Lab 4 Separation of Benzoic Acid, 3-Nitroaniline, and Naphthalene

Objectives

- Separate organic compounds based on functional groups
- Use pH changes to separate compounds

Background

Separations of Immiscible Liquids

Throughout organic experiments, multiple different solvents get used, such as a variety of organic solvents and water. Many organic solvents, like ether and dichloromethane, are not miscible with water, so mixtures of these solvents can easily be separated into layers. The compounds soluble in each layer are also separated, allowing purification of reaction products and separations of mixtures based on different solubilities.

In large scale experiments, the separation of immiscible solutions is usually performed in a separatory funnel, as seen in Figure 1. The liquids in a separatory funnel can be shaken together, using the stopcock to vent any built-up pressure during mixing, and then allowed to settle into layers and drained separately through the stopcock. Microscale experiments often mix the solutions in a test tube or small flask, and the layers are removed with a pipette. The position of the layers after settling depends on the density of each layer. Most organic solvents are less dense than water, but dichloromethane is a notable exception that is denser than water and appears as the bottom layer.

Figure 1 Separatory funnel for macroscale separation of organic and aqueous layers

There are two common processes using the separation of immiscible solutions. A wash is the term for the addition of solvent to wash away impurities while the compound of interest stays in its original layer. The most common wash is the addition of water itself, to wash away water-soluble reagents or byproducts. Extractions use solubility or reactivity to pull the compound of interest from one layer into the other. One common example is the addition of organic solvent to extract an organic natural product from its source.

Altering the Solubility of Organic Bases

Extractions often use pH changes to manipulate the solubility of different compounds so that they can be separated from a mixture. If a mixture dissolved in an organic solvent contains an organic base, extraction with an acid solution protonates the base, forming the conjugate acid salt, as shown in Figure 2. The conjugate acid salt is an ionic compound that is soluble in water, separating it from the original organic solution and any other organic compounds there. After separating the layers, the isolated conjugate acid can be deprotonated with the addition of base to reconstitute the organic base. A final extraction with the addition of an organic solvent moves the now organic-soluble base back into an organic solution.

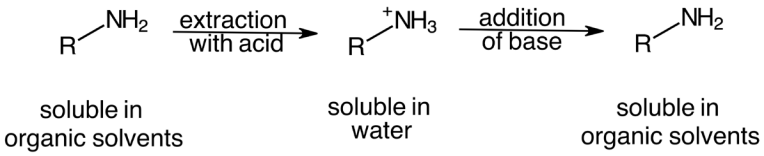

Figure 2 General scheme of organic base extractions

Altering the Solubility of Organic Acids

Organic acids can be isolated using the same general process as for bases. Mixing an organic acid solution with an aqueous base results in the water-soluble conjugate base salt, as shown in Figure 3. Once the conjugate base salt is separated out, the addition of acid reconstitutes the organic acid and allows it to be extracted into a now pure organic solution.

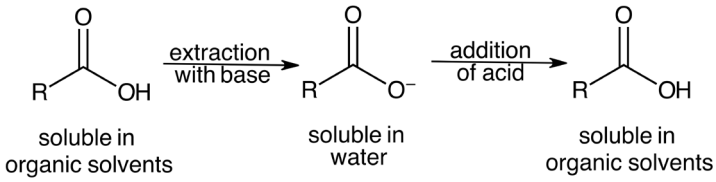

Figure 3 General scheme of organic acid extractions

In this experiment, a mixture of benzoic acid, 3-nitroaniline, and naphthalene is separated by manipulating the solubility of the organic acid and base in multiple steps of extraction. It is extremely important to understand where each compound ends up after each layer separation as the compounds move between the organic and aqueous layers depending on the reagent solution at each step. To follow the whole extraction process, it is helpful to write out a flow chart like the one in Figure 4. While working, carefully label the layers so that you do not mix up the steps or which layer is which.

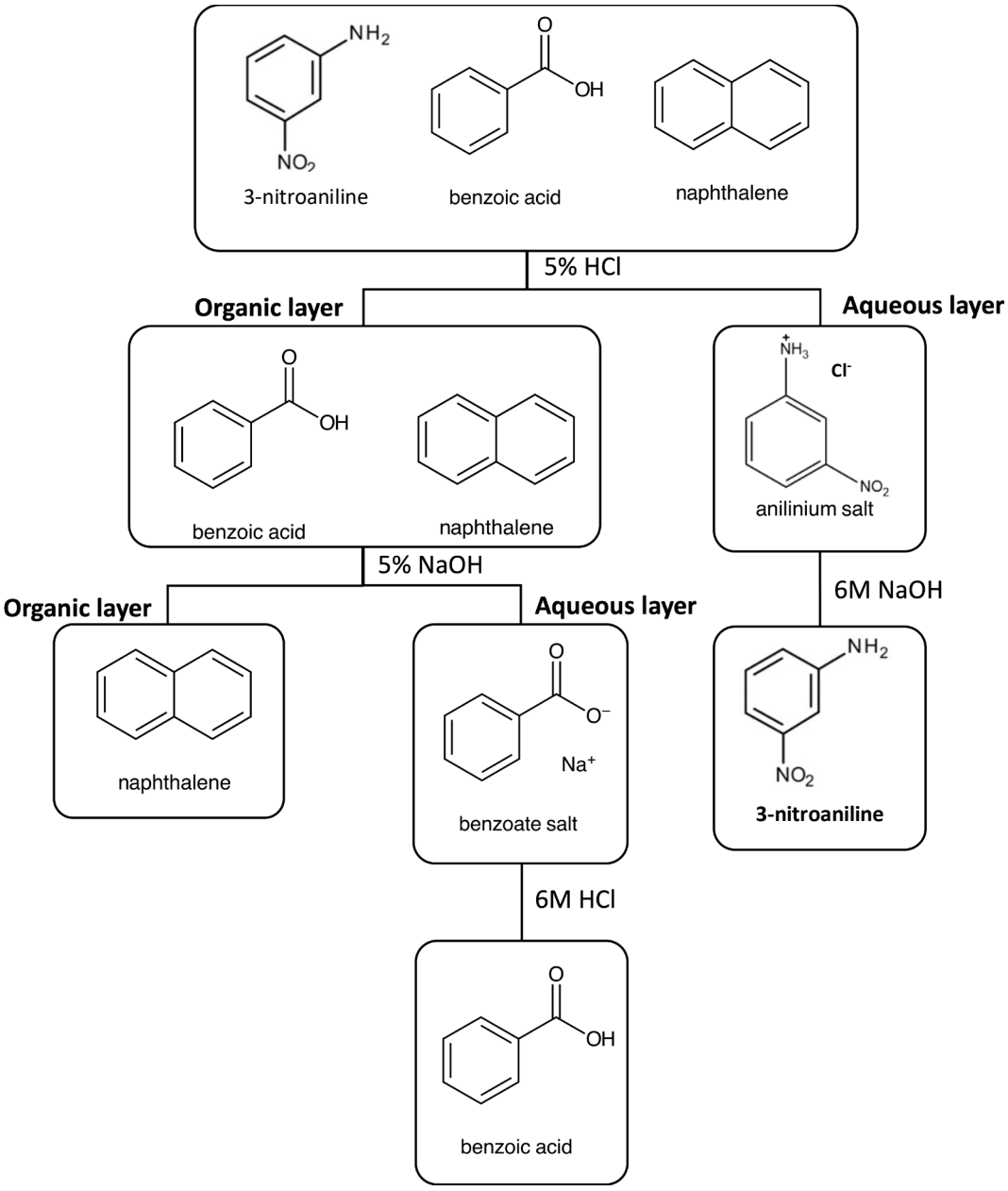

Figure 4 Summary flow chart of the separation of 3-nitroaniline, benzoic acid, and naphthalene

Materials

- Mixture of benzoic acid, naphthalene, and 3-nitroaniline
- Dichloromethane
- 5% HCl solution
- 5% NaOH solution
- 6M HCl
- 6M NaOH
- Anhydrous magnesium sulfate
- Microscale glassware kit
- Test tubes
- Pasteur pipette
- Air stream or warm water bath

Safety goggles are required!

Benzoic acid is corrosive and will cause skin irritation. 3-Nitroaniline is flammable, toxic, and can cause skin irritation. Naphthalene is flammable and toxic and its vapors can cause nausea. Dichloromethane is toxic and will cause skin and eye irritation; keep in the hood when open. Sodium hydroxide is toxic and corrosive. Hydrochloric acid is toxic and corrosive.

Procedure

Separation of Benzoic Acid, Naphthalene, and 3-nitroaniline

1. Weigh, record and place approximately 1.50 g of the mixture of benzoic acid, naphthalene, and 3-nitroaniline in a round bottom flask. Add ~3 mL of dichloromethane (DCM).
2. Place 2.5 mL of 5 % HCl solution in the flask and shake well to allow the organic and inorganic layers to mix thoroughly.
3. Identify the aqueous layer in the flask based on the density of the solvents.
4. Remove the aqueous layer using a long Pasteur pipette and put it in a labeled test tube.
5. Place another 2.5 mL of 5% HCl in the flask, shake, and remove the aqueous layer, placing it in the same test tube.
6. Add 1.0 mL of water to the flask and shake well to remove any remaining HCl that may have been left behind in the organic layer.
7. Remove the aqueous layer and place it in the labeled test tube containing the HCl solution layers where all the protonated 3-nitroaniline should now be located. Note – think about how you will obtain accurate masses of the final compounds. What can you do beforehand to the test tube?
8. Place 2.5 mL of 5 % NaOH solution in the flask and shake well.
9. Remove the aqueous layer and place it in a different labeled test tube.
10. Place another 2.5 mL of 5% NaOH in the flask, shake, and remove the aqueous layer, placing it in the same test tube.
11. Add 1.0 mL of water to the flask and shake well to remove any remaining NaOH that may have been left behind in the organic layer.

12. Remove the aqueous layer and place it in the labeled test tube containing the NaOH solution layers.
13. Add 0.05 g of anhydrous magnesium sulfate to the organic layer in the flask and swirl.
14. Filter the solution to remove the magnesium sulfate and place the solution, which should be only naphthalene in dichloromethane, in a labeled and tared test tube.
15. Measure the mass and volume of the naphthalene solution in dichloromethane.
16. Add 6 M NaOH to the HCl solution layers you previously collected, slowly mixing thoroughly as you add it until the solution tests basic according to litmus paper.
17. Add 2.5 mL of dichloromethane to the now basic solution and mix well.
18. Remove the organic layer and place it in a labeled test tube.
19. Add 0.05 g of anhydrous magnesium sulfate to dry the organic solution.
20. Filter the solution to remove the magnesium sulfate and place the solution, which should now be only 3-nitroaniline in dichloromethane, in another labeled test tube.
21. Measure the mass and volume of the 3-nitroaniline solution in dichloromethane.
22. Add 6 M HCl to the NaOH solution layers you previously collected, slowly mixing thoroughly as you add it until the solution tests acidic according to litmus paper.
23. Add 2.5 mL of dichloromethane to the now acidic solution and mix well.
24. Remove the organic layer and place it in a labeled test tube.
25. Add 0.05 g of anhydrous magnesium sulfate to dry the organic solution.
26. Filter the solution to remove the magnesium sulfate and place the solution, which should now be only benzoic acid in dichloromethane, in another labeled test tube.
27. Measure the mass and volume of the benzoic acid solution in dichloromethane.
28. Use a light stream of air or a warm water bath to remove the solvent. Perform this in a fume hood.
29. Determine the masses of each compound, the percent by mass, and the overall percent recovery. Show all calculations.

Pre-Lab Questions

Prepare for lab by completing and understanding the answers to these questions. Refer to the Background or another resource, such as your textbook, if necessary.

1. What precautions should one use when working with naphthalene?

2. What precautions should one use when working with sodium hydroxide?

3. What is the process of acidifying a basic solution?

4. What is the process of making an acidic solution basic?

5. What is the basis of the separation being performed in this experiment?

Lab 4: Separation of Benzoic Acid, Naphthalene, and 3-nitroaniline Report Sheet

Name _____
Date _____
Section _____
Instructor _____

Original Mixture

Mass of original mixture (g) _____

Naphthalene Component

Mass of naphthalene recovered (g) _____

% by mass of naphthalene in mixture _____

3-nitroaniline Component

Mass of 3-nitroaniline recovered (g) _____

% by mass of 3-nitroaniline in mixture _____

Benzoic Acid Component

Mass of benzoic acid recovered (g) _____

by mass of benzoic acid in mixture _____

Total percent recovery _____

Show All Calculations:

Post-lab Questions

1. You find a separatory funnel set up in a fume hood. There are clearly two visible layers. Describe a method you could use to determine which layer is the aqueous layer.

2. If you had a mixture of butyric acid and hexane, how would you separate the two compounds?