Experiment 4: Soaps and Detergents

Background

There is some evidence that soap-making was known to the Babylonians in 2800 BC and to the Phoenicians around 600 BC. Surprisingly enough, it seems that soap was first used for cleaning textile fibers such as wool and cotton in preparation for the dyeing process and not for personal hygiene. Wool obtained from sheep has a coat of grease that interferes with the application of the dyes. In those days colorful garments were very valuable and our ancestors figured out that they could remove that layer of grease with a mixture of tallow (rendered fat from cattle and sheep) and ashes.

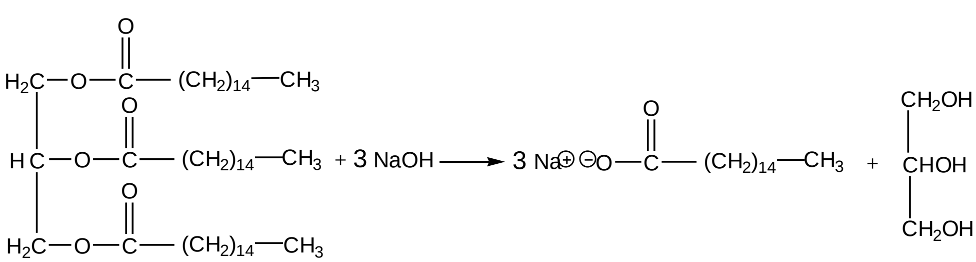
According to a Roman legend soap got its name from mount Sapo, a place where the Romans offered animal sacrifices. Apparently the fat from the animals got mixed with the wood ashes and got washed downhill where the women noted that using that mixture to do their wash made their clothes cleaner.

Throughout 18th century Europe soap was a luxury item and as such it was heavily taxed. It was mainly used by the very wealthy.
Modern soap-making began in the 19th century with the work of Eugène Chevreul who discovered the chemical nature of soap.

Today soap is manufactured much like it was over a hundred years ago: fats or oils are heated in the presence of a strong base (NaOH or KOH) to produce fatty acid salts and glycerol in what is called the saponification reaction. The salt of a fatty acid is the soap, a soft and waxy material that improves the cleaning ability of water.

The Saponification Reaction

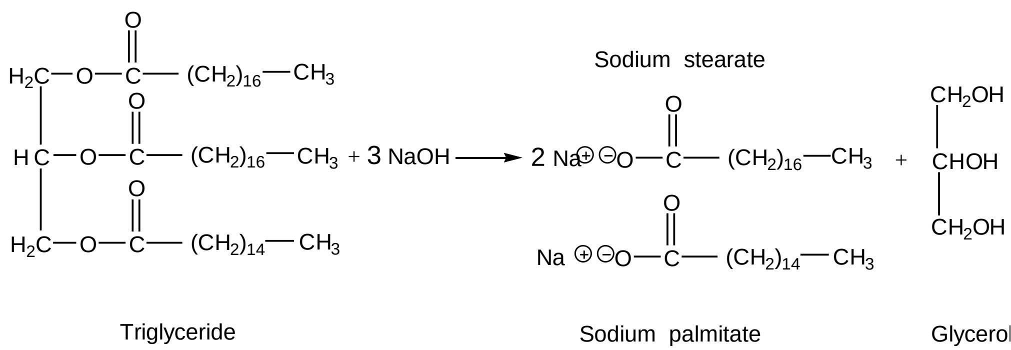
An example of a saponification reaction is indicated below.



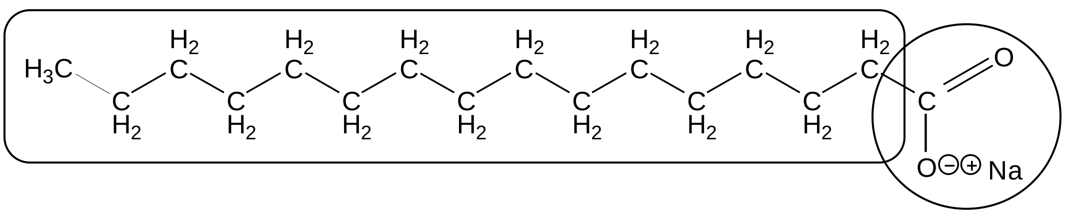
Triglyceride Sodium palmitate Glycerol

Sodium palmitate $CH_3(CH_2)_{14}COO^- Na^+$ is the salt of palmitic acid $CH_3(CH_2)_{14}COOH$, a fatty acid with a 16 carbon chain. Fatty acids are straight-chain monocarboxylic acids with a general formula $CH_3(CH_2)_nCOOH$ where *n* usually varies between 8 and 18. In nature, most fatty acids are present as triglycerides. Natural fats and oils usually include different fatty acids. For example, the saponification reaction of a component of olive oil would produce the salts of palmitic acid and stearic acid.

The Cleaning Power of Soap

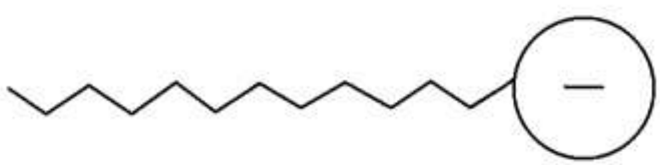


Notice the particular structure of the soap molecule: it has a long nonpolar tail (the hydrocarbon chain of the fatty acid) and a highly polar end (the ionic group COO^-). The non polar or hydrophobic tail can dissolve the grease and dirt whereas the polar or hydrophylic end is attracted to water molecules.



Hydrophobic tail (non-polar) **Hydrophilic head (polar)**

It is common to represent the non-polar portion with a zig-zag line and the polar head with a circle.



Adjacent negatively charged heads repel each other forcing the soap molecules into a spherical shape, a micelle.The soap molecules orient themselves with the non polar tails towards the center of the micelle and the COO^- groups facing the water. In the presence of oil (or dirt) the non polar tails interact with the oil that ends up at the center of the micelle. This is how soap cleans: the dirt and the grease stay at the center of the micelles who repel each other due to the negatively charged outer surface. Rinsing with water washes the micelles (and the dirt) away. Soap is acting as an emulsifying agent. Recall that an emulsion is the dispersion of a liquid in a second immiscible liquid.

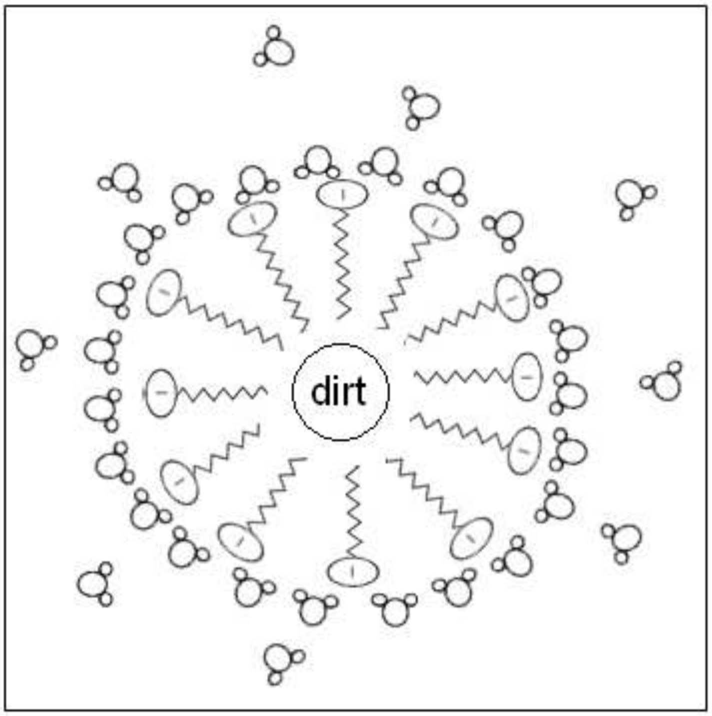


Diagram of a soap micelle

The nonpolar tails of the soap molecules attract dirt and the polar heads attract water molecules.

Problems with using soap

The cleaning properties of soap are intimately related to the fact that there is a highly polar head and a nonpolar tail in each soap molecule. If the ionic charge of the polar head were to disappear, the soap molecules would not be able to interact with water, micelles would not form, and soap would not clean. This is what happens in acidic or hard water. In acidic water the COO^- group gets protonated and the fatty acid precipitates, being now water insoluble.

For example:

$$CH_3(CH_2)_{14}COO^-Na^+ + H^+ \rightarrow CH_3(CH_2)_{14}COOH + Na^+$$

In hard water (water with a high concentration of mostly magnesium and calcium) these ions react with the carboxyl end forming insoluble salts (commonly called “bathtub ring” or “scum”).

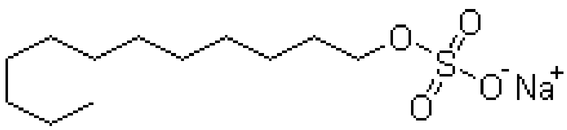
$$CH_3(CH_2)_{14}COO^-Na^+ + Ca^{2+} \rightarrow (CH_3(CH_2)_{14}COO^-)_2Ca \text{ (insoluble)}$$

Once those salts precipitate the soap cannot clean.

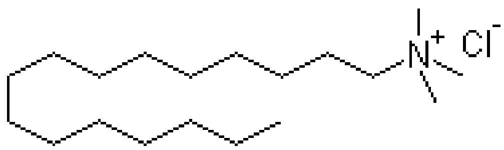
Detergents

The manufacturing of soap took a turn during World War I when the first synthetic detergent (or simply “detergent”) was produced. Synthetic detergents are non-soap cleaning products that were developped as a response to the shortage of fats and because of the need for a cleaning agent that would work well in hard water.

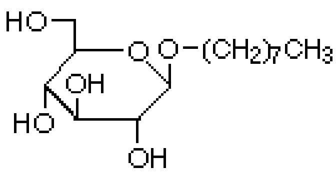
Today there are a variety of detergents, which in general contain a surfactant, a builder, and other additives (such as bleaching agents and enzymes). The surfactants are the chemical equivalent of the soap and they are responsible for the cleaning properties of the detergent. Some of them are anionic, some of them are cationic and some of them are non-ionic. For example:



sodium dodecyl sulfonate (anionic)



trimethylhexadecyl ammonium chloride (cationic)



octyl glucoside (non-ionic)

The builders are compounds responsible for removing the calcium and magnesium ions in hard water. Often times phosphates are used as builders which causes rather serious environmental problems. Detergents containing phosphates end up in wastewater where they cause excessive growth of algae and other aquatic plants. When those die, bacteria in the dead matter consume oxygen and less oxygen is available for fish and other aquatic life.

Today you can read in the list of ingredients of any detergent whether they include phosphates or not and so you can make a more informed choice as a consumer.

Another issue is the biodegradability of some of the components in the detergent. For instance, whereas soaps are biodegradable (can be degraded by bacteria), many of the surfactants initially used in detergents were not. Today most developed countries have switched to detergents made from biodegradable surfactants that do not contain phosphates. Some of the additives found in detergents, though, are non biodegradable.

In this experiment we will prepare soap and compare its properties to those of a commercial soap and a detergent.

Safety Hazards

NaOH is corrosive to skin and clothing. Avoid contact. Wash hands before leaving the laboratory. Ethanol is flammable so be sure that there are no open flames in the laboratory.

Experimental Procedure

A. Preparation of the soap

1. Place 20g of vegetable oil (roughly 22-23 mL) in a 250 mL beaker and add 20 mL of ethanol. Your teacher may give you the option of choosing among a variety of different types of oil. The ethanol and the oil will separate in two layers. Swirl the beaker well.

2. Add 25 mL of 5M NaOH solution. Mix well.

3. Heat gently on a hot plate. Stir with a glass rod until the solution turns into a paste. As soon as the consistency begins to turn pasty stir carefully to avoid foaming. The paste is made up of glycerol and soap (this step takes about thirty minutes).

4. When all the paste has formed, let the beaker cool on your bench top.

5. After the paste is cold add 100 mL of saturated NaCl. Stir thoroughly, breaking the pieces of paste against the walls of the beaker. This is called the "salting out step" where the Na^+ and Cl^- ions bind to water molecules and help separate them from the soap.

6. *Optional:* add 3 or 4 drops of a scented essential oil (for example lavender or jasmine)

7. Use suction filtration to separate the soap from the rest. Wash the soap with 25 mL of ice water through the suction filter. Continue filtering for about ten minutes to help dry the soap.

8. Prepare a test solution of your prepared soap (solution 1) by dissolving one gram of soap in 100 mL of warm deionized water. Two other solutions will be available to you for the remainder of the lab: a solution of a commercial soap (solution 2) and a solution of a detergent (solution 3)

B. Comparison of the properties of the prepared soap, a commercial soap and a commercial detergent

1. pH testing
Use a clean glass rod to transfer a drop of solution 1 onto a strip of universal indicator. Repeat with solutions 2 and 3. Record your results.

solution	Color of the indicator	pH
1. prepared soap		
2. commercial soap		
3. commercial detergent		

2. Emulsifying properties
Add one drop of food coloring to 5 mL of water in a test tube. Note how they mix and how the water "takes up" the color (a)
Add one drop of food coloring to 2 mL of vegetable oil in a test tube. Note how they don't mix and how the food coloring does not impart any color to the oil (b).
Add 2mL of vegetable oil to 5mL of water in another test tube. Add one drop of food coloring, stopper and shake for 20 seconds.

Do you observe one or two layers? ________________________

What happens after 5-10 minutes? What color are these layers? (c) ________________________
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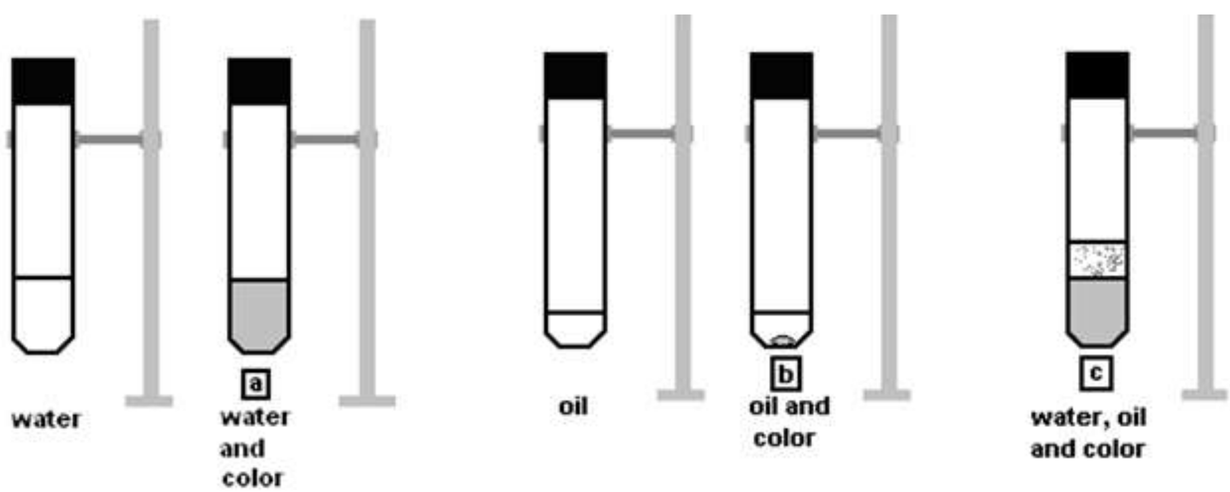
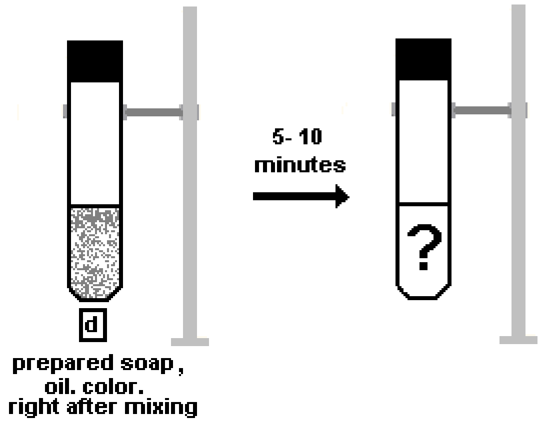


As you already knew, water and oil do not mix together. Because the color remains mostly with the water phase, we can monitor "where the water goes" by "following the color". In the rest of this experiment you will assess who is better at "helping water and oil mix" (who is the best emulsifying agent), your soap, the commercial soap or the detergent.

Repeat the procedure with:
d) 5mL of prepared soap (solution 1), 2 mL of oil, one drop of food coloring
e) 5mL of commercial soap (solution 2), 2 mL of oil, one drop of food coloring
f) 5mL of commercial detergent (solution 3), 2 mL of oil, one drop of food coloring



Record your observations after10 minutes. Can you determine which solution has the best emulsifying properties?

solution	Observations after 10 minutes
1. prepared soap	
2. commercial soap	
3. commercial detergent	
4. water	

Solution with the best emulsifying properties: ____

3. Behavior in acidic water
Place 10 mL of each of the prepared solutions in separate test tubes. Add 5 drops of 3M HCl to each tube, stopper and shake for 20 seconds. Record your observations about the sudsing properties of each solution (do you see any foam being formed?).
Now add 2 mL of vegetable oil and one drop of food coloring to each tube. Stopper the tubes, shake for 20 seconds and record your observations about the emulsifying properties of all three solutions in acidic water. Wait for 10 minutes and record your observations again.

solution	Sudsing properties	Emulsifying properties after 20 seconds	Emulsifying properties after 10 minutes
1. prepared soap			
2. commercial soap			
3. commercial detergent			

4. Behavior in hard water

A solution containing $CaCl_2$ and $MgCl_2$ (75 mg/L of each) will be used to represent a sample of hard water. Place 10 mL of each prepared solution in a different test tube with 2 mL of hard water. Stopper, shake for 20 seconds and record your results. Do you see cloudiness, a precipitate, a film? Record your results again after 10 minutes.

solution	Observations after 20 seconds	Observations after 10 minutes
1. prepared soap		
2. commercial soap		
3. commercial detergent		

5. Testing for the presence of phosphates

We will use a 0.5% solution of ammonium molybdate to look for phosphates in the prepared solutions.
Add 2 mL of each of the prepared solutions to 3 mL of 6M HNO_3 and 2 mL of 0.5% ammonium molybdate. A yellow solution or precipitate indicates the presence of phosphates. If no reaction is apparent warm the solutions in a water bath to a temperature of about 60°C for a few minutes.

$$PO_4^{3-} + 12\ (NH_4)_2MoO_4 + 24\ H^+ \rightarrow (NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4^+ + 12H_2O$$

solution	Testing for phosphates
1. prepared soap	
2. commercial soap	
3. commercial detergent	

6. Cleaning properties

Wash your hands with some of the prepared soap. See how well it lathers (or does not!). Spread some of the vegetable oil on your hands and try washing it off with tap water. Repeat using your prepared soap. Record your observations.

	Tap water alone	Using prepared soap
Lathering		
Cleaning properties		

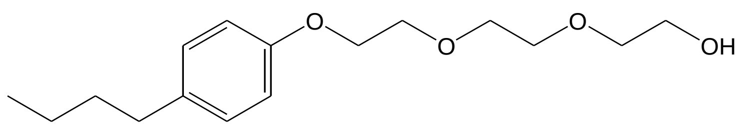
Follow-up questions

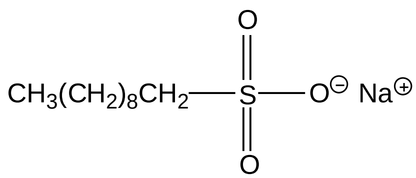
1. Explain in your own words how soap cleans.

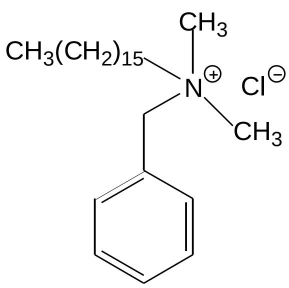
2. Complete the following table about the advantages and disadvantages of soaps against detergents.

	soaps	detergents
Clean in acid water		
Clean in hard water		
Biodegradability		
Damage to the environment		
Cost		
Which one would you buy as a consumer?		

3. Label the following detergents as anionic, cationic or non-ionic.







Pre-lab Assignment—To be completed BEFORE lab!

1. Why do we add ethanol to the oil and the NaOH when we start preparing the soap? (Hint: Consider polarities)

2. Draw the expanded structure of myristic acid, $CH_3(CH_2)_{12}COOH$ and of its corresponding salt, the soap sodium myristate $CH_3(CH_2)_{12}COO^-Na^+$. Indicate the polar and non-polar portions of each molecule.

3. Draw the micelle formed by molecules of sodium myristate. Use the abbreviated form that we learned for fatty acid salts (use a circle for the polar head and a zig-zag for the hydrocarbon chain)

4. What is hard water and why does it prevent soap from cleaning?