10. Extraction: Separation of Acidic Substances

Chemists frequently find it necessary to separate a mixture of compounds by moving or partitioning a component from one solution or mixture to another. The process most often used for this is called extraction.

There are two common types of extraction, one of which is solid-liquid extraction. The brewing of tea or coffee is an example of this type. Some of the components (caffeine and other substances) of the original solid (the tea leaves or the ground-up coffee beans) are extracted into the liquid (the hot water). A future experiment will include a solid-liquid extraction.

The other common type of extraction is liquid-liquid extraction. In this type, a component of a liquid mixture is extracted into a different liquid. In other words, a solute is transferred from one solvent to a different solvent.

Liquid-liquid extractions can be subdivided into two types. One type includes extractions in which the separation is based purely on the solute being much more soluble in the extraction solvent than in the original solvent. In another type of liquid-liquid extraction, a chemical reaction converts the solute to a form in which it is more soluble in the extraction solvent. Acid-base extractions, such as this week's experiment, are the most common example of liquid-liquid extractions involving reactions. In today’s experiment benzoic acid and 2-naphthol will be separated by employing an acid-base extraction technique using sodium bicarbonate and sodium hydroxide.

Extractions may involve separating two desirable compounds from one another or removing a desired substance in a mixture from undesirable ones, or removing undesired contaminants from a mixture.

PRE-EXPERIMENT ASSIGNMENT

Study this chapter of the manual, the lecture notes on the 2230L web site, and pages 95-107 of Klein. Do the first seven sections of your notebook write-up from date through references. Be sure to write the correct reactions, not just structures in your lab notebook.

A student who has prepared for the Extraction (Separation of Acidic Substances) experiment should be able to:

1. Define and explain the processes of liquid-liquid extraction involving acids, bases, ions and neutral substances.
2. Predict the product of the reactions of benzoic acid and 2-naphthol with NaOH and NaHCO₃ solutions, and of their conjugate bases with HCl.
3. Explain Ka and pKa, and how they relate to the direction of a reaction.
4. If given two or more molecules, be able to predict which will be more soluble in an aqueous solvent, and which in an organic solvent.
5. If given an acidic molecule, be able to draw the conjugate base. If given a basic molecule be able to draw the conjugate acid.
6. If given an acid-base reaction be able to identify the acid and base on each side of the arrow. Furthermore, if given pKas be able to predict if the reaction will proceed in the forward direction or not.
7. Draw and label the apparatus used for this experiment (a separatory funnel) and explain how to use it. Predict the consequences of improper use (including failure to vent fumes through the stopcock).
8. Draw the structure given the name, or give the name from the structure, of the compounds used in the day's experiment, and give the role of each (reactant, solvent, catalyst, etc.).
9. Identify and explain safety considerations for this experiment.
10. Perform the day's experiment safely and successfully.

Quizzes given after the experiment has been performed may also include:

11. Given starting materials and procedures for extraction experiments, predict what substance will appear in what layer.
12. Predict what will happen if you make changes in the procedure (for example, use more extractions with smaller volumes of solvent, and extract with NaOH and NaHCO₃ in the wrong order).

**Safety Considerations**

Concentrated hydrochloric acid (HCl) is a very strong corrosive acid that will cause rapid destruction of any tissue it encounters. Wear eye goggles and a lab coat at all times during this lab. It is advisable to wear gloves when manipulating the hydrochloric acid. Open HCl bottles and use HCl only in the fume hoods. Avoid HCl contact with skin, eyes and clothes. If contact is made, wash immediately with copious amounts of water. Inform instructor. Neutralize and clean up any spills.

Sodium hydroxide (NaOH) is caustic. Avoid contact with skin, eyes and clothes. If any contact is made, wash area with plenty of water.

Two precautions should be taken whenever working with separatory funnels. Because gaseous products often form and because most extraction solvents are volatile, pressure often builds up during the extraction process. To prevent accidents caused by the pressure, frequent venting of the funnel is necessary as described in the procedure that follows.

When venting the funnel, always make sure that the opening is pointed away from yourself or anyone else because the pressure may force some of the contents to spurt out with the released gases.

It is very important that waste from this experiment is disposed of in the correct manner. All excess sodium bicarbonate solution, excess hydrochloric acid and the waste from the vacuum flask is aqueous and not organic. Aqueous waste needs to be disposed of down the drain with copious amounts of water.
Do not place excess sodium bicarbonate solution, excess hydrochloric acid or the waste from the vacuum flask in the “Non-halogenated liquid organic waste”. If sodium bicarbonate and acid are mixed in a bottle and sealed, gasses will form and the container can rupture. If the container is glass, as organic waste containers typically are, this can cause dangerous flying glass shards. Be very careful about proper waste segregation for this lab.

Here are some other precautions. They aren't safety precautions, but failure to observe them can cost you money and/or points.

Because of the pressure and the tendency of ground glass apparatus to “freeze”, the cap or stopper should only be placed on the funnel when it is being shaken. When it is upright or when it is stored in your locker, always remove the stopper.

Finally, it is a good practice to keep a beaker or Erlenmeyer flask big enough to hold all of the contents of the funnel under the funnel. This will allow you to recover from stopcock leaks or from accidentally pouring a liquid into a funnel with an open stopcock.

EXPERIMENT

This is a very time intensive lab. Be sure to arrive fully prepared and on time to class. You must work very efficiently during your class time to complete the experiment within the allotted time. Read over the notes and procedures several times before class to familiarize yourself with each step.

In a 100 mL graduated cylinder obtain approximately 20 mL saturated sodium bicarbonate in water. Do not waste time getting exactly 20.0 mL, but do record the volume used.

In a 10 mL graduated cylinder obtain approximately 10 mL water. Again do not waste time getting exactly 10.00 mL. The exact volume of this is not important.

In a 10 mL graduated cylinder obtain approximately 10 mL of 1.5 M sodium hydroxide in water. Again do not waste time getting exactly 10.00 mL. Record volume used in notebook.

Place the target volume of a solution of benzoic acid and 2-naphthol in tert-butyl methyl ether (MTBE) in the separatory funnel. The target volume is probably 30.0 mL but check with your instructor before obtaining. The concentration of this solution is $2.50 \times 10^{-2}$ g/mL of each material. Double check this concentration with the solution label and your instructor. Be sure to write these values in your notebook. The stating volume and concentration determine the starting mass of benzoic acid and 2-naphthol. Your instructor may elect to grade this experiment based, in part, on your recovery. If so, he or she may dispense the solution to you to insure fairness. If not, you will find the solution in one of the hoods. Often the solution is affixed with an auto-dispensing head. Each pull up and depression dispenses a fixed amount of liquid. Consult your instructor as to how many pumps are desired. Use the volume and concentration to determine the mass of each compound.
You may place the solution directly into your separatory funnel. If you dispensed the MTBE solution to a transfer vessel, rinse the vessel with a few milliliters of MTBE and add that to the separatory funnel as well.

Add approximately 10 mL of water to the separatory funnel and note and document which layer (aqueous or organic) is on top. Remember to always write your data and observations directly in your lab notebook.

Drain the bottom layer into a flask or beaker. The stopper must be removed in order for the separatory funnel to drain. Note how the meniscus moves as the stopcock is opened. Do not allow any of the MTBE solution to drain into the flask. Discard the water.

**Sodium Bicarbonate Extraction**

Add approximately 10 mL of saturated sodium bicarbonate solution to the separatory funnel. Swirl the funnel for a short period of time (5-10 seconds), vent. Put the top on the funnel and turn it upside down, while holding the top firmly in place. Open the stopcock to vent the funnel. (Carbon dioxide gas is formed when sodium bicarbonate reacts with acids. Therefore, it is very important to vent the funnel frequently while shaking to release pressure.)

Close the stopcock and shake or swirl the funnel for a short period of time, then open the stopcock or stopper to vent. Repeat multiple times to mix the contents well. Vent the funnel frequently. This is necessary not only because additional carbon dioxide may form, but also because MTBE is very volatile and its vapors may cause a pressure buildup as your hands and the heat of the reaction warm the funnel.

Return the funnel to the ring stand, remove the stopper, and allow the layers to separate undisturbed. After the layers have separated, open the stopcock and drain the lower layer into a 50 mL Erlenmeyer flask or beaker labeled “flask 1.” Leave the top layer in the funnel. Do not allow any MTBE to drain into flask 1. If MTBE is accidentally drained, pour the entire contents of the flask back into the separatory funnel and again drain off the aqueous layer.

The sodium bicarbonate extraction is not very efficient; therefore this entire process is repeated with a new 10 mL aliquot of sodium bicarbonate solution. The new lower layer is combined with the first lower layer in “flask 1”.

What is in “flask 1”?

**Sodium Hydroxide Extraction**

Add approximately 10 mL of a 1.5M aqueous sodium hydroxide solution to the liquid remaining in the separatory funnel. (Two layers should form at this point. If you don’t have two layers, then you probably have the wrong layer in flask 1.) Stopper the funnel, and mix the layers as described above.

Return the funnel to the ring stand, remove the stopper, and allow the layers to separate
completely. Note and document what you see. Drain the lower layer into a 50 mL Erlenmeyer flask or beaker labeled “flask 2.”

What is in “flask 2”?

**Recovery of the Solutes**

The solutions in both flasks 1 and 2 must be acidified by adding concentrated hydrochloric acid until the solution reaches a pH of about 1. First add about 3 mL of the acid to the flask. Swirl the flask gently to ensure that the acid has mixed with the contents of the flask. Next, check the pH using a strip of pH paper on a watch glass. To do this, stir the solution in the flask with a clean stirring rod and touch the wet rod to the pH paper. Compare the color of the paper to the chart on the container and read the pH. (Note: Litmus paper should also be used in this way. Never dip the paper into the solution to be tested, because indicator chemicals from the paper will contaminate your sample.)

Acidification of the solutions should cause precipitates to form in each flask. (Why?) If precipitation does not occur, swirl the flask again, and check the pH again, adding acid as necessary.

To recover the precipitates, use suction filtration. Attach a Büchner funnel to a filter flask and clamp the flask to a ring stand. Place a piece of 70 mm filter paper in the Büchner funnel so that it sits flat on the bottom of the funnel, covering all of the holes. Wet the filter paper with some of the solvent (water, in this case) of the solution you will be filtering so that the paper clings to the flat bottom of the funnel.

Connect the vacuum line to the sidearm of the flask. Turn the vacuum on all the way. Left or counterclockwise is open, right or clockwise is closed. This will cause the filter paper to sit down on the funnel holes.

Carefully pour all of the solution from flask 1 onto the paper in the funnel. Scrape out as much solid from the flask as possible and add it to the filter. Once all of the liquid has been removed, pop the funnel off the vacuum flask.

Transfer the filter paper from the funnel to a dry piece of filter paper or watch glass and allow them to air-dry. Clean the funnel quickly, place a new piece of filter paper in the funnel, and repeat the process to recover the solid from flask 2.

Weigh both crude samples and obtain a melting point of each. Turn the samples in to your instructor for grading if required.

**CLEANUP**

The liquid in the separatory funnel is MTBE. Place this in the non-halogenated liquid waste container in the hood. If your instructor does not collect the benzoic acid and 2-naphthol you isolate, place them in the non-halogenated solid waste container.

The liquid in the suction flask is water. Pour down the drain with plenty of water. Any residual sodium bicarbonate solution should be poured down
drain. And residual hydrochloric acid should be neutralized and poured down sink.

**It is very important that the sodium bicarbonate and acid aqueous waste be put down sink and not in the liquid organic waste container.** If sodium bicarbonate and acid are mixed in a glass bottle and sealed, the bottle can easily rupture explosively sending glass shard flying. This can be very dangerous.

Using a sponge, clean up your work area. Clean the separatory funnel, Büchner funnel, flasks and all other materials with soap and water. Acetone may have to be used to clean residue from separatory funnel.

**POST-EXPERIMENT ASSIGNMENT**

Complete your datasheet. Turn your notebook pages and datasheet into your instructor. Prepare for the separation of acidic substances portion of the next quiz.

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