

Extraction: Separation of Acidic Substances

Chemists frequently find it necessary to separate a mixture of compounds by moving 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 a solution in one solvent to a solution in 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 these.

Extractions may involve removing a desired substance in a mixture from undesirable ones. They may also be done to remove the undesirable components of a mixture, leaving the desirable components behind.

PRE-EXPERIMENT ASSIGNMENT

Study this chapter of the manual, the lecture notes on the Chemistry Department web site, and pages 95-107 of Klein. Do the first seven parts of your notebook writeup from date through references.

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 K_a and pK_a, 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. 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 pK_a s 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 Notes

Concentrated hydrochloric acid (HCl) is a very strong acid that will cause rapid destruction of any tissue it encounters. Wear eyegoggles and a lab coat at all times during this lab. It is advisable to wear gloves when manipulating the hydrochloric acid. HCl fumes. 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.

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

inverted. 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.

Preparation

Obtain the target volume of a solution of benzoic acid and 2-naphthol in *tert*-butyl methyl ether (MTBE). The target volume is probably 30.0 mL but check with your instructor before obtaining. The concentration of this solution is 2.50×10^{-2} g/mL of each material. Double check this concentration with the solution label and your instructor. 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.

Place the MTBE solution in 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 (deionized, of course) 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.

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 (about 10 seconds). 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 immediately to release the 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 at least three 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 cap, 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.

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. Remember to hold the cap firmly in place while swirling or shaking and to vent the funnel frequently to release the pressure that builds up. 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, disconnect the tubing from the vacuum line and then turn the vacuum off.

Transfer the solid from the filter paper on the funnel to a dry piece of filter paper and allow them to air-dry. Clean the apparatus, including the inside of the funnel, and repeat this 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

Put your used MTBE 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 at the bottom of the suction flask should be water with all of the organic materials removed. Pour down the drain with plenty of water.

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.