Soap

In chemistry, soap is a salt of a fatty acid. Soaps are mainly used as surfactants for washing, bathing, and cleaning, but they are also used in textile spinning and are important components of lubricants.

(Soaps are water-soluble sodium or potassium salts of fatty acids. Soaps are made from fats and oils, or their fatty acids, by treating them chemically with a strong alkali.)

Soaps for cleansing are obtained by treating vegetable or animal oils and fats with a strongly alkaline solution. Fats and oils are composed of triglycerides; three molecules of fatty acids are attached to a single molecule of glycerol. The alkaline solution, which is often called lye (although the term "lye soap" refers almost exclusively to soaps made with sodium hydroxide), brings about a chemical reaction known as saponification. In this reaction, the triglyceride fats are first hydrolyzed into free fatty acids, and then these combine with the alkali to form crude soap, an amalgam of various soap salts, excess fat or alkali, water, and liberated glycerol (glycerin). The glycerin is a useful by-product, which can be left in the soap product as a softening agent, or isolated for other uses.

Soaps are key components of most lubricating greases, which are usually emulsions of calcium soap or lithium soaps and mineral oil. These calcium- and lithium-based greases are widely used. Many other metallic soaps are also useful, including those of aluminium, sodium, and mixtures of them. Such soaps are also used as thickeners to increase the viscosity of oils. In ancient times, lubricating greases were made by the addition of lime to olive oil. Soap is very important for effective hand washing and hygiene, but if it is not available in difficult situations, then clean ash or sand / soil can be used as substitute as recommended by e.g. World Health Organization.

Mechanism of cleansing soaps

When used for cleaning, soap allows insoluble particles to become soluble in water and then be rinsed away. For example: oil/fat is insoluble in water, but when a couple of drops of dish soap are added to the mixture, the oil/fat apparently disappears. The insoluble oil/fat molecules become associated inside micelles, tiny spheres formed from soap molecules with polar hydrophilic (water-attracting) groups on the outside and encasing a lipophilic (fat-attracting) pocket, which shields the oil/fat molecules from the water making it soluble. Anything that is soluble will be washed away with the water. Synthetic detergents operate by similar mechanisms to soap.

Effect of the alkali

The type of alkali metal used determines the kind of soap product. Sodium soaps, prepared from sodium hydroxide, are firm, whereas potassium soaps, derived from potassium hydroxide, are softer or often liquid. Historically, potassium hydroxide was extracted from the ashes of bracken or other plants. Lithium soaps also tend to be hard—these are used exclusively in greases.
Effects of fats

Soaps are derivatives of fatty acids. Traditionally they have been made from triglycerides (oils and fats). Triglyceride is the chemical name for the triesters of fatty acids and glycerin. Tallow, *i.e.*, rendered beef fat, is the most available triglyceride from animals. Its saponified product is called sodium tallowate. Typical vegetable oils used in soap making are palm oil, coconut oil, olive oil, and laurel oil. Each species offers quite different fatty acid content and, hence, results in soaps of distinct feel. The seed oils give softer but milder soaps. Soap made from pure olive oil is sometimes called Castile soap or Marseille soap, and is reputed for being extra mild. The term "Castile" is also sometimes applied to soaps from a mixture of oils, but a high percentage of olive oil.

Soap-making processes

The industrial production of soap involves continuous processes, such as continuous addition of fat and removal of product. Smaller-scale production involves the traditional batch processes. The three variations are: the 'cold process', wherein the reaction takes place substantially at room temperature, the 'semiboiled' or 'hot process', wherein the reaction takes place near the boiling point, and the 'fully boiled process', wherein the reactants are boiled at least once and the glycerol is recovered. There are two types of 'semiboiled' hot process methods. The first is the ITMHP (in the mold hot process) and the second is the CPHP (crockpot hot process). Typically soapmakers choose the hot process methods if they wish to reduce the cure time to a three-day air dry process. Most soapmakers, however, continue to prefer the cold process method. The cold process and hot process (semiboiled) are the simplest and typically used by small artisans and hobbyists producing handmade decorative soaps. The glycerine remains in the soap and the reaction continues for many days after the soap is poured into moulds. The glycerine is left during the hot-process method, but at the high temperature employed, the reaction is practically completed in the kettle, before the soap is poured into moulds. This simple and quick process is employed in small factories all over the world.

Handmade soap from the cold process also differs from industrially made soap in that an excess of fat is used, beyond that needed to consume the alkali (in a cold-pour process, this excess fat is called “superfattening”), and the glycerine left in acts as a moisturizing agent. However, the glycerine also makes the soap softer and less resistant to becoming “mushy” if left wet. Since it is better to add too much oil and have left-over fat, than to add too much lye and have left-over lye, soap produced from the hot process also contains left-over glycerine and its concomitant pros and cons. Further addition of glycerine and processing of this soap produces glycerin soap. Superfatted soap is more skin-friendly than one without extra fat. However, if too much fat is added, it can leave a “greasy” feel to the skin. Sometimes, an emollient additive, such as jojoba oil or shea butter, is added “at trace” (i.e., the point at which the saponification process is sufficiently advanced that the soap has begun to thicken in the cold process method) in the belief that nearly all the lye will be spent and it will escape saponification and remain intact. In the case of hot-process soap, an emollient may be added after the initial oils have saponified so they remain unreacted in the finished soap. Superfattting can also be accomplished through a process known as “lye discount” in which the soap maker uses less alkali than required instead of adding extra fats.
Hot processes

Hot-processed soaps are created by encouraging the saponification reaction by adding heat to speed up the reaction. In contrast with cold-pour soap which is poured into moulds and for the most part only then saponifies, hot-process soaping for the most part saponifies the oils completely and only then is poured into moulds.

In the hot process, the hydroxide and the fat are heated and mixed together at 80–100 °C, a little below boiling point, until saponification is complete, which, before modern scientific equipment, the soapmaker determined by taste (the sharp, distinctive taste of the hydroxide disappears after it is saponified) or by eye; the experienced eye can tell when gel stage and full saponification has occurred. Beginners can find this information through research and classes. Tasting soap for readiness is not recommended, as sodium and potassium hydroxides, when not saponified, are highly caustic.

An advantage of the fully boiled hot process in soapmaking is the exact amount of hydroxide required need not be known with great accuracy. They originated when the purity of the alkali hydroxides were unreliable, as these processes can use even naturally found alkalis, such as wood ashes and potash deposits. In the fully boiled process, the mix is actually boiled (100+ °C), and, after saponification has occurred, the “neat soap” is precipitated from the solution by adding common salt, and the excess liquid is drained off. This excess liquid carries away with it much of the impurities and color compounds in the fat, to leave a purer, whiter soap, and with practically all the glycerine removed. The hot, soft soap is then pumped into a mould. The spent hydroxide solution is processed for recovery of glycerine.

Chemistry of Soap

The basic structure of all soaps is essentially the same, consisting of a long hydrophobic (water-fearing) hydrocarbon "tail" and a hydrophilic (water loving) anionic "head":

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}^- \text{ or } \text{CH}_3(\text{CH}_2)_n\text{COO}^-$$

The length of the hydrocarbon chain ("n") varies with the type of fat or oil but is usually quite long. The anionic charge on the carboxylate head is usually balanced by either a positively charged potassium (K⁺) or sodium (Na⁺) cation. In making soap, triglycerides in fat or oils are heated in the presence of a strong alkali base such as sodium hydroxide, producing three molecules of soap for every molecule of glycerol. This process is called saponification.

Like synthetic detergents, soaps are "surface active" substances (surfactants) and as such make water better at cleaning surfaces. Water, although a good general solvent, is unfortunately also a substance with a very high surface tension. Because of this, water molecules generally prefer to stay together rather than to wet other surfaces. Surfactants work by reducing the surface tension of water, allowing the water molecules to better wet the surface and thus increase water's ability to dissolve dirty, oily stains.
In studying how soap works, it is useful to consider a general rule of nature: "like dissolves like." The nonpolar hydrophobic tails of soap are lipophilic ("oil-loving") and so will embed into the grease and oils that help dirt and stains adhere to surfaces. The hydrophilic heads, however, remain surrounded by the water molecules to which they are attracted. As more and more soap molecules embed into a greasy stain, they eventually surround and isolate little particles of the grease and form structures called micelles that are lifted into solution. In a micelle, the tails of the soap molecules are oriented toward and into the grease, while the heads face outward into the water, resulting in an emulsion of soapy grease particles suspended in the water.

With agitation, the micelles are dispersed into the water and removed from the previously dirty surface. In essence, soap molecules partially dissolve the greasy stain to form the emulsion that is kept suspended in water until it can be rinsed away.

As good as soaps are, they are not perfect. For example, they do not work well in hard water containing calcium and magnesium ions, because the calcium and magnesium salts of soap are insoluble; they tend to bind to the calcium and magnesium ions, eventually precipitating and falling out of solution. In doing so, soaps actually dirty the surfaces they were designed to clean. Thus soaps have been largely replaced in modern cleaning solutions by synthetic detergents that have a sulfonate (R-SO$_3^-$) group instead of the carboxylate head (R-COO$^-$). Sulfonate detergents tend not to precipitate with calcium or magnesium ions and are generally more soluble in water.
Objective: To prepare soap by alkaline hydrolysis (saponification) of natural fats and test some of the chemical properties and cleansing power of soap relative to detergent.

Introduction

Soaps are the sodium and potassium salts of long chain fatty acids that are generally made by saponification (alkaline hydrolysis) of natural fats, such as animal fats or palm oil. Prior to World War II, most soap was prepared in the home by boiling animal fat with lye (commercial sodium hydroxide). Soap is not particularly good for cleaning in hard water (water with high concentrations of Ca^{2+}, Mg^{2+} and/or Fe^{3+} ions) because it forms insoluble complexes with divalent (or trivalent) cations. Organic sulfonic acid and phosphoric acid salts, commonly known as detergents, were found to be much more effective cleaning agents because they do not readily form insoluble complexes with the ions in hard water. Modern cleansers labeled "soft soap" are, in fact, detergents rather than soap. Check the labels for ingredients of some cleansers you have around the home, including shampoo.

The phosphate detergents caused environmental problems in waterways, not because they are toxic, but because they are nutrients and resulted in an overabundance of plant growth, or algal blooms. Consequently phosphate detergents have been replaced with other alternatives. Today there are a wide variety of synthetic detergents available for various purposes. Some representative detergents and a soap are shown below.

Sodium Stearate (a soap) vs. Sodium Dodecyl Sulfate (an anionic detergent) vs. Benzalkonium Chloride (a cationic detergent) vs. Phosphatidyl Choline (Lecithin) (a natural detergent)

In this experiment you will prepare soap from a fat and determine some of its properties relative to a detergent. See the chemical equation for saponification on the next page.

Materials and Reagents

Shortening, tallow or coconut oil, 20% NaOH solution, 20% NaCl solution, 400 mL beaker, 125 mL Erlenmeyer flask, ice, universal pH paper, 0.3 % detergent (or sodium dodecylsulfate) solution, 0.3% calcium chloride solution, filter paper, filtration apparatus, and test tube (6pcs).
Procedure

Part A. Preparation of Soap.

1. Take about 2 gm of coconut oil or fat (fat should be taken in liquid form by heating) to a 125 mL Erlenmeyer flask.

2. Pour 30 mL of 20% NaOH solution to the above flask and shake vigorously.

3. Place the flask containing the fat solution in the water bath and fasten it with a clamp to hold it upright in the water bath. Place a small watch glass over the mouth of the flask to minimize evaporation.

4. Allow the fat-alcoholic NaOH solution to heat at 80-90 oC for at least 2h. If you observe undissolved fat in the flask, add 10 ml of NaOH solution to the flask and shake vigorously.

5. After 2h min, test the fat solution to see if saponification is complete by placing a few drops of the solution in a test tube of deionized water. If you see fats droplets float to the top, the saponification is not complete and allow it to boil for an additional 15 min.
6. While the saponification proceeds, prepare a salt solution by completely dissolving 20 g NaCL in 100 mL deionized water in a 250 mL beaker. After the salt completely dissolves, transfer about half of this salt solution to another beaker and place both beakers of salt solution on ice to cool them.

7. When saponification is complete, carefully pour the hot reaction mixture slowly into one beaker of salt solution (called "salting out" method) and stir for a minute or two. Place the mixture on ice to cool it before filtering.

8. Set up a suction filtration apparatus with a Buchner funnel and filter paper (Aspirator or vacuum filtration apparatus). Filter the mixture from step 7, and wash the soap (remaining in the Buchner funnel) twice with ice cold salt water (from the second beaker). Draw air through the soap for a few minutes to remove most of the water (using drier).

9. Remove the soap cake from the Buchner funnel and save it for the following tests.

**Part B. Comparison of the Properties of Soap with Detergent.**

**B-1. Alkalinity or pH test**

1. Prepare a 0.3% soap (prepared) solution in 100 mL of warm distilled water.

2. Use a glass stirring rod to place a drop of the soap solution on a piece of universal pH paper to determine whether the solution is alkaline, neutral or acid. Record your observation on the Report Sheet.

3. Prepare a 0.3% detergent or soap (standard) solution or soap solution in 100 mL distilled water warm and test it as above.

**B-2. Lathering Power or Foam test**

1. Add about 2 mL of distilled water to four large test tubes.

2. Add an equal amount (10 mL of 0.3%) of soap solution to one test tube of water and shake vigorously by placing a stopper in the tube for 10 sec. This should give a permanent lather that lasts for at least 30 sec Observe and record the amount of suds or foam each soap solution produces.
3. Add an equal amount of detergent solution to another test tube of water and shake vigorously. Test it as above.

4. Add 2 mL of 0.3% \( \text{Ca}^{2+} \) solution to each of the two remaining test tubes of water. \( \text{CaCl}_2 \) or \( \text{MgCl}_2 \) or \( \text{FeCl}_2 \)

5. Add an equal amount of soap solution to one of the tubes containing \( \text{Ca}^{2+} \) ion and shake vigorously for 10 sec. Notice whether this solution forms a permanent lather and note whether there is any floculent precipitate in the tube. Does the precipitate float or sink?

6. Add an equal amount of detergent solution to the other tube containing \( \text{Ca}^{2+} \) ion and shake vigorously to get a permanent lather. Test it as above.

**B-3. Cleansing Power**

1. Place a drop of used oil on four separate thin strips of filter paper.

2. Place one filter paper with oil spot in the tube containing soap 10 mL of 0.3% in water. Place another in the tube containing detergent or soap and water. Place a third strip in the tube containing soap in \( \text{Ca}^{2+} \) solution. Place the fourth strip of oily paper in the tube containing detergent and \( \text{Ca}^{2+} \) solution. Shake each one well and make sure the filter paper is immersed in the solution.

3. After 2 min remove the filter paper and rinse with tap water. Did the oil get washed out of the filter paper strip? Compare the cleaning power of soap vs detergent on the Report Sheet.