too much nor too little. Because 95% ethyl alcohol is very volatile, you need to perform this entire procedure fairly rapidly. Otherwise, you may lose solvent nearly as quickly as you are adding it, and this procedure will take a very long time. The time from the first addition of solvent until the solid dissolves completely should not be longer than 10–15 minutes.

Crystallization

Remove the flask from the heat and allow the solution to cool *slowly* (see Section 11.3, Part C, p. 655, for suggestions). Cover the flask with a small watch glass or stopper the flask. Crystallization should begin by the time the flask has cooled to room temperature. If it has not, scratch the inside surface of the flask with a glass rod (not fire-polished) to induce crystallization (Technique 11, Section 11.8, Part A, p. 664). When it appears that no further crystallization is occurring at room temperature, place the flask in an ice-water bath using a beaker (Technique 11, Section 11.8, p. 664). Be sure that both water and ice are present and that the beaker is small enough to prevent the flask from tipping over.

Filtration

When crystallization is complete, vacuum filter the crystals using a Hirsch funnel (see Technique 8, Section 8.3, and Figure 8.5, p. 622). (If you will be performing the Optional Exercise at the end of this procedure, you must save the mother liquor from this filtration procedure. Therefore, the filter flask should be clean and dry.) Moisten the filter paper with a few drops of 95% ethyl alcohol and turn on the vacuum (or aspirator) to the fullest extent. Use a spatula dislodge the crystals from the bottom of the flask before transferring the material to the Hirsch funnel. Swirl the mixture in the flask and pour the mixture into the funnel, attempting to transfer both crystals and solvent. You need to pour the mixture quickly, before the crystals have completely resettled on the bottom of the flask. (You may need to do this in portions, depending on the size of your Hirsch funnel.) When the liquid has passed through the filter, repeat this procedure until you have transferred all the liquid to the Hirsch funnel. At this point, there will usually be some crystals remaining in the flask. Using your spatula, scrape out as many of the crystals as possible from the flask. Add about 1 mL of *ice-cold* 95% ethyl alcohol (measured with a calibrated Pasteur pipet) to the flask. Swirl the liquid in the flask and then pour the remaining crystals and alcohol into the Hirsch funnel. Not only does this additional solvent help transfer the remaining crystals to the funnel but the alcohol also rinses the crystals already on the funnel. This washing step should be done whether or not it is necessary to use the wash solvent for transferring crystals. If necessary, repeat with another 1-mL portion of ice-cold alcohol. Wash the crystals with a total of about 2 mL of ice-cold solvent.

Continue drawing air through the crystals on the Hirsch funnel by suction for about five minutes. Transfer the crystals onto a preweighed watch glass for air-drying. (Save the mother liquor in the filter flask if you will be doing the Optional Exercise.) Separate the crystals as much as possible with a spatula. The crystals should be completely dried within 10–15 minutes. You can usually determine if the crystals are still wet by observing whether or not they stick to a spatula or stay together in a clump. Weigh the dry crystals and calculate the percent recovery. Determine the melting point of the pure sulfanilamide and the original impure material. At the option of the instructor, turn in your crystallized material in a properly labeled container.

Comments on the Crystallization Procedure

1. Do not heat the crude sulfanilamide until you have added some solvent. Otherwise, the solid may melt and possibly form an oil, which may not crystallize easily.

2. When you are dissolving the solid in hot solvent, the solvent should be added in small portions with swirling and heating. The procedure calls for a specific amount (about 0.25 mL), which is appropriate for this experiment. However, the actual amount you should add each time you perform a crystallization may vary, depending on the size of your sample and the nature of the solid and solvent. You will need to make this judgment when you perform this step.
3. One of the most common mistakes is to add too much solvent. This can happen most easily if the solvent is not hot enough or if the mixture is not stirred sufficiently. If too much solvent is added, the percent recovery will be reduced; it is even possible that no crystals will form when the solution is cooled. If too much solvent is added, you must evaporate the excess by heating the mixture. Using a nitrogen or air stream directed into the container will accelerate the evaporation process (see Technique 7, Section 7.10, p. 611).
4. Sulfanilamide should crystallize as large, beautiful needles. However, this will not always happen. If the crystals form too rapidly or if there is not enough solvent, they will tend to be smaller, perhaps even appearing as a powder. Furthermore, many substances crystallize in other characteristic shapes, such as plates or prisms.
5. When the solvent is water or when the crystals form as a powder, it will be necessary to dry the crystals longer than 10–15 minutes. Overnight drying may be necessary, especially with water.

Optional Exercise

Transfer the mother liquor to a tared (preweighed) test tube. Place the test tube in a hot water bath and evaporate all the solvent from the mother liquor. Use a stream of nitrogen or air directed into the test tube to speed up the rate of evaporation (see Technique 7, Section 7.10, p. 611). Cool the test tube to room temperature and dry the outside. Weigh the test tube with solid. Compare this to the weight calculated in the Pre-Lab Calculations. Determine the melting point of this solid and compare it to the melting point of the crystals obtained by crystallization.

3B EXPERIMENT 3B

Microscale Crystallization—Craig Tube

This experiment assumes familiarity with the general microscale crystallization procedure (Technique 11, Section 11.4, p. 656). In this experiment, Step 2 in Figure 11.6 (removal of insoluble impurities) will not be required. Although the impure sample may have a slight color, it also will not be necessary to use a decolorizing agent (Section 11.7, p. 663). Leaving out these steps makes the crystallization easier to perform. Furthermore, very few experiments in this textbook require either of these techniques. When a filtration or decolorizing step is required, Technique 11 describes these procedures in detail.

Pre-Lab Calculations

1. Calculate how much 95% ethyl alcohol will be required to dissolve 0.1 g of sulfanilamide at 78°C. Use the data from the introduction to this

experiment to make this calculation. Make this calculation so that you will know the approximate amount of hot solvent you will be adding.

2. Using the volume of solvent calculated in Step 1, calculate how much sulfanilamide will remain dissolved in the mother liquor after the mixture is cooled to 0°C.

To dissolve the sulfanilamide in the minimum of hot (boiling or almost boiling) solvent, you must keep the mixture at (or near) the boiling point of 95% ethyl alcohol during the entire procedure. You will likely add more solvent than the amount you calculated because some solvent will evaporate. Use this calculated amount only as a guide: you should follow the procedure to determine the correct amount of solvent needed.

PROCEDURE

Preparations

Weigh 0.10 g of impure sulfanilamide[3] and transfer this solid to a Craig tube. To a small test tube, add 2–3 mL of 95% ethyl alcohol and a boiling stone. Heat the solvent on a *warm (not hot)* hot plate with an aluminum block until the solvent is boiling.[4] Setting the temperature of the hot plate too high will result in too much loss of solvent through evaporation.

CAUTION

In performing the following procedure, keep in mind that the mixture in the Craig tube may erupt out of the tube if it becomes superheated. You can prevent this by stirring the mixture constantly with the spatula and by avoiding overheating the mixture.

Dissolving the Sulfanilamide

Before heating the Craig tube containing the sulfanilamide, add enough hot solvent with a Pasteur pipet to barely cover the crystals. Then heat the Craig tube containing the sulfanilamide until the solvent is boiling. At first, this may be difficult to see because so little solvent is present. Add another small portion of solvent (one or two drops), continue to heat the Craig tube, and stir the mixture by rapidly twirling a microspatula between your fingers. When you have stirred the mixture for 10–15 seconds, check to see whether the solid has dissolved. If it has not, add another portion (one or two drops) of solvent. Heat the Craig tube again with stirring until the solvent boils. Then stir the tube for 10–15 seconds. Continue repeating this process of adding solvent, heating, and stirring until all the solid has dissolved completely. Note that is it essential to add just enough solvent to dissolve the solid—neither too much nor too little. Because 95% ethyl alcohol is very volatile, you need to perform this entire procedure fairly rapidly. Otherwise, you may lose solvent nearly as rapidly as you are adding it, and this procedure will take a very long time. The time from the first addition of solvent until the solid dissolves completely should be no longer than 10–15 minutes.

[3] See footnote 1, p. 23.

[4] You may also use a hot water bath to heat the solvent in the test tube and to heat the Craig tube. The temperature of the water bath should be about 80°C.

Crystallization

Remove the Craig tube from the heat and insert the inner plug into the opening. Allow the Craig tube to cool slowly to room temperature by placing it into a 10-mL Erlenmeyer flask (see Section 11.4C, p. 658). Crystallization should begin by the time the Craig tube has cooled to room temperature. If it has not, *gently* scratch the inside surface of the tube with a glass rod (not fire-polished) to induce crystallization (Technique 11, Section 11.7, Part B, p. 664).[5] When it appears that no further crystallization is occurring at room temperature, place the Craig tube in an ice-water bath using a beaker (Technique 6, Section 6.5, p. 595). Be sure that both water and ice are present and that the beaker is small enough to prevent the Craig tube from tipping over.

Isolation of Crystals

When crystallization is complete, place the Craig tube in a centrifuge tube and separate the crystals from the mother liquor by centrifugation. Follow the procedure in Technique 11, Section 11.7, p. 663.

Using the copper wire, pull the Craig tube out of the centrifuge tube. If the crystals collected on the end of the inner plug, remove the plug and scrape the crystals with a spatula onto a preweighed watch glass for air-drying. Otherwise, it will be necessary to scrape the crystals from the inside surface of the outer part of the Craig tube. If you will be doing the Optional Exercise, save the mother liquor in the centrifuge tube. Separate the crystals as much as possible with a spatula. The crystals should be completely dried within 5–10 minutes. You can determine if the crystals are still wet by observing whether or not they stick to a spatula or stay together in a clump. Weigh the dry crystals and calculate the percent recovery. Determine the melting point of both the pure sulfanilamide and the original impure material. At the option of the instructor, turn in your crystallized material in a properly labeled container.

For additional information about crystallization, see "Comments on the Crystallization Procedure," p. 24.

Optional Exercise

See "Optional Exercise" on p. 25.

3C **EXPERIMENT 3C**

Selecting a Solvent to Crystallize a Substance

In this experiment you will be given an impure sample of fluorene.[6] Your goal will be to find a good solvent for crystallizing the sample. You should try water, methyl alcohol, and toluene. After you have determined which is the best solvent, crystallize the remaining material. Finally, determine the melting point of the purified compound and of the impure sample.

[5] An alternative method for inducing crystallization is to dip a microspatula into the solution. Then allow the solvent to evaporate so that a small amount of solid will form on the surface of the spatula. When placed back into the solution, the solid will seed the solution.

[6] The impure fluorene contains 5% fluorenone, a yellow compound.

PROCEDURE

Selecting a Solvent

Perform the procedure given in Section 11.6 on p. 662 with three separate samples of impure fluorene. Use the following solvents: methyl alcohol, water, and toluene.

Crystallizing the Sample

After you have found a good solvent, crystallize the impure fluorene using a semimicroscale (Erlenmeyer flask and Hirsch funnel) or a microscale (Craig tube) procedure. Use 0.3 g of impure fluorene if you follow the semimicroscale procedure, or use 0.05 g if you follow the microscale procedure. Weigh the impure sample carefully, and be sure to keep a little of the impure sample on which to perform a melting point. If you perform a semimicroscale crystallization, you may need to use a size of Erlenmeyer flask different from the one specified in the procedure. This decision should be made based on the amount of sample you will be crystallizing and how much solvent you think will be needed. Transfer the crystals to a preweighed watch glass and allow them to air-dry. If water was used as the solvent, you may need to let the crystals sit out overnight for drying because water is less volatile than most organic solvents. Weigh the dried sample and calculate the percent recovery. Determine the melting point of both the pure sample and the original impure material. At the option of the instructor, turn in your crystallized material in a properly labeled container.

3D EXPERIMENT 3D

Mixture Melting Points

In Experiments 3A and 3B of this experiment, the melting point was used to determine the purity of a known substance. In some situations the melting point can also be used to determine the identity of an unknown substance.

In Experiment 3D, you will be given a pure sample of an unknown from the following list:

Compound	Melting Point (°C)
Acetylsalicylic acid	138–140
Benzoic acid	121–122
Benzoin	135–136
Dibenzoyl ethylene	108–111
Succinimide	122–124
o-Toluic acid	108–110

Your goal is to determine the identity of the unknown using the melting-point technique. If all of the compounds in the list had distinctly different melting points, it would be possible to determine the identity of the unknown by just taking its melting point. However, each of the compounds in this list has a melting point that is close to the melting point of another compound in the list. Therefore, the melting point of the unknown will allow you to narrow down the choices to two compounds. To determine the identity of your compound, you must perform mixture melting points of

your unknown and each of the two compounds with similar melting points. A mixture melting point that is depressed and has a wide range indicates that the two compounds in the mixture are different.

PROCEDURE

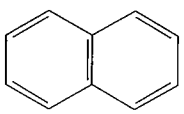
Obtain an unknown sample and determine its melting point. Determine mixture melting points (see Technique 9, Section 9.4, p. 630) of your unknown and all compounds from the previous list that have similar melting points. To prepare a sample for a mixture melting point, use a spatula or a glass stirring rod to grind equal amounts of your unknown and the known compound in a watch glass. Record all melting points and state the identity of your unknown.

3E EXPERIMENT 3E

Critical Thinking Application

The goal of the exercise is to find an appropriate solvent to crystallize a given compound. Rather than doing this experimentally, you will try to predict which one of three given solvents is the best. For each compound, one of the solvents has the desired solubility characteristics to be a good solvent for crystallization. In a second solvent, the compound will be highly soluble, even at room temperature. The compound will be relatively insoluble in the third solvent, even at the boiling point of the solvent. After making your predictions, you will check them by looking up the appropriate information in *The Merck Index*.

For example, consider naphthalene, which has the following structure:



Naphthalene

Consider the three solvents ether, water, and toluene. (Look up their structures if you are unsure. Remember that ether is also called diethyl ether.) Based on your knowledge of polarity and solubility behavior, make your predictions. It should be clear that naphthalene is insoluble in water because naphthalene is a hydrocarbon that is nonpolar and water is very polar. Both toluene and ether are relatively nonpolar, so naphthalene is most likely soluble in both of them. One would expect naphthalene to be more soluble in toluene because both naphthalene and toluene are hydrocarbons. In addition, they both contain benzene rings, which means that their structures are very similar. Therefore, according to the solubility rule "Like dissolves like," one would predict that naphthalene is very soluble in toluene. Perhaps it is too soluble in toluene to be a good crystallizing solvent. If so, then ether would be the best solvent for crystallizing naphthalene.

These predictions can be checked with information from *The Merck Index*. Finding the appropriate information can be somewhat difficult, especially for beginning organic chemistry students. Look up *naphthalene* in *The Merck Index*. The entry for *naphthalene* states, "Monoclinic prismatic plates from

ether." This statement means that naphthalene can be crystallized from ether. It also gives the type of crystal structure. Unfortunately, sometimes the crystal structure is given without reference to the solvent. Another way to determine the best solvent is by looking at solubility-vs.-temperature data. A good solvent is one in which the solubility of the compound increases significantly as the temperature increases. To determine whether the solid is too soluble in the solvent, check the solubility at room temperature. In Technique 11 on page 647, you were instructed to add 0.5 mL of solvent to 0.05 g of compound. If the solid completely dissolved, then the solubility at room temperature was too great. Follow this same guideline here. For naphthalene, the solubility in toluene is given as 1 g in 3.5 mL. When no temperature is given, room temperature is understood. By comparing this to the 0.05 g in 0.5 mL ratio, it is clear that naphthalene is too soluble in toluene at room temperature for toluene to be a good crystallizing solvent. Finally, *The Merck Index* states that naphthalene is insoluble in water. Sometimes no information is given about solvents in which the compound is insoluble. In that case, you would rely on your understanding of solubility behavior to confirm your predictions.

When using *The Merck Index,* you should be aware that alcohol is listed frequently as a solvent. This generally refers to 95% or 100% ethyl alcohol. Because 100% (absolute) ethyl alcohol is more expensive than 95% ethyl alcohol, the cheaper grade is usually used in the chemistry lab. Finally, benzene is frequently listed as a solvent. Because benzene is a known carcinogen, it is rarely used in student labs. Toluene is a suitable substitute; the solubility behavior of a substance in benzene and toluene is so similar that you may assume any statement made about benzene also applies to toluene.

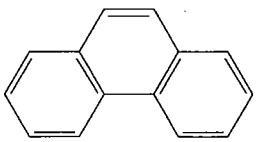
Exercise. For each of the following sets of compounds (the solid is listed first, followed by the three solvents), use your understanding of polarity and solubility to predict

1. The best solvent for crystallization
2. The solvent in which the compound is too soluble
3. The solvent in which the compound is not sufficiently soluble

Then check your predictions by looking up each compound in *The Merck Index.*

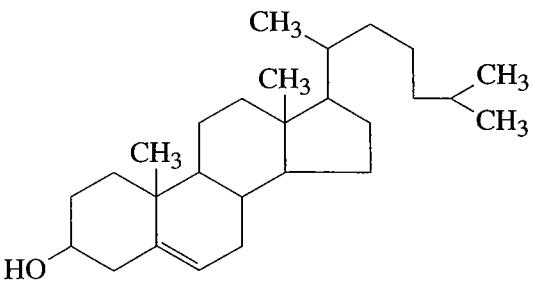
1. Phenanthrene; toluene, 95% ethyl alcohol, water

Phenanthrene

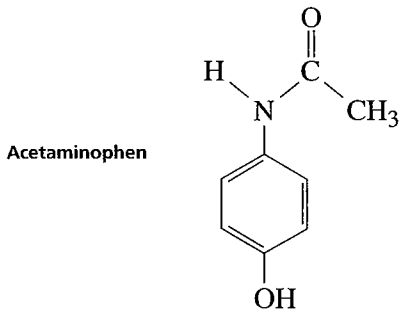


2. Cholesterol; ether, 95% ethyl alcohol, water

Cholesterol

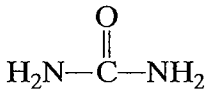


3. Acetaminophen; toluene, 95% ethyl alcohol, water



Acetaminophen

4. Urea; hexane, 95% ethyl alcohol, water



Urea

REPORT

Experiments 3A and 3B

1. Report the melting points for both the impure sulfanilamide and the crystallized sulfanilamide and comment on the differences. Also, compare these to the literature value. Look up the literature value and include this in your report. Report both the original weight of the impure sulfanilamide and the weight of the crystallized sulfanilamide. Calculate the percentage recovery and comment on several sources of loss.
2. If you completed the Optional Exercise (isolating the solid dissolved in the mother liquor), do the following:
   - **a.** Make a table with the following information:
     - **i.** Weight of impure sulfanilamide used in the crystallization procedure
     - **ii.** Weight of pure sulfanilamide after crystallization
     - **iii.** Weight of sulfanilamide plus impurity recovered from the mother liquor (see p. 25 or p. 27)
     - **iv.** Total of items ii and iii (total weight of sulfanilamide plus impurity isolated)
     - **v.** Calculated weight of sulfanilamide in the mother liquor (see p. 23)
   - **b.** Comment on any differences between the values in items i and iv. Should they be the same? Explain.
   - **c.** Comment on any differences between items iii and v. Should they be the same? Explain.
   - **d.** Report the melting point of the solid recovered from the mother liquor. Compare this to the melting points of the crystallized sulfanilamide. Should they be the same? Explain.

Experiment 3C

1. For each of the three solvents (methyl alcohol, water, and toluene), describe the results from the tests for selecting a good crystallizing solvent for fluorene. Explain these results in terms of polarity and solubility predictions (see "Guidelines for Predicting Polarity and Solubility," p. 639).
2. Report the melting points for both the impure fluorene and the crystallized fluorene and comment on the differences. What is the literature value for the

melting point of fluorene? Report the original weight of both the impure fluorene and the weight of the crystallized fluorene. Calculate the percentage recovery and comment on several sources of loss.

3. The solubility of fluorene in each solvent used in Experiment 3B corresponds to one of the three curves shown in Figure 11.1 (p. 648). For each solvent, indicate which curve best describes the solubility of fluorene in that solvent.

Experiment 3D Record all melting points and state the identity of your unknown.

Experiment 3E For each compound assigned, state your predictions, along with an explanation. Then give the relevant information from *The Merck Index* that supports or contradicts your predictions. Try to explain any differences between your predictions and information found in *The Merck Index*.

QUESTIONS

1. Consider a crystallization of sulfanilamide in which 10 mL of hot 95% ethyl alcohol is added to 0.10 g of impure sulfanilamide. After the solid has dissolved, the solution is cooled to room temperature and then placed in an ice-water bath. No crystals form, even after scratching with a glass rod. Explain why this crystallization failed. What would you have to do at this point to make the crystallization work? (You may need to refer to Figure 11.2 on p. 648.)
2. Benzyl alcohol (bp 205°C) was selected by a student to crystallize fluorenol (mp 153–154°C) because the solubility characteristics of this solvent are appropriate. However, this solvent is not a good choice. Explain.
3. A student performs a crystallization on an impure sample of biphenyl. The sample weighs 0.5 g and contains about 5% impurity. Based on his knowledge of solubility, the student decides to use benzene as the solvent. After crystallization, the crystals are dried and the final weight is found to be 0.02 g. Assume that all steps in the crystallization are performed correctly, there are no spills, and the student lost very little solid on any glassware or in any of the transfers. Why is the recovery so low?

4 EXPERIMENT 4

Extraction

Extraction

Critical thinking application

Extraction is one of the most important techniques for isolating and purifying organic substances. In this method, a solution is mixed thoroughly with a second solvent that is **immiscible** with the first solvent. (Remember that immiscible liquids do not mix; they form two phases, or layers.) The solute is extracted from one solvent into the other because it is more soluble in the second solvent than in the first.

The theory of extraction is described in detail in Technique 12, Sections 12.1–12.2, pp. 669–671. You should read these sections before continuing this experiment. Because solubility is the underlying principle of extraction, you may also wish to reread the introduction to the experiment on solubility.