

Chem 355 Jasperse

RECRYSTALLIZATION-Week 2

1. Mixed Solvent Recrystallization of Acetanilide
2. Mixed Solvent Recrystallization of Dibenzylacetone
3. Recrystallization of an Unknown

Background

Review: Recrystallization is an important technique for purifying organic solids. The contaminated solid is dissolved in a minimum of hot solvent, then cooled. The amount of solvent that is used should be just enough so that the solvent is just barely saturated or almost saturated when it is boiling hot. Upon cooling the solubility decreases, and crystal formation can occur. The new crystals are purer than the original because impurities are left in the solvent. Slow, gradual cooling is best for formation of pure crystals. Filtration then provides purified material. Some mass loss always occurs, because the solvent holds not only the impurities but also some of the desired material as well. Additional unnecessary mass loss can occur if you use too much solvent, don't heat your solution to boiling in the process of dissolving your sample, if you don't cool adequately, or if you wash your product crystals excessively. An appropriate solvent needs to have mediocre dissolving power: strong enough to dissolve the sample when boiling hot, but not able to dissolve too much of the sample when cold.

General Mixed Solvent Procedure, Concept: Often it's difficult to find a single solvent with appropriate dissolving power. Further, it's often difficult to decide exactly how much of the solvent is ideal. Frequently the use of mixed solvents is a practical and convenient solution.

In the usual mixed solvent recrystallization procedure, dissolve your sample in a sufficient quantity of your "better" solvent by heating it up to the boiling point. A 4 mL/1 g ratio is the default starting guess. Add more solvent if necessary, or boil some off if you judge it's obviously way more than needed. Then add "bad" solvent (usually hot water), until either you reach a visible "saturation" point (the "lucky" situation, where you can see crystals or slight cloudiness beginning to form) or until you have a 1:1 solvent ratio. Let cool so as to grow more crystals and harvest by filtration.

An alternative and often preferred strategy is if you intentionally or unintentionally start with a solvent that does not have enough dissolving power to dissolve the solid, even when hot. You can then add as much hot "better solvent" as needed to barely dissolve the sample (while boiling hot.)

When mixed solvents are used, it is essential that they be co-soluble. Otherwise the bad solvent will simply create a second layer, but the sample can remain soluble in the original layer.

Ethanol/water combinations are commonly used because ethanol has good dissolving ability for many organics, but is also infinitely co-soluble with water. Addition of water can rapidly and dramatically reduce the solubility of many organics and thus induce crystallization. While organic mixtures are also frequently useful, the difference in character between two organics is rarely as dramatic as the difference between water and an organic solvent.

Difficult Crystallizations: Sometimes crystallization is slow or difficult. Crystallization must start on some nucleation center. (Crystals grow when molecules "fit" onto some preexisting surface.) Sometimes this will happen spontaneously, but sometimes it is difficult. The formation of "supersaturated" solutions, in which the solvent holds more sample than it could if equilibrium existed, are routine. Some common techniques for initiating crystallization include:

- Seeding the saturated solution with some of the desired sample that is already in solid form.
- Scratching the insides of your flask with a rough glass rod. (By scratching the surface of your glass, you can get a rough edge which may coincidentally serve as a crystallization surface.)
- Using old, scratched up flasks!
- Leaving a boiling stick, preferably broken off so it has rough shards sticking out at the end.
- Adding an ice chip. (The surface is often rather rough, and can serve as a nucleation site. In addition, because the surface is pure water, the solvent composition near the ice chip is not representative of the bulk solvent distribution. Being water-rich, solubility may be especially poor resulting in crystal initiation. The ice chip serves to provide a local area of extremely "bad solvent".)
- Wait a long time!
- Find a better solvent.

Crystallization Summary

1. **Choosing the Solvent.** “Like dissolves like.” Some common solvents are water, methanol, ethanol, ligroin, and toluene. When you use a solvent pair, dissolve the solute in the better solvent and add the poorer solvent to the hot solution until saturation occurs. Some common solvent pairs are ethanol-water, diethyl ether-ligroin, toluene-ligroin, and t-butyl methyl ether-hexane.
2. **Dissolving the solute.** To the crushed or ground solute in an Erlenmeyer flask, add solvent, add a boiling stick, and heat the mixture to boiling. Add more solvent as necessary to obtain a hot, saturated solution. (Do not use a beaker, because the large mouth allows solvent evaporation to be too fast and uncontrolled.)
3. **Filtering suspended solids (if necessary).** If it is necessary to remove suspended solids, dilute the hot solution slightly to prevent crystallization from occurring during filtration. Filter the hot solution. Add solvent if crystallization begins in the funnel. Rinse thoroughly. Concentrate the filtrate to obtain a saturated solution.
4. **Crystallizing the solute.** Let the hot saturated solution cool spontaneously to room temperature. Do not disturb the solution. Slow cooling gives the best crystals. Cooling while clamped in the air, or while standing on a watch glass that is resting on your round-bottomed flask holder is a good way to do it. Put a watch glass or inverted beaker over the top of your flask so that solvent doesn't evaporate away while still hot. Then cool it in ice. If crystallization does not occur, scratch the insides of the container, add seed crystals, or for many solvents add ice chip(s).
5. **Collecting and washing the crystals.** Collect the crystals using a Hirsch funnel (<0.2 grams) or a Buchner funnel (>0.2 g), a filter flask, and aspirator suction. Place a filter paper on the surface, wet the filter paper with solvent, and apply suction to make sure the paper seals. Break the vacuum, add crystals and liquid, and apply vacuum. After solvent disappears, break vacuum, add cold wash solvent, apply vacuum, and repeat until crystals are clean and filtrate comes through clear. The wash solvent is normally either a small amount of an ice-cold portion of the main recrystallization solvent, or else a somewhat “worse” solvent (although it shouldn't normally be a totally “bad” solvent). For example, if 80% ethanol/water is used for a recrystallization, it would be common to wash with 60% ethanol/water to avoid dissolving much crystal.
6. **Drying the product.** Aspirate the sample for as long as is convenient. Press the product on the filter to remove solvent. Then remove it from the filter, squeeze it between sheets of filter paper to remove more solvent, and spread it on a watch glass to dry
7. **Analyzing the product.** Take a melting point of the final product. But since incomplete drying will contaminate the crystal and depress the melting point, it is sometimes best to wait for 15 hours or more before doing so.

Part I: Mixed Solvent Recrystallization of Acetanilide (partner permitted). (Supersaturation).

Purpose: Do mixed solvent recrystallization involving “super-saturation”, where no visible saturation appears; practice tricks for inducing difficult crystallization.

Detailed Procedure: Add about 50-mL of hot water to each of two 150-mL beaker, and warm these on each of your two hot plates. Warm to ~70-85° but less than boiling. Use a thermometer to monitor, supported by metal ring clamped above bath. Typically set your hot-plate power to 4 to achieve a good temperature. (You may perhaps need to adjust slightly.)

Weigh about 2 g (write down exactly) of acetanilide, and place it in a 25-mL Erlenmeyer flask. Add a boiling stick. Add 4 mL of ethanol and heat this to boiling by placing the flask into the hot water bath. Once it has dissolved, add three pipet squirts of hot water (instructor will demonstrate). You can transfer hot water directly from your hot water bath by pipet. In this example of “super-saturation” (review prelab intro), visible crystals/cloud-point will not appear. After the 3 pipets of water (~50% water), don’t add anymore. (In general, if you’ve added 50% water and still haven’t seen visible saturation, assume you have super-saturation as in this example.)

Let the solution cool slowly to room temp, and further cool on ice. If crystallization does not ensue, try standard crystallization tricks (scratch, add broken boiling stick, add ice crystals, seed, see instructor...). Once crystals have formed and are cold, filter using your Buchner funnel and the aspirator. Wash using some ice-cold 50-50 ethanol-water. Vacuum for as long as is convenient, so the sample is as dry as possible. Weigh the product. You can take your melting point same day or later during the week. Acetanilide mp: 112-115

Part II: Mixed Solvent Recrystallization of Dibenzalacetone (partner permitted). (Saturation)

Purpose: Observe how dramatically a “bad solvent” (water) can induce visible saturation/crystallization, when “super-saturation” does not occur.

Procedure: Weigh about 1 g (write down exactly) of dibenzalacetone and place it in a 25-mL Erlenmeyer flask. Add 4 mL of ethanol and heat to boiling by placing it in a hot water bath, as in Part I. Once you have the solution dissolved, add water slowly, dropwise, until the solution reaches a “cloud point”. (Try to count your drops). At this cloud point, your solution is visibly saturated!

Let the solution cool slowly to room temp, and further cool on ice for at least 5 minutes. Once crystals have formed and are cold, filter using your Buchner funnel and the aspirator. Wash using some ice-cold ethanol, and aspirate thoroughly under vacuum. Get your yield. You can take your melting point same day or later during the week. Pure dibenzalacetone mp: 108-111

Part III: Recrystallization and Identification of an Unknown. (work solo)

Purpose: To identify a suitable recrystallization solvent (or solvent combination) for an unknown; to do a recrystallization without instructions; and to identify an unknown.

Choose one of the unknowns (make sure you write down your letter in your lab report!) **Screen various solvents** (as we did last week) to determine which might be suitable for recrystallizing your particular unknown. Weigh out about 0.16 g of the solute, and divide it into four roughly equal piles. Place these into four test tubes. Add 1 mL of each of the four solvents. Check the solubility at room temperature and at hot temperature. Solvents available: water, ethanol, pentanone, toluene.

After identifying a reasonable solvent, or one that could be used as the “good” solvent in a solvent pair (normally in combination with water or pentanone), **proceed to actually recrystallize about 1 g** (write down exactly) **of your unknown**. Start with 4mL of your primary solvent per the one gram of solute. Choose ethanol if possible as your solvent, because it “solvent pairs” so beautifully. Water can be subsequently added if you want to diminish dissolving power; pentanone can be added to improve dissolving power. (Do not exceed 3 pipets water.) However, using ethanol or mixed solvents won’t always be appropriate, it depends on your unknown. **Rinse with whatever solvent or solvent blend that you recrystallized with.**

Get your final yield, and take your melting point same day or later during the week. If you have been successful, your melting point should be sufficiently accurate so that you can identify your unknown from the list of candidates on following page.

Note: The solvent/solid ratio in the solvent screening is 1 mL/0.04 g, which is 25mL/1g. Normally you start with a 4ml/1g ratio as your first guess for the bulk recrystallization. As a result of this difference in solvent/solid ratio, some solvents that look to have satisfactory dissolving power in the solvent screening tests don’t come close to fully dissolving the sample when you try the actual bulk recrystallization. In such cases, rather than adding enough solvent to reach the 25mL/g ratio, the easier and higher-yielding solution is normally to add some “better solvent” to get the crystals to dissolve. (All of this done with hot solvents, of course.)

Review: Two Ways To Achieve Just-Barely-Saturated/Just-Barely-Dissolved Borderline.

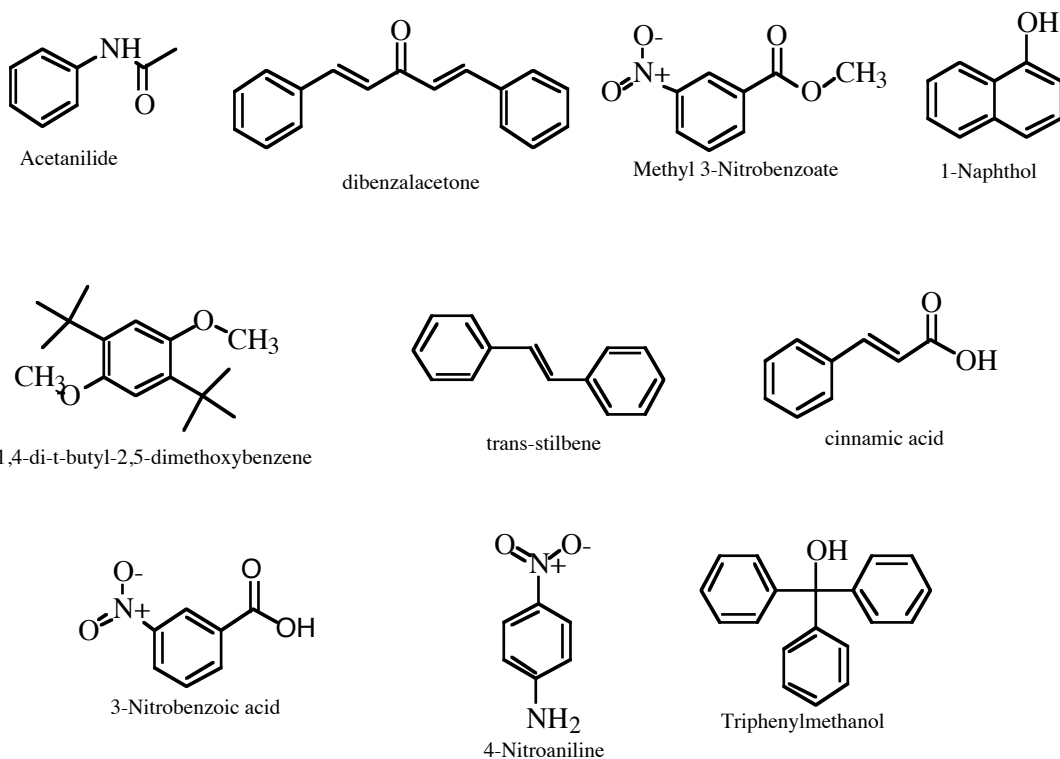
In all cases, heat to boiling, and only adjust by adding “hot” solvent, whether that be superior solvent or “bad” solvent.

- Add some hot superior solvent (if solubility is too low. Preferred route)
- Add some hot ‘bad solvent’ (if solubility is too high)
- Other possibility is to simply add more of the same solvent, if your solubility is too low; or to boil some of your solvent away, if the solubility is too high. But usually the first two options are faster and more convenient.

SOLVENTS	H_2O	$HO-CH_2-CH_3$	$CH_3-CO-CH_2-CH_2-CH_3$	$C_6H_5-CH_3$
	water ("W")	ethanol ("E")	pentanone ("P")	toluene ("T")

Recrystallization Unknown Candidates:

methyl 3-nitrobenzoate	78-80	cinnamic acid	133-134
1-naphthol	95-96	3-nitrobenzoic acid	140-142
1,4-di-t-butyl-2,5-dimethoxybenzene	104-105	4-nitroaniline	148-150
trans-Stilbene	121-122	triphenylmethanol	160-165

Recrystallization Unknown Candidates

Name: _____

Recrystallization #2 Lab Report (may work with partner)

Part 1: Acetanilide

Initial Mass: _____ Final Mass: _____ % Yield: _____ Melting Range: _____

To the best of your knowledge, how much water did you add?

If you needed any “tricks” to induce crystallization, what did you try and what worked?

Any problems, difficulties, excuses, or interesting observations?

Part 2: Dibenzalacetone (may work with partner)

Initial Mass: _____ Final Mass: _____ % Yield: _____ Melting Range: _____

To the best of your knowledge, how much water did you add?

Any problems, difficulties, excuses, or interesting observations?

Part 3: Unknown (work solo)

Initial Mass: _____ Final Mass: _____ % Yield: _____ Melting Range: _____

Which unknown letter did you use? _____

What was the chemical identity of your unknown? _____
(See list of candidates on page 26)

Solvent Screening:

Water			Ethanol			Pentanone			Toluene		
RT	Hot	Extra Solvent	RT	Hot	Extra Solvent	RT	Hot	Extra Solvent	RT	Hot	Extra Solvent

What solvent or solvent mixture did you choose?

Approximately how much of each solvent did you use?

Any problems, difficulties, excuses, or interesting observations?

