Experiment 8: Acid/Base Extraction: Separation of Acidic and Neutral Substances

Your task in this lab is to separate and identify two compounds in a mixture by taking advantage of their acidity differences. The “unknown” mixture you will be given contains equal amounts of an acidic and a neutral compound. The acidic compound will be either benzoic acid (pKa 4.2) or 2-naphthol (pKa 9.5). The neutral compound will be naphthalene (smells like mothballs!).

These three compounds are soluble in diethyl ether (slightly polar extracting solvent) and essentially insoluble in cold water. When reacted with a base of appropriate strength, the acidic compounds get deprotonated and become converted to their ionic, conjugate base forms which are now soluble in water.

As salts, they are highly polarized and can easily hydrogen bond to water molecules, thus dissolving into the solution. The surrounding of a molecule by solvent molecules is called “solvation”.

The neutral compound, naphthalene, is unreactive in the presence of aqueous base due to the lack of an acidic proton.

Two bases, of different strength, will be used to deprotonate the appropriate acidic compound and therefore extract it from the organic layer into the aqueous layer. Sodium bicarbonate (a weaker base) is sufficiently strong to react with the more acidic benzoic acid.
Bronsted-Lowry Acid-Base reactions:

**Equilibrium Direction?**

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\[
\begin{align*}
&\text{Forwards reaction. Works well...} \\
&\text{And now?} \\
&\text{Reverse reaction. Doesn't work!}
\end{align*}
\]
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An even stronger base, such as sodium hydroxide, is required to deprotonate the weaker acid, 2-naphthol.

Keep in mind that if the base is strong enough, then the uncharged, free acid form dissolved in diethyl ether becomes deprotonated, forming a polar ionic salt and becomes water-soluble (“extracted” into the aqueous layer).

**Why is it a problem if 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.

**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 whatever 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 components. 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 neutral naphthalene that is soluble in the relatively non-polar 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 remove water-soluble impurities.
   - To remove acids, we add bases.
   - To remove bases, we add acids.
   - To remove salts, we just sometimes wash with water.

“Extracting” a component from a liquid using a second liquid (“liquid-liquid extraction”) requires that the two liquids being used to be immiscible. In this lab we rely on the fact that diethyl ether and water (or aqueous solutions of sodium bicarbonate and sodium hydroxide) do not dissolve well in each other and will form layers. These layers will be placed in a **separatory funnel** with the less dense liquid floating on top of the more dense one. Shaking the two layers, however, allows transfer of components between them (partitioning) so that a compound will be moved or **extracted** into the phase in which it is most soluble. While neutral, all of the organic compounds will be dissolved in the diethyl ether organic solvent. Once charged and highly polarized, the organic compound in its ionic salt form will be soluble in the aqueous layer. You will do two sequential liquid-liquid extractions on an ether solution of your mixture.

You will first use an aqueous sodium bicarbonate solution (weaker base) followed by an aqueous sodium hydroxide solution (stronger base). Your acidic compound (in its ionic, conjugate base form) will be in one of the two aqueous solutions extracts, depending on its acidity. The identity of the unknown will be known by which base it reacts with, if you do this process correctly.
The uncharged, free acids will be found in either Flask 1 or 2 and will be recovered as solids by adding a strong acid to the aqueous solution of the conjugate bases, protonating them and causing them to precipitate (water insoluble).

\[
\begin{align*}
\text{Flask 1:} & \quad \text{water-soluble} \quad & \text{HCl} \quad (H^+) \quad \rightarrow \quad \text{not water-soluble} \\
\text{Flask 2:} & \quad \text{water-soluble} \quad & \text{HCl} \quad (H^+) \quad \rightarrow \quad \text{not water-soluble}
\end{align*}
\]

The neutral compound (naphthalene) that remains in the diethyl ether solution will be isolated as a solid by first drying, then allowing the solvent to evaporate in the hood.

"Drying the Product":

Water must commonly be removed from liquid organic compounds, after washes/extractions with aqueous solutions. In today's lab, the neutral compound, naphthalene or biphenyl, are 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 or a "neat" liquid compound, where "neat" means "without solvent, just the liquid compound", 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 move or 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, flask or whatever container you are using.

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. Note also that when wet, an organic solvent often looks cloudy but when dry, it becomes clear.

There are several drying agents to choose from, including magnesium sulfate (MgSO$_4$), potassium carbonate (K$_2$CO$_3$) 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 from the product using a gravity filtration with fluted filter paper, as long as the product stays dissolved in the ether solution. This is a gravity filtration that 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. The MgSO$_4$ large surface area could be a detriment as the product would cling to the surface of the drying agent and you would lose compound, if you did not rinse it.

Both compounds will be purified by recrystallization and their identities confirmed using melting point analysis.

**FOR YOUR SAFETY**

1. Concentrated hydrochloric acid is corrosive and an irritant. Avoid skin contact by wearing gloves and, as always, goggles must be worn. In case of contact with skin, wash thoroughly with running cold water immediately.
2. Sodium bicarbonate solution will exothermically produce CO$_2$ gas when mixed with acid. Acid must be added cautiously to such solutions to control the reaction. Also, this will cause a pressure build-up in a closed container such as a stoppered separatory funnel. Frequent venting of the pressure is required to prevent uncontrolled pressure release.

**Experimental Procedure (Week 1)**

1. Weigh approximately 2 g of the solid mixture and transfer it to a 100 mL beaker. Record the exact mass used in your notebook.
2. Set up your separatory funnel-support it in an iron ring that is clamped on a bench frame. Close the stopcock and place a 125 mL Erlenmeyer flask underneath the stem.

3. Add 30 mL of diethyl ether to the beaker containing your mixture. Swirl gently to dissolve the solid and transfer to the separatory funnel using a glass funnel. Use a small amount of additional diethyl ether (2-3 mL) to wash the residual compound in the beaker and transfer to the separatory funnel.

4. Add 10 mL of DI water to the separatory funnel. You should see two layers. Which is the aqueous and which is the organic (diethyl ether) layer? Confirm with your instructor before you proceed to the next step.

5. Add 10 mL of 10% sodium bicarbonate solution to the separatory funnel.
   
   **CAUTION:** When the bicarbonate solution is mixed with diethyl ether, CO$_2$ gas may be generated causing a pressure buildup in the separatory funnel. You must vent the funnel frequently, as demonstrated by your instructor, to release the pressure.
   
   Place the stopper in the funnel and while holding the stopper tightly shake the funnel several times. Immediately vent the funnel, with the stem pointing upwards and away from you (and other students), by opening the stopcock. Close the stopcock and repeat the process 4-5 times, venting the pressure each time until no more CO$_2$ is given off. The two layers inside the separatory funnel must mix well so that solutes can partition into the phase in which they are most soluble.

6. Place the separatory funnel back in the iron ring, remove the stopper right away and allow the layers to fully separate. Then, drain the lower layer into a 125 mL Erlenmeyer flask, labeled as "Aqueous Flask 1". With the organic layer remaining in the separatory funnel, repeat the extraction sequence 2 more times, using 10 mL of 10% sodium bicarbonate (no added water) each time. Add these new aqueous extracts to the aqueous layer already in "Aqueous Flask 1".

7. To the organic layer remaining in the separatory funnel after the third extraction sequence from above, add 10 mL of 5% aqueous sodium hydroxide solution. Place the stopper in the funnel and while holding the stopper tightly shake the funnel several times. Immediately vent the funnel, with the stem pointing upwards and away from you (and other students), by opening the stopcock. Close the stopcock and repeat the process 4-5 times, venting the pressure each time. Place the separatory funnel back in the iron ring, remove the stopper right away and allow the layers to fully separate. Then, drain the lower layer into a 125 mL Erlenmeyer flask, labeled as "Aqueous Flask 2".

8. With the organic layer remaining in the separatory funnel, repeat the extraction sequence 2 more times using 10 mL of 5% aqueous sodium hydroxide solution each
time. Add the new aqueous extracts to the aqueous layer already in "Aqueous Flask 2".

9. At the end of the third extraction sequence in Step 8, drain the diethyl ether layer that remains in the separatory funnel in a 50 mL Erlenmeyer flask. Label this as "Organic Flask 3". Add enough anhydrous magnesium sulfate drying agent to the ether extract and swirl the flask.

   What is the role of the drying agent and how much of it is enough?
   The drying agent absorbs any residual water that is present in the organic layer. You will know that you have added enough when the drying agent no longer clumps or sticks to the walls of the glassware.

10. Label a clean, dry 50 mL beaker as "Organic Beaker 4" along with your name and lab section and obtain its mass. Filter the ether solution from step 9 into this beaker by doing a gravity filtration (use a glass short-stem funnel and fluted filter paper). Use a few mL of diethyl ether to wash the remaining magnesium sulfate and ensure all of the organic compound has been transferred to the filtrate. Your instructor will assist in evaporating the ether in the fume hood.

Lab partners can now each take one of the Aqueous Flasks and acidify:

11. Obtain "Aqueous Flask 1". Place a magnetic stir bar in it and stir at medium speed (setting 5-6) using your stirrer hotplate (HEAT OFF). Cautiously and in small portions, add 5 mL of concentrated hydrochloric acid using a Pasteur pipette. You will observe vigorous bubbling at the beginning of the addition and therefore you should only use small amounts initially. Use pH paper to check that the solution is pH = 1 at the end of the addition (additional hydrochloric acid may be added if necessary until pH 1 is reached). When using pH paper, remember to always use a stirring rod or pipette tip to place a drop on the test paper rather than dipping the paper directly into the solution. Record observations. Did a solid form? What was the color and appearance/form of the solid? Once done, set aside this flask.

12. Obtain "Aqueous Flask 2". Place a magnetic stir bar in it and stir at medium speed using your stirrer hotplate (HEAT OFF). Cautiously and in small portions, add 5 mL of concentrated hydrochloric acid using a Pasteur pipette. You will observe vigorous bubbling at the beginning of the addition and therefore you should only use small amounts initially. Use pH paper to check that the solution is pH = 1 at the end of the addition (additional hydrochloric acid may be added if necessary until pH 1 is reached). When using pH paper, remember to always use a stirring rod or pipette tip to place a drop on the test paper rather than dipping the paper directly into the solution. Record observations. Did a solid form? What was the color and appearance/form of the solid? Once done, set aside this flask.
At this stage, you should have a significant amount of solid in either “Aqueous Flask 1” or “Aqueous Flask 2”, depending on which acidic compound was part of your mixture, but not in both! If you have solid in both, consult with your instructor before proceeding.

13. Place the flask that contains the solid (either “Aqueous Flask 1” or “Aqueous Flask 2”) on the hotplate and begin magnetic stirring. Set the hotplate to a setting of 6 and begin heating the solid suspension. Add an additional 50 mL of DI water to the flask.

14. Continue heating the mixture until the solution is boiling. If there is undissolved material then add small portions of water using a Pasteur pipette until it is completely dissolved (do not use more than 15 mL of water). If you observe small amounts of an oily substance that will not dissolve even after adding more water then go to step 15. Otherwise, remove the flask from the hotplate, turn off the hotplate and allow the flask to cool on the bench for a few minutes. Then, continue to step 16.

15. Perform only if you observe an insoluble oily substance in step 14! Set up a hot gravity filtration apparatus—a 250 mL Erlenmeyer flask with 10 mL of water in it and a short stem glass funnel with fluted filter paper in it. Place apparatus on the hotplate. When the water in the Erlenmeyer flask is boiling, pre-wet the filter paper and carefully filter the solution from step 14 (use a hot glove!). Keep the filtration flask on the hotplate until the filtration is complete. Then, remove the flask from the hotplate and allow it to cool on the bench for a few minutes. Turn off your hotplate and proceed to step 16.

16. Place your flask in an ice bath and allow the solution to cool completely to ice bath temperature. Once crystallization is complete, isolate the crystals by vacuum filtration. Wash the crystals with a small amount of ice-cold water and leave under vacuum for a few minutes. Once dry, store Buchner funnel containing your product in your drawer until next week.

17. Obtain "Organic Beaker 4" from step 10. Using a spatula, scrape down the solid from the walls of the beaker so that it collects at the bottom of the beaker. Reweigh the beaker to obtain the crude mass of the solid.

18. Add 4 Pasteur pipettes of methanol to the solid from step 17 and gently swirl the beaker. Set hotplate to a setting of 2.5 and place beaker on the hotplate. Cover the top of the beaker with a watch glass to prevent evaporation of the solvent and continue heating until it boils. Add additional methanol dropwise as necessary until all solids dissolve. Remove the beaker from the hotplate, turn off the hotplate and allow the flask to cool on the bench for a few minutes. Once cooled, place beaker in an ice bath (remember that slow cooling gives better crystals).
19. Set up a vacuum filtration apparatus and isolate your crystals from the previous step. Wash the beaker with a small amount of ice-cold methanol to transfer most of the pure compound in the Buchner funnel. Leave product under vacuum for a few minutes to dry.

20. Transfer the crystals to a clean, dry, pre-weighed sample vial labeled as “Organic Beaker 4”. Loosely cap and store the compound in your locker until the next lab. [Note: the naphthalene slowly sublimes and so mass loss may occur if the naphthalene is stored on the Buchner funnel for a prolonged period.]

**Waste Disposal**

Pour the methanol filtrate and any unused methanol in the methanol/acetone waste bottle.

The aqueous filtrate from the recrystallization and the aqueous solution that did not produce any solid should be placed in the aqueous acid waste container.

**Experimental Procedure (Week 2)**

1. Weigh an empty sample vial with cap and transfer (using a powder funnel) the product from Flask 1 or 2 to it. Reweigh the sample vial/cap/product. Record both weights.
2. Reweigh the sample vial/cap that contains the naphthalene from Beaker 4. Record this weight.
3. Obtain melting points on your two compounds.
   a. Take a fast run of BOTH compounds at the same time using the following Digimelt settings: **START temp: 50°C**, RAMP rate: **20°C/min**, **STOP temp: 140°C**. Record both fast mp ranges.
   b. After determining the Ball-Park temperatures for each, adjust the START temp accordingly for the Beaker 4 Compound and perform its slow run (RAMP RATE: 2°C/min, STOP temp: 140°C).
   c. Then raise the START temp accordingly for the Flask 1/2 Compound and perform its slow run (RAMP RATE: 2°C/min, STOP temp: 140°C).
4. Obtain an IR spectrum on your acidic compound, if directed to do so by your instructor then submit your two product vials to your instructor.