Lab 4B • 10/06/11

{description of separation scheme; already covered in lab 2B and 3B}

Recrystallization

Let me tell you first about the idea case of recrystallization. Recrystallization means dissolve your compound and pull it back out as a crystal again. First thing you have to do is choose a solvent. {using water for benzoic acid} The ideal behavior would be that you have zero solubility at room temperature or in an ice bath and virtually infinite solubility at high temperature. Why? Because if you didn't have zero solubility when cold, that means some compound's always going to be left behind in the solvent. In real life, that is what happens. If you have very low solubility, that means you'll have very low loss, but that means you're going to have loss in recrystallization. Because of that, you want very high solubility at high temperatures, so that you use the minimum amount of solvent possible, so that the least amount of compound remains behind once you cool it off. Ideal solvent behavior for recrystallization: the target solute should have zero solubility at room temperature (RT) and virtually infinite solubility near the solvent's boiling point. In reality (whatever that is), solutes will have trace solubility, even below room temperature, so the minimum possible quantity of solvent should be used to minimize loss of product.

Given that our goal is to use the minimum amount of solvent as possible, here's what I recommend: I would recommend using a hot plate with a sand bath and then have two beakers or Erlenmeyers – I tend to prefer Erlenmeyes because they've got some sort of constriction at the top that prevents things from splattering out in case you don't heat quite correctly. In one of them, you'll have the solvent; in the other one, you'll have your target solid compound. You heat both of them up until you get to the point where the solvent is about to boil. Your solid might melt; not a problem, but something you've got to watch out for as you're trying to do the following: you first take a little bit of that hot solvent (use a pipette) and transfer maybe 0.5 mL or so to the solid container. If you're worried about how much [solvent] do you really need, we could easily look up the solubility of the solute in that solvent. Transfer a little bit over. Let it heat up again, because as you pull it out, as soon as you pull it out, it's cooling down. Once you put that solvent with the solid, let it heat for a moment and stir it.

In this case, don't use the magnetic stirrer, since it's going to be off-center from your plate most likely, so it won't stir well, and so you don't have the stirbar blocking your view of the solution. What you're looking for is the following: if you add the solvent over and the solid completely dissolves, then you've added enough – or possibly too much – solvent, cause it's all gone. What hopefully will happen the first time you transfer is that it won't all disappear. Some of it will dissolve, some of it remains behind. You keep doing these small-portion transfers until you get barely to the point where all of the solvent disappears. If you do it that way, you've minimized the solvent, so you're going to minimize your solvent loss. Another possibility, though, is that you get two layers of liquid. That happens if your solid melts during this process. If you get two layers, that means there's not enough solvent to take that liquid solute and dissolve it. So even if it melts, if you have enough solvent, you'll only have one layer. If you have two layers, again, that means not everything has dissolved yet.

To summarize that, you're going to transfer small portions of the solvent one at a time into the solid. Doesn't work, do it again, and keep doing it only up to the point where that solid barely disappears. Watch out for layers forming, which indicates melted but not-yet-dissolved solid.

Once you have done this process, you've dissolved it; now, you need to get your crystals back again. Take it off the heat source, let it cool down to room temperature first, then place it in an ice bath. Why do it like that? Two reasons. Even though this is strong lab glassware, a strong thermal shock could still potentially break your glassware, so you don't want to take boiling-hot glassware and place it straight into an ice bath. The other reason is that, in general, slower cooling encourages larger crystal growth, so it'll make it easier to isolate your compound. Some of you are going to get powdery solid, some of you are going to get crystalline, some of you are going to get something that looks like a paste – it all depends on how much water is around and how quickly the crystals formed once it cooled down. Then you're going to collect your crystals on a Hirsch funnel. I recommend that you wash your crystals with a small portion of ice-cold water to make sure you've washed through any potential water-soluble impurities. The point of recrystallization is that once the crystals form, the impurities stay behind.

What if you accidentally add way too much solvent? You could boil off the solvent, but that means you're leaving the impurities behind again.

One thing that can happen in the process of recrystallization is that you do everything right, you know you used that minimum amount of solvent, but you can't get your crystals to reform. That can happen if you form a supersaturated solution, where the solution cools down enough that it should form a precipitate, but somehow physically the solute and solvent are so [strongly] interacting, that the solute just doesn't clump together and fall out of solution. You have to physically disturb the solution. Sometimes just stirring it, agitating it aggressive, that'll make the crystals form.

Sometimes, for whatever reason, you can scratch carefully the inside glass of the container, which I presume opens up little rough spots which allows sites for nucleation to occur; sometimes that will induce crystallization. Either agitation or scraping the inside of your glassware (but don't scrape so hard you break your glassware) can initiate crystallization.

_____

Recrystallization

Ideal solvent behavior – The solute should have zero solubility at RT and virtually infinite solubility near the solvent's boiling point.
In reality, solutes will have trace solubility even below RT, so the minimum possible amount of solvent should be used to minimize loss of product.

– Transfer small (0.5 mL – 1 ml) portions of the solvent (water for this lab) to the solid and attempt to dissolve the solid. Repeat this process until the point when the solid barely dissolves. Watch out for layers, which indicates the solute melted but didn't dissolve.
– Once the solid dissolves, cool first to RT then place in an ice bath. Collect the crystals on a Hirsch funnel then allow to air dry.water. If only clumps are visible, more drying agent should be added to ensure complete dryness.