Lab 3: An ester hydrolysis and a carbon dioxide extraction

Objective:

Introduction: In this experiment, you are going to make orange-scented soap. This requires two parts: first, the extraction of the orange scent (a compound called limonene from orange rind) and, second, the making of the soap (to which the extract of limonene will be added).

An extraction is the process of separating desired compounds from a solid material or solution by means of a cunningly-chosen solvent. By “cunningly-chosen”, I mean that the solvent is chosen based on its polarity, the polarity of the desired compound to be extracted, and practical factors, such as the ease of removing the solvent once the extraction is complete. For instance, a traditional way to remove non-polar compounds such as caffeine and limonene has been to use non-polar solvents such as benzene or slightly polar solvents such as isopropanol.

In this experiment, you will use liquid carbon dioxide to remove limonene from orange rind. Carbon dioxide is non-polar and will do the job, but the drawback is that liquid carbon dioxide can be achieved only above pressures of 55 atmospheres. Fortunately, plastic centrifuge tubes can withstand such pressures and thus the extraction can be performed in them.

In the second part, soaps can be made through a process called saponification. Fats and oils, also known as triacylglycerides (or even more briefly, triglycerides), are types of lipids. Fats (animal origin) and oils (vegetable origin) are high-molar mass esters of carboxylic acids (fatty acids) attached to a glycerol molecule. The acids can be hydrolyzed from the triglyceride under alkaline conditions; it is this base-catalyzed hydrolysis of a tryglyceride that is called saponification.

\[
\text{O}\\ R_1\text{C} - \text{O} \quad \text{CH}_2 \\
\text{O}\\ R_2\text{C} - \text{O} \quad \text{CH} \\
\text{O}\\ R_3\text{C} - \text{O} \quad \text{CH}_2 \\
\text{R}_1\text{COO}^- \text{Na}^+ \quad \text{HO} - \text{CH}_2 \\
\text{NaOH} \\
\text{saponification} \\
\text{R}_2\text{COO}^- \text{Na}^+ + \text{HO} - \text{CH} \\
\text{R}_3\text{COO}^- \text{Na}^+ \quad \text{HO} - \text{CH}_2 \\
\text{Triglycerides} \quad \text{carboxylic acid salts (soap)} \quad \text{glycerol}
\]
The naturally-occurring acids are rarely of a single type in any given triglyceride. In fact, a single triglyceride molecule may contain three different acid residues (R₁COOH, R₂COOH and R₃COOH), and not every triglyceride in the substance will be identical. Each fat or oil, however, has a characteristic statistical distribution of the various types of fatty acids.

In this experiment, you will make soap from animal fat (lard), vegetable oil (olive oil) and a combination of the two. The fats and oils that are most common in soap preparations are lard and tallow from animal sources, and coconut, palm and olive oils from vegetable sources. The length of the hydrocarbon chain and the number of double bonds in the carboxylic acid portion of the fat or oil determine the properties of the resulting soap. For example, a salt of a saturated fatty acid makes a harder, more insoluble soap; longer chain fatty acids also make a more insoluble soap. Solubility is more important because the “softer” (more soluble) a soap is, the more it will lather.

Oleic acid: \( \text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH} \)

Palmitic acid: \( \text{CH}_3(\text{CH}_2)_14\text{COOH} \)

Stearic acid: \( \text{CH}_3(\text{CH}_2)_16\text{COOH} \)

Lauric acid: \( \text{CH}_3(\text{CH}_2)_10\text{COOH} \)

Myristic acid: \( \text{CH}_3(\text{CH}_2)_12\text{COOH} \)

Tallow is the principal fatty material used in making soap. The solid fats of cattle are melted with steam and the tallow layer formed at the top is removed. Soapmakers usually blend tallow with coconut oil and saponify this mixture. The resulting soap contains mainly the salts of palmitic, stearic and oleic acids from the tallow, and the salts of lauric and myristic acids from the coconut oil. The coconut oil is added to produce a softer, more soluble soap. Lard (from hogs) differs from tallow (from cattle or sheep) because lard contains more oleic acid.

Pure coconut oil yields a soap that is very soluble in water. The soap is, essentially, the salt of lauric acid with some myristic acid. It is so soft that it will lather even in seawater. Palm oil contains mainly two acids, palmitic acid and oleic acid in about equal amounts. Saponification of this oil yields a soap that is an important constituent of toilet soaps. Olive oil contains mainly oleic acid; it is used to prepare Castile soap, named after the region in Spain in which it was the first made.

Toilet soaps generally have been carefully washed free of any alkali remaining from the saponification. As much glycerol as possible is usually left in the soap, and perfumes and medicinal agents are sometimes added. Floating soaps are produced by blowing air into the soap as it solidifies. Soft soaps are made by using potassium hydroxide, yielding potassium salts rather than the sodium salts.
of the acids. They are used in shaving cream and liquid soaps. Scouring soaps have abrasives (such as fine sand or pumice) added.

More information about soap-making can be found at: millersoap.com/soapdesign.html

**Safety issues:** Hot potassium hydroxide is used in this lab, so goggles must be worn. The cap of the pressurized centrifuge tube may fly off violently; work in the hood and avoid “aiming” the top of the tube towards any person.

Disposal: Check solutions to be discarded for excessive alkalinity (use the pH paper); if the pH is less than 10, the solutions may be poured down the sink; otherwise, they must go in the base waste container. Used orange rind can be discarded in the trash.

**Materials**

- electronic balance
- distilled water
- 10 mL Erlenmeyer flask
- Buchner funnel with filter paper
- 25 mL Erlenmeyer flasks
- glass stirring rod
- two 50 mL beakers
- sand bath with thermometer
- 10 mL graduated cylinder
- pH paper (to test discard alkalinity)
- AND A BUNCH OF CHEMICALS (see question 2 below)

**Procedure**

For the limonene extraction part, each student should **extract his/her own limonene**. Unfortunately, all I could find was the carbon dioxide extraction of eugenol (clove oil), and who wants clove-scented soap? Nevertheless, it will serve as a useful guide. Modify the procedure so that it is appropriate for 2.5 g of grated orange rind; the extraction will be done in a 15-mL centrifuge tube. (see question 4 below)

For the soap-making part, work in **groups of three**. Each person in the group will use one of the following for their triglyceride; all three triglyceride combinations should be done by the group (in other words, coordinate with each other!):  

| Triglyceride #1: | 0.75 grams lard |
| Triglyceride #2: | 0.75 grams olive oil |
| Triglyceride #3: | 0.375 grams lard and 0.375 grams olive oil |

1. Make a solution of about 0.75 g sodium hydroxide in a mixture of 3 mL distilled water and 3 mL 95% ethanol in a 10 mL Erlenmeyer flask.

2. Measure out and place your triglyceride in a 25 mL Erlenmeyer flask and add the sodium hydroxide solution to it. Heat the mixture in a sand bath at about 120°C. Place an inverted 50 mL beaker over the neck of the flask to help reduce evaporation. Swirl the Erlenmeyer flask every few minutes.
3. The soap often begins to precipitate from the boiling mixture within about 20 minutes. If it appears that some of the alcohol and water is evaporating from the flask, you may add up to 1 mL of a 50/50 water/ethanol mixture to replace the solvent that is lost. Heat the mixture for a total of 25 minutes in the sand bath.

4. Put 10 mL saturated sodium chloride solution in a 50 mL beaker and transfer the saponified mixture from the Erlenmeyer flask to the beaker. Stir the mixture while cooling the beaker in an ice-water bath. Collect the prepared soap on a Buchner funnel by vacuum filtration on filter paper.

5. Wash the soap with two 5 mL portions of ice-cold distilled water to remove any excess sodium hydroxide. Continue to draw air through the filter for a few minutes to partially dry the product.

6. Test your soap while it is still damp by removing a small piece (size of a pea) from the filter paper and placing it in a clean 10 mL graduated cylinder. Add 3 mL distilled water, place your thumb over the opening of the cylinder and shake the mixture vigorously for about 15 seconds. After about 30 seconds, measure the level of the foam inside the cylinder (you may wish to set up a data table to record not only your soap, but your partners’ soaps as well).

7. Add two drops of 4% calcium chloride solution to the soap mixture. Shake the mixture for 15 seconds and allow it to stand for about 30 seconds. Measure the level of the foam inside the cylinder, and record that in your data table.

8. Add 0.5 g trisodium phosphate to the soap mixture. Shake the mixture for 15 seconds and allow it to stand for about 30 seconds. Measure the level of the foam inside the cylinder, and record that in your data table.

9. Examine the dried soap you and your partners made. Compare and record (again in table format) the hardness of each soap.

Questions

1. Write a scientific objective (in other words, don’t write “we’re making soap”) for this experiment in the appropriate section of your lab notebook. The objective should not be long, but contain enough words to account for the major goal(s) of this lab.

2. Finish the materials portion of the writeup (I’ve left out all of the chemicals for both parts).

3. Look up the structure of limonene and draw it in the reaction scheme section, which should either be just before or just after the materials/procedure section.

4. Modify the attached “eugenol from cloves extraction” procedure to accommodate extracting limonene from orange rind. Don’t worry about the
spectroscopy or other non-procedural parts of the attached writeup; focus on the procedure.

5. I’ll really be looking for the two data tables, so make sure that you have your partners’ results as well, and make the whole thing legible and logically organized.

6. During the filtration process, what is the purpose of washing the soap with successive 5 mL ice-cold water portions?

7. Why do you suppose a mixture of ethanol and water (instead of simply water) is used for saponification?

8. Explain the results of the “foaming test” for any of the soaps before and after the calcium chloride is added, and after the trisodium phosphate is added. Use chemical equations as part of your explanation as appropriate.

9. Which soap (of the three that were made by your group) gave the best lather (lots of foam)? Describe the differences in lathering properties and relate them to the differences in chemical structure between the soaps.

10. Describe the connection between the hardness of the soap and the state of the original triglyceride material.

11. Read the attached “Principles of Green Chemistry”. In the past, you would have extracted the limonene from orange rind using benzene. By using carbon dioxide instead of benzene, explain which (there are more than one) of the principles of green chemistry we are following.