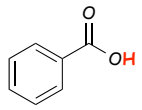
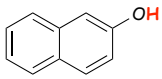
Experiment 3: Acid/base Extraction and Separation of Acidic and Neutral Substances

Introduction

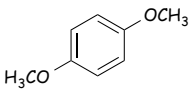
You will be given a mixture that contains three substances in equal amounts: benzoic acid, 2-naphthol and 1,4-dimethoxybenzene (*p*-dimethoxybenzene):



benzoic acid
pK_a 4.17



2-naphthol
pK_a 9.5



p-dimethoxybenzene

Your task: to separate these three compounds by taking advantage of differences in their acidity.

Definitions:

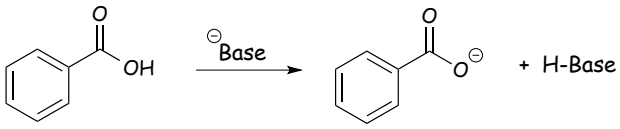
There are two terms we use when separating compounds from organic products:
1. *To remove organic compounds (what you want)* from aqueous solutions (or what you don't want), we perform an "**extraction**". For neutral organic compounds, we often add an organic solvent to dissolve a neutral organic compound to separate it away from inorganic, aqueous soluble "trash". In today's lab, we are adding a base to form an ionic salt from the organic compound, which will make it water soluble to separate it from the compound(s) still soluble in the ether solvent.

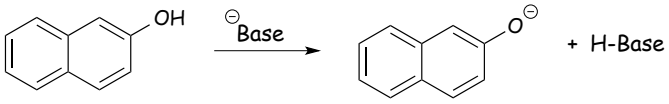
2. *To remove inorganic unwanted compounds* from what we want, we perform a "**wash**". We add aqueous solutions to our organic compounds so they **"wash" away impurities**.

- To remove acids, we add bases.
- To remove bases, we add acids.
- To remove salts, we just sometimes wash with water.

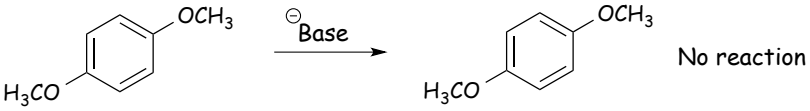
Today you will be extracting your compounds from a mixture.

In their neutral, covalent forms, all three compounds are soluble in a slightly polar organic solvent such as diethyl ether ($CH_3CH_2OCH_2CH_3$) but are fairly insoluble in water. This is because they are composed of many non-polar C-C and C-H bonds and have only a couple polar covalent bonds. Generally they are relatively non-polar, and only relatively non-polar organic solvents want to surround them. However, benzoic acid and 2-naphthol are acidic due to their –OH groups and so will be converted to their ionic salt forms on reaction with an appropriate base.





Note that 1,4-dimethoxybenzene has no acidic proton and cannot become an ionic salt:



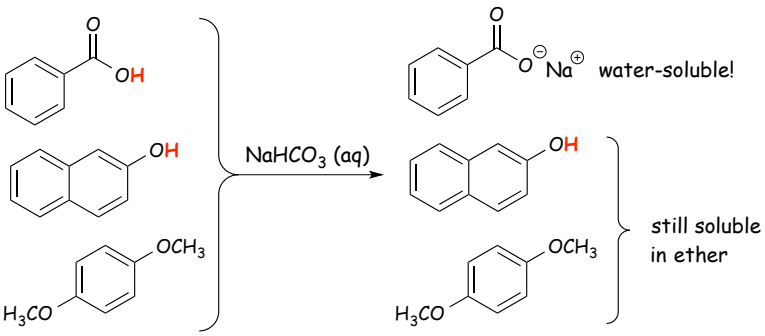
Once an organic compound becomes a salt, it possesses a highly polarized area inside its structure. When this highly polarized area forms, polar water molecules flock to it, surround it (we call this "solvation") and ultimately dissolve it.

So, two of the compounds can be turned into ionic salts and separated from the one compound that cannot be ionized. Separation of the two potential ionic compounds themselves can be accomplished by the use of different bases. Carboxylic acids (like that in benzoic acid) have a pKa between 4-5 while phenols (seen in 2-naphthol) have a pKa of 9-10.

Which compound is more acidic?

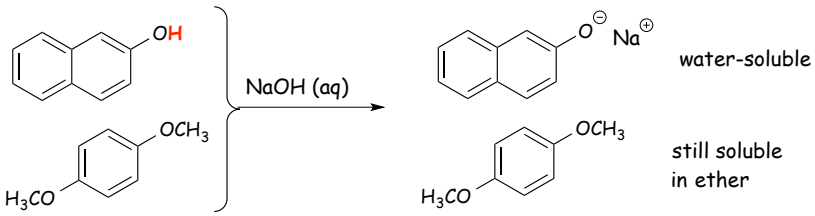
Benzoic Acid

Use of two different bases with two different strengths allows for selective reaction of the stronger acid versus the weaker acid. The weaker base, sodium bicarbonate, is strong enough to react with the stronger acid, benzoic acid, but not strong enough to react with the weaker acid, 2-naphthol. The sodium salt that forms is ionic, highly polarized and soluble in water. Therefore a neutral compound dissolved in diethyl ether can be **extracted** from the mixture into an aqueous base solution if the base is strong enough:



You can see that only one compound, benzoic acid, is an ionic salt when the mixture is treated with sodium bicarbonate, and only benzoic acid becomes water-soluble. The other two compounds remain neutral, still dissolved in the diethyl ether.

A stronger base, sodium hydroxide, is required to react with the less acidic 2-naphthol. The remaining two-component mixture in the ether layer can then be separated and 2-naphthol is then **extracted** from the remaining mixture:

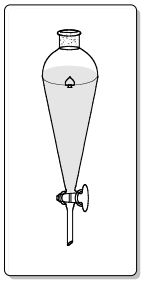


Note that 1,4-dimethoxybenzene does not have any acidic proton and cannot react with either base. It will remain in the ether layer.

Why is it a problem is you were to accidentally use the stronger base first?

If your base is too strong, you will form ionic salts from both the carboxylic acid (benzoic acid) and the phenol (2-naphthol) and both will dissolve in the aqueous base, thus NOT separating.

Diethyl ether and water (think water whenever using "***aqueous*** solutions") do not dissolve well in each other ("***immiscible***") and will form layers in a container with the less dense liquid floating on top of the denser one. The piece of equipment that is used for separating these layers (or more generally, for doing "*liquid-liquid extractions*") is called a **separatory funnel** (or "sep funnel"), shown at right.



Both "washes" and "extractions" are done in a separatory funnel, when working on a larger scale. The separatory funnel has a stopcock on the bottom to help drain out the bottom layer. We use a glass stopper to plug up the top, when you want to shake and mix the layers.

To properly use a sep funnel, one uses an iron ring to hold the separatory funnel during layer separation. Be sure to pick an iron ring that is properly sized - too big and the iron ring will let the separatory funnel fall straight through and break on the counter!

First, place your sep funnel in the iron ring, then add the organic and aqueous solutions. Now, place the stopper on top. Invert the sep funnel, shake to mix the layers well, then "vent". To "vent" a sep funnel, simply open the stopcock, while the funnel is inverted

upside-down, after allowing the liquid to settle away from the stopcock. This releases any built-up gases inside the sep funnel. Be sure not to point the opening of the sep funnel towards yourself or anyone else in the lab. The sep funnel is then turned right side up and set into the iron ring while the two layers separate. It is recommended that you wear gloves while working with a sep funnel – in case the stopper comes loose, you don't want the liquid layers to leak onto your hand.

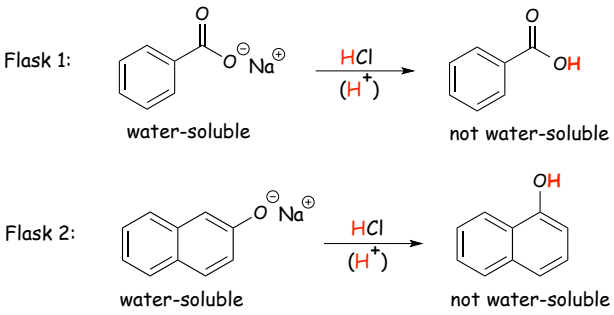
Once the layers are separated, **the stopper is removed** and the bottom layer is carefully drained from the bottom.

Why must the stopper be removed?
To prevent formation of a vacuum inside the separatory funnel (keeps the liquids from draining out the bottom)

Once the bottom layer is drained out the bottom, the top layer is poured out the top opening. This prevents the top layer from being drained through the area where remnants of the bottom layer can re-mix with your newly separated top layer.

Finishing the lab:

Once all of the compounds have been separated, the neutral compounds may then be recovered as solids by adding a strong acid to the aqueous solutions of the sodium salts, causing them to precipitate from the aqueous solution in separate flasks (neutral organic compounds are no longer highly polarized and generally not soluble in aqueous solutions):



The neutral, non-acidic compound that remains in the ether solution can be isolated as a solid by simply allowing the ether to evaporate, after the ether solution has been "dried". This brings up another new technique needed today:

"Drying the Product":
Water must commonly be removed from liquid organic compounds, after washes/extractions with aqueous solutions. In today's lab, the neutral product, 1,4-dimethoxybenzene, is exposed in multiple extractions with aqueous basic solutions. While the bulk of water is usually separated away using the separatory funnel, trace amounts of water may still remain in the organic solution. **Trace amounts** must be

removed using what is called a "**drying agent**". [Note – that's TRACE amounts – not big globs of water!]

Drying agents are anhydrous compounds that form hydrates, meaning water molecules adhere to the drying agent to form complexes. The job of the drying agent is to enter a liquid (either a solution where something is dissolved in an organic solvent, like the 1,4-dimethoxybenzene, or a neat liquid compound, where "neat" means "without solvent, just the liquid compound") and search to find water molecules and complex with them. When the drying agent is filtered away, so are the water molecules.

How do you know when a solution is dry?
When drying agents are dry, they freely float in a solution. Some drying agents in a dried solution commonly remind you of those tourist toys, where the ball has the snowflakes you shake up. Others may just roll around in the bottom of your flask or vial – but the key is that they are MOVING, not stuck to the bottom or sides of the vial.

When a drying agent finds water and complexes to form the hydrate, the drying agent becomes sticky and heavy. Typically, the drying agent falls to the bottom of the flask or vial and sticks there, not moving around. And once it sticks, it stays stuck… Expect your flasks or vials to have some drying agent stuck to the bottom or sides. These will remain stuck always. Look beyond what is already stuck to what is happening in the solution inside the flask or vial.

Ideally, when your solution is dry, there should be ***some amount* of drying agent freely floating in the solution**. Seeing this tells you there are no longer any water molecules left in the solution.

There are several drying agents to choose from, including magnesium sulfate ($MgSO_4$), potassium carbonate (K_2CO_3) and calcium chloride ($CaCl_2$). In this experiment, we will use magnesium sulfate, which has a consistency like flour and readily floats in a dry solution (think about one of those tourist globes with sparkly snow flakes that float when shaken). The magnesium sulfate has a large surface area and is a fast drying agent.

The magnesium sulfate is easily filtered away using a gravity filtration with fluted filter paper from the product, which is dissolved in the ether solution. This is a gravity filtration but does not need to be hot – the compound in the ether layer stays dissolved regardless of the temperature. Rinsing of the drying agent and filter paper is performed to prevent a loss in product.

Finally: All three separated compounds may be purified by recrystallization and their identities confirmed using melting point analysis.