Lab 3A • 10/03/11

If you have to make a change in your lab book, how do you do it? The best way to show that in a lab book is to just put one line through whatever quantity it was, so you could see what you had originally, then write the correction next to it. Let's say that, in the future, you figure out that you really that the correct quantity written down the first time; then you could still see that original quantity. In real life, mistakes are perfectly fine to make, but you document so you can have a trail of what your thought process was. Lab books should technically never be written in pencil or anything erasable; everything's supposed to be a permanent record.

{Lab directions}

What are doing with the aqueous layer? Why are you adding HCl? To protonate the benzoate, which makes it non-polar again. The whole point of this extraction is that we started out with benzoic acid that's non-polar, and naphthalene that's non-polar. The two of them both dissolved in the same solvent, so we wanted some trick to be able to separate them apart. What we did is react it with sodium hydroxide, which will react with the benzoic acid, but not with the naphthalene. Benzoic acid becomes far more polar when it is benzoate, so that's why it's able to slip into the aqueous layer. For the aqueous layer, which is the sodium hydroxide layer, you're going to acidify until a precipitate forms. How do you know enough acid is in there? You're going to make the precipitate. If you don't make a precipitate, that probably means you need to add more acid. How do you know how much acid you need? You know the strength of the sodium hydroxide that you used; you can estimate the volume that you used. So you know the moles of sodium hydroxide, so you should be able to calculate how much of the hydrochloric acid you would need.

{explanation of isolating solid}

Benzoic acid is not very soluble in water, and the cold the water is, the less soluble benzoic acid is. If you've added your hydrochloric acid in, you've got your precipitate, and you need to filter ....

{explanation of Hirsch funnel}
{measuring mass of flasks ahead of precipitations or evaporations}

Drying agents

A drying agent is often a dehydrated hydrate, so something that is a desiccant. A desiccant is a fancy word for drying agent. Magnesium sulfate, calcium sulfate, zinc sulfate, all three are often used as drying agents. They might be a fine powder, they might be a larger-grain material, usually some kind of powder form. The purpose of a drying agent is not to get rid of liquid; dry doesn't mean liquid-less, it means waterless. The drying agent's only purpose is to get rid of water that might still be stuck in your organic layer. The magic questions: how do I know how much to add? how do I know when it's done drying? Neither of those questions I can answer, because I'm not the one doing the experiment. Here's how you can tell if you've added enough, though. You add some drying agent, a spatula tip-full is a usual recommendation – and that means, whatever the tip of your spatula is, fill it up and dump that much in. Swirl it around for a few minutes. If you only put a little bit of drying agent in, and there's a lot of water around, it's going to clump up, it's going to make clumps of material. There won't be any of that fine, powdery drying agent left. You know it's working if it clumps. If you add in some and no clumping occurs, it might mean you didn't have much water to begin with either. But if clumping occurs, you know it's removing water. How do you know if it's been sitting around long enough? If you can find any drying agent that's still in powdery form, that hasn't clumped up, that means that there was more drying agent there than needed for the water that was removed, that means it did it's job. If you end up with just clumps, you can't tell if it's done or not; you have to add more drying agent and see if it remains granular or see if that clumps together.

When you add the drying agent, you'll see clumps form (most likely). If, after that clump is formed, you still have leftover granular drying agent, then the drying agent did its job.

Usually a drying agent will clump together in the presence of water. If, after drying has occurred, there is still powderized drying agent, in addition to any clumped material, enough drying agent was added. Some of you, if you did the separation really well, you might never see clumped material, which just means you didn't have much water, and you'll never see the clumping. If you wait some time, and you've just got powdery drying agent, that means it was dry to begin with.

What do you do at that point? Gravity filtration. We use glass funnels with a piece of filter paper in it. The simplest way to fold is to do the following: fold it in half, fold it again in half to make quarters, and three of the four quarters keep clumped together, just one of the four pull out, and then that's made a little paper funnel.

{waste guidelines}

If you have something solid in a container that's labeled liquid, that's fine. If you have something that's labeled solid, you should not put liquid in it. Anything that's liquid need to be labeled liquid no matter how little liquid there is.

When you pour the drying agent and solution through, the drying agent will be caught in the paper, which is what you want, and only the liquid's going to come through. You might want to take a little bit more ether, wash the whole beaker that sample just came from. As you are going to discover, as soon as that ether evaporates, a residue is left behind. To make sure you recover as much of your product as possible, you might want to rinse out that beaker and then pour that through.

How are you going to evaporate the solvents?

Ether's got a really low boiling point, 37.5° C. Lower than body temperature. You only need to very gently heat ether in order to get it to evaporate. Another temperature we should care about is its auto-ignition point, which means get it this hot, and it bursts into flames all by itself. The fires that I have had while at De Anza have both been ether fires. They were both because students were impatient [or unaware] and turned their hotplates all the way up and the stuff auto-ignited, it got hot enough where it just caught on fire. If you're going to evaporate ether, you've got to keep your temperature comfortably below 160° C.

You could have an Erlenmeyer in which you'd have a stir bar. Below that you'd have a stirring hotplate. Each one of you should have a hotplate in your fumehood, either in the fumehood itself or one of the cabinets below the fumehood. Each one's got a label on it saying which fumehood it should be in. If you get to your fumehood and you don't have two of them, that means someone next to you took one and you should go hunt it down and reclaim it for your own. The way these things work is they've got a heating element in them, but they've also got a large magnet that turns. If you put a little stirbar magnet in your beaker or your Erlenmeyer, then, as the large magnet of the hotplate turns, it will force the magnet inside the container to turn as well, which means you can get nice, consistent stirring without you ever having to do the stirring; you just sit and let it go. So, you and get a stirring solution and heat it gently, keeping it way below the 160 °C mark.

For other solvents that are a bit more recalcitrant, a bit trickier to evaporate, instead of doing it at atmospheric pressure, with just an open container, we might, instead, do it under vacuum. You might remember that boiling point is where the vapor pressure equals surrounding atmospheric pressure. If you change surrounding atmospheric pressure, it doesn't change the vapor pressure, it just changes the boiling point. If we put something under vacuum, the boiling point drops, because evaporation is still occurring at the same rate. What you could do is use a pear-shaped flask. Because the flask comes down to a point, it would be better to use your spinvane, something that's more compatible shapewise with that. Attach to that the flow control adapter, and then attach that to the vacuum. What you're doing is using the vacuum to pull all your solvent off. The reason you don't want to hook it straight up to vacuum – control. If, all of a sudden, you establish vacuum, because, in either's case, it's such a low boiling-point material, when you put it under vacuum, it may all suddenly bump, it may all get sucked in at once. So you have this control knob so you can controllably introduce vacuum to the system, or shut it back off if you need to. With ether, at room temperature you can sit there with it spinning under vacuum and it will evaporate that way as well. You also could use a combination of the two. If you really wanted to hurry it along, heat it a little bit and have it stirring [under vacuum] at the same time.

I really recommend indirect heating, which means you're gonna use a sand bath. Just put this container on top of your hotplate, settle your beaker inside of here. The more you bury it, the more heat contact that you're going to get, but the heat is more diffuse, more spread out, than just by contacting that hot bit of hot plate. Would that stop the stirbar from working? No, if you get it settled far enough down, the magnet in the stir plate will get it to spin anyways. It can have issues, you sometimes have to play with it a little bit, but they're usually good enough that it'll push through.

{lab directions}

I'm going to recommend that you use a tared flask. That way, once your stuff is stuck on there, instead of spending half an hour scraping it out, if all you care about is the mass you obtained, then you can get that mass by difference.

Whatever you do, never heat it up if it's not an open system. Vacuum, because it's a mechanical device constantly pulling air in, you can count that as an open system. If you were going to heat something that was closed, pressure builds up and … <pop>.

{Part B}

In part B, in addition to benzoic acid and naphthalene, you now also have 2-naphthol. The 2- comes from the way that nomenclature of these [fused] ring systems is handled. Numbering begins towards the inside of the compound. That -ol ending in the name, that is the designation that it is an alcohol. Just as with benzoic acid, 2-naphthol is mostly non-polar. You have this -OH group, but the larger portion of the molecule – naphthalene portion of the molecule – is symmetric and non-polar.

If you were to take these three compounds and put them in an organic solvent, they're all three going to dissolve, and it would be difficult, just on the basis of solubility tricks, to separate one from the other. We're doing an acid-base extraction, where we're purposely changing the functional group, changing the polarity to make it go into the aqueous layer. Except, we're using two different base this time: sodium hydroxide and sodium bicarbonate.

Carbonic acid is the parent of sodium bicarbonate. What do you know about carbonic acid? Are we going to isolate that material somehow during our experiment? We'll form it; if we're using bicarbonate as a base, we're going to make carbonic acid. Are we going to end up with any? The answer is no because, it's going to decompose into carbon dioxide and water. If you took water, put it under a pressure of carbon dioxide, that's how you make carbonate drinks, that's what carbonic acid is. You don't form it as an isolatable compound, but I'm putting carbonic acid name down so I can tell you it has a pKa of 6.9. I'll also tell you that the pKa of 2-naphthol is 9.51, and I'll remind you that the pKa of benzoic acid is 4.2. Why do we care about these numbers? You have three compounds in one sample, and you through sodium bicarbonate at it as the first extraction. Let's see what would happen with these three compounds.

Naphthalene, I'll just tell you, nothing happens. You can assume it's non-acid. Remember, just saying it's non-acid doesn't mean it's basic – it just means it's non-acidic. Then we have these two other compounds. I could show benzoic acid reacting with sodium bicarbonate, which makes sodium benzoate plus, before it decomposes, for just a moment we're going to have carbonic acid. Between these two acids, which one's the stronger one, benzoic acid or carbonic acid? Benzoic acid. {Need to review pKa} Since the pKa of benzoic acid is lower than carbonic acid, it is the stronger acid. When we figure out which one is the stronger acid, that means its conjugate is going to be weaker, because strong means it loves to lose its proton, so why would it want its proton back again. So the weaker base will be on the right. Carbonic acid, being the weaker acid, means its conjugate is the stronger base, the stronger conjugate. This means this neutralization is going to occur.

Let's throw the same equation up using 2-naphthol instead. 2-naphthol, reacting with bicarbonate (if it occurs), is going to form an anion – sodium 2-naphthoxide, and (before it decomposes) carbonic acid. But is this going to happen, if I tell you that the pKa values are 9.51 versus 6.9? Which one of these two compounds is the weaker acid this time? The 2-naphthol is weaker because it has the higher pKa; higher pKa, lower Ka, lower amount of dissociation, weaker acid. If it's a weaker acid, that means it doesn't want to be a base, so the base would be stronger. That means, in this particular neutralization, it's not going to occur, because you're trying to make a weak acid and weak base dissociate – which they don't want to – to make a stronger acid and stronger base – which would react and go right back to where you started at.

So, you have three compounds in solution, but because you've carefully chosen the conjugate base of an acid that has pKa in between the two compounds we want to target, we're able to target those two different compounds. In a mixture of multiple acids with distinct pKa values, you can isolate one from the other by starting with a weak base and then increasing the base strength each time you do the next subsequent extraction.

You start with three compounds together: the naphthalene, the 2-naphthol, and the benzoic acid. You dissolve them up in diethyl ether. You then add to the separatory funnel not sodium hydroxide first, but sodium bicarbonate. Since it's a weak base, it can't force a weak acid to react, but the stronger acid – benzoic acid – can react. You end up with two layers. Since ether is again the solvent you're using, ether will again appear on top. We'll have ether with the 2-naphthol and the naphthalene. The bottom later will have water plus benzoate. So, you targeted one compound and brought it out of the mixture. You're going to separate out the water layer and reacidify to cause a precipitate and filter that out. The top layer, you're going to leave it in there and add your second extract, you're going to do a back-to-back extraction. You leave it in the separatory funnel and add sodium hydroxide. Again, you're going to form two layers, and again the ether layer will be on top. Because sodium hydroxide is a stronger base, now it will react with the 2-naphthol, so all you're going to have [in the top layer] is ether and naphthalene. The aqueous layer will now have the water plus 2-naphthoxide. You'll separate that out, acidify and filter, and then the organic layer you'll dry, filter, and evaporate.

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Benzoic acid can be washed with small quantities of ice cold water. Benzoic acid has lower solubility in cold water, but not zero solubility.
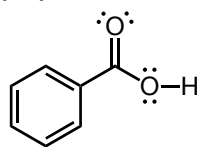
drying agent – usually a dehydrate hydrate, such as MgSO4, CaSO4, ZnSO4. used to remove water (not just any liquid) from an organic solution.
– usually, a dry agent will clump together in organic solution in the presence of water. It, after drying has occurred, there is still powderized drying agent left over (in addition to the clumped material), enough drying agent was added.
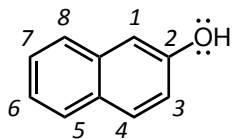
In a mixture of acids with distinct pKa values, the acids can be individually isolated by extracting first with a weak base, then using a stronger base for each subsequent extraction.
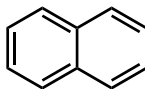
Structures

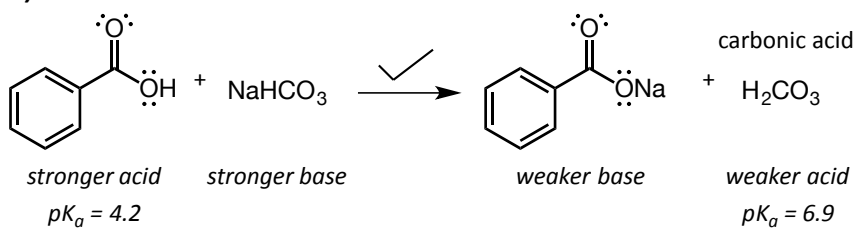*10/03/11 lab • 1*

benzoic acid
$pK_a = 4.2$

2-naphthol
$pK_a = 9.51$

naphthalene

10/03/11 lab • 2

carbonic acid

stronger acid
$pK_a = 4.2$

stronger base

weaker base

weaker acid
$pK_a = 6.9$

10/03/11 lab • 3

weaker acid
$pK_a = 9.51$

weaker base

sodium 2-naphthoxide
stronger base

stronger acid
$pK_a = 6.9$