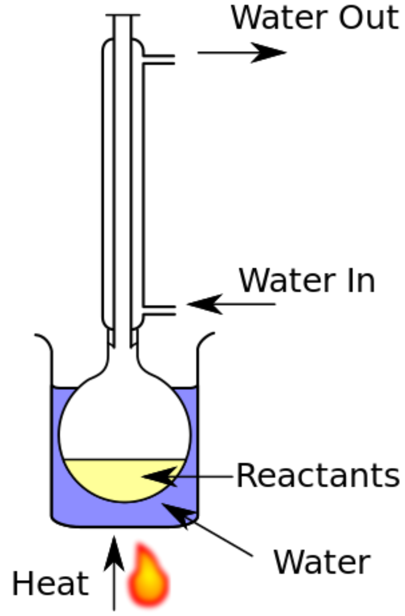
Cathkin High School
CfE Higher Chemistry

Soaps, Detergents and Emulsions

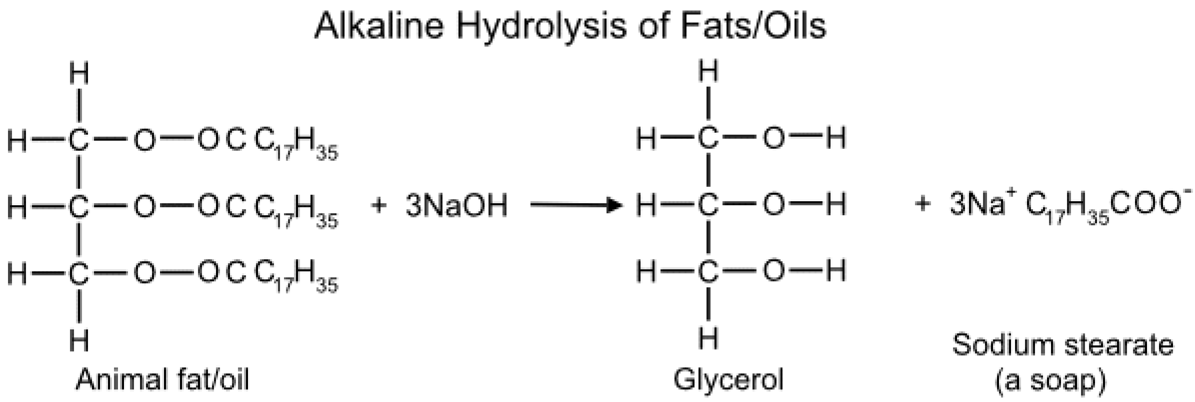
No.	Learning Outcome	Understanding?
1	Soaps are produced by the alkaline hydrolysis of the ester links in fats and oils to form water-soluble ionic salts.	☺ 😐 ☹
2	Soap ions have a long covalent tail, readily soluble in covalent compounds. This tail is hydrophobic.	☺ 😐 ☹
3	Soap ions have an ionic carboxylate head which is negatively charged and water soluble. This head is hydrophilic.	☺ 😐 ☹
4	When cleaning using soaps and detergents, the hydrophobic tails dissolve in a droplet of grease or oil whilst the hydrophilic heads face out into the surrounding water.	☺ 😐 ☹
5	Agitation of the mixture results in a ball-like structure forming with the hydrophobic tails on the inside and the negative hydrophilic heads on the outside.	☺ 😐 ☹
6	Repulsion between the negatively charged hydrophilic heads results in an emulsion being formed and the dirt released.	☺ 😐 ☹
7	Detergents are particularly useful in hard water areas.	☺ 😐 ☹
8	An emulsion contains small droplets of one liquid dispersed in another liquid. Emulsions in food are mixtures of oil and water.	☺ 😐 ☹
9	To prevent oil and water components separating into layers, a soap-like molecule known as an emulsifier is added.	☺ 😐 ☹
10	Emulsifiers for use in food are commonly made by reacting edible oils with glycerol to form molecules in which either one or two fatty acid groups are linked to a glycerol backbone. This is different to the three fatty acids usually found in edible oils.	☺ 😐 ☹
11	The one or two hydroxyl groups present in these emulsifier molecules are hydrophilic whilst the fatty acid chains are hydrophobic.	☺ 😐 ☹
12	The ionic (hydrophilic) head in a soapless detergent does not form a solid precipitate with calcium ions or magnesium ions (which are found in hard water).	☺ 😐 ☹

Making Soaps

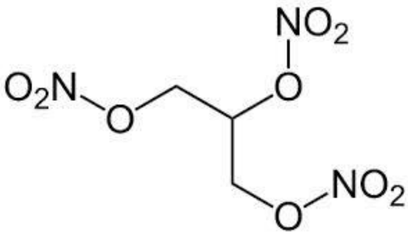
Soaps **are formed by the alkaline** ***hydrolysis*** **(breaking up) of fats and oils by sodium or potassium hydroxide by boiling under reflux conditions:**



Reflux Apparatus

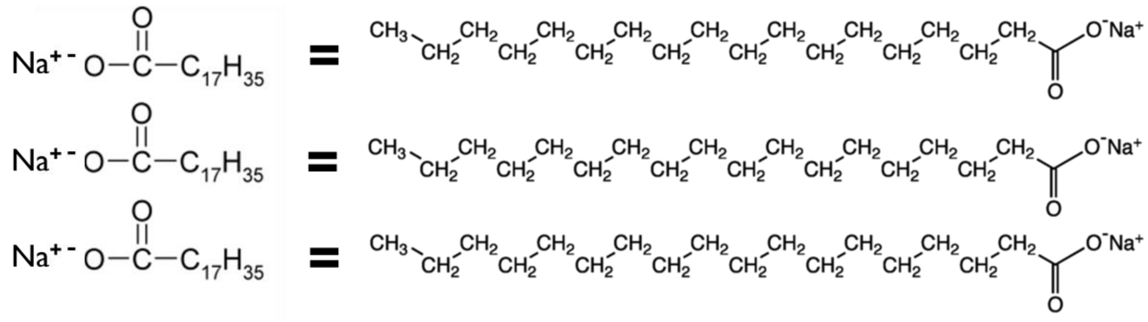


Glycerol is produced as a by-product of the hydrolysis of fat and is separated and used as a raw material for other processes and preparations for example antifreeze. In food and beverages, glycerol serves as a humectant (keeps the food moist), solvent, sweetener and emulsifier (see later). Glycerol is used to produce trinitroglycerin, which is an essential ingredient of various explosives such as dynamite, gelignite, and smokeless propellants like cordite.

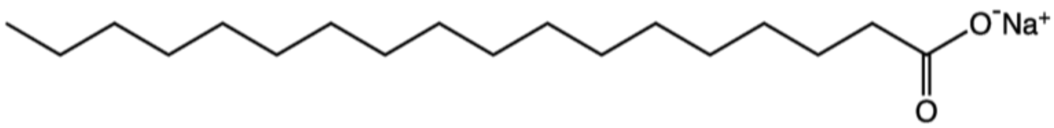


Hydrolysis of esters such as fats/oil produces glycerol and *fatty acids*. Fats and oils are triglycerides meaning they are esters which contain 3 molecules of fatty acid condensed to 1 molecule of the *trihydric alcohol*, glycerol. So during hydrolysis, three molecules of soap are made per molecule of glycerol. (3:1 ratio of fatty acid:glycerol)
The hydrolysis is carried out using alkalis (NaOH or KOH) as catalyst and the fatty acids formed are changed into sodium or potassium salts (soaps) such as sodium stearate, $C_{17}H_{35}COO^{-}Na^{+}$ in a neutralisation reaction. **The soaps are ionic and water-soluble.**

The long covalent hydrocarbon chain that makes up the tail section of a soap structure can be represented in a number of ways, either in the shorthand notation shown below or as a bond-stick representation, shown at the bottom of the page. The charged carboxylate group represents the head section of the soap structure.



Soap can also be illustrated like this



Practical Activity

Soap can be made from castor oil in about 40 minutes. 5 cm^3 of ethanol is added dropwise to 2 cm^3 of castor oil. 10 cm^3 of 5 mol l^{-1} sodium hydroxide is then added, and the solution warmed in a waterbath containing near-boiling water for five minutes. 10 cm^3 of saturated sodium chloride solution is then added to the beaker and the mixture stirred. The mixture is cooled in a cold water bath (or an ice bath if available). Soft, white lumps of the soap will gradually form in the mixture. Leave for a few minutes to improve the yield. During this time the soap may rise to the surface and form a soft crust on cooling.

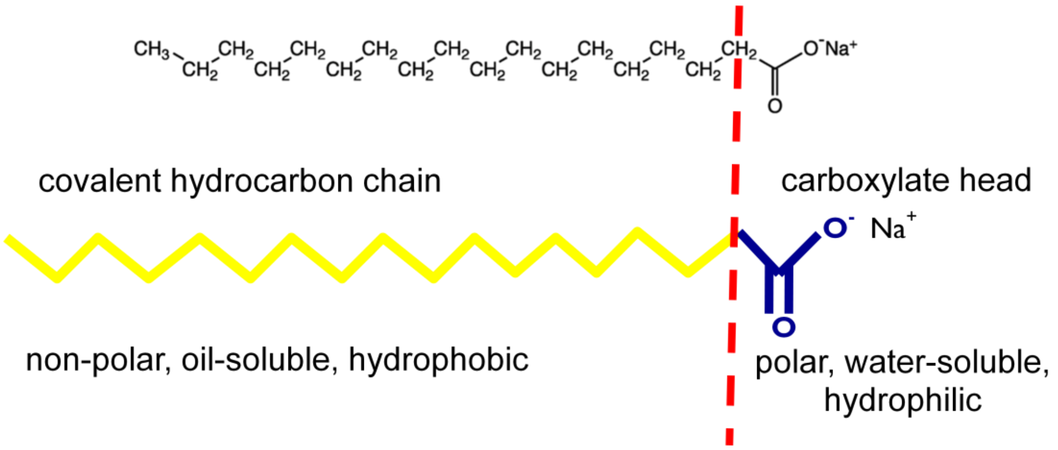
A quicker method of making soap takes under five minutes. In this method around 2g of mutton fat is dissolved in 8 cm^3 of ethanol in a boiling tube. One pellet of KOH is added, and the mixture boiled in a water bath for 2 minutes during which the cloudy mixture becomes clear. When the contents of the tube are poured into a beaker containing saturated NaCl solution the soap precipitates and floats on the surface.

Why do we need Soap or detergent to clean?

Cleaning with water alone has little effect when stains consist of non-polar substances, such as grease and sweat since fats do not dissolve in water. This is because water is a polar solvent but fats and oils are non polar.

The structure of soap

The long covalent hydrocarbon chain gives rise to the *hydrophobic* (water hating) and oil-soluble (non-polar) properties of the soap molecule (represented in yellow). The charged carboxylate group (represented in blue) is attracted to water molecules (*hydrophilic*). In this way, soaps are composed of a hydrophilic head and a hydrophobic tail:

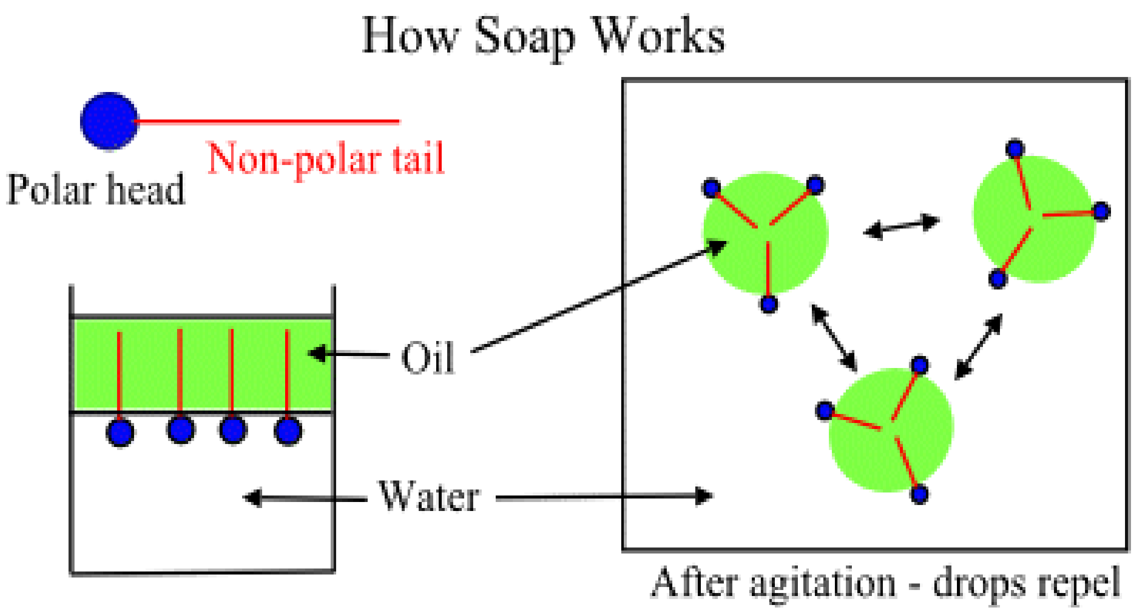


In solution a soap molecule consists of a long non-polar hydrocarbon tail (e.g. $C_{17}H_{35}$-) and a polar head (-COO^-).

The non-polar tail is soluble in non-polar substances such as oil while the polar head is soluble in polar substances such as water. As the non-polar tail is repelled by water, it is described as hydrophobic (water hating). The head is described as hydrophilic (water loving) Agitation of the oil and water produces oil droplets surrounded by negatively-charged heads and these repel similar charges on other oil droplets.

How Soaps Work

The following ball and stick diagram represents the initial interaction of soap on addition to water and material with a grease stain.



This repulsion prevents the oil droplets re-joining and helps disperse the oil.

Practical Activity

The detergent action of soaps can be demonstrated using very finely divided MnO_2 or very finely divided charcoal as "dirt". 50 cm^3 of water is placed in one 100 cm^3 measuring cylinder, and 50 cm^3 of soap solution in another. A pinch of simulated "dirt" is added to each, and the two cylinders shaken. The two cylinders are set aside for some time. In the control cylinder containing water, the "dirt" settles down on the bottom of the cylinder, whilst in the soap solution the powder remains suspended.

The Cleansing Action of Soaps

When used for cleaning in combination with water, soap serves as a *surfactant*. Surfactants are the main contributors to detergents' cleaning performance.

The bulk components of detergents are surfactants; other key ingredients include:

- bleach, to enhance the appearance and effect of whiteness
- polymers, for binding to and removing certain types of dirt
- builders: to provide the formulations (liquids, gels, capsules and tablets) with consistency
- enzymes, to remove biological stains, including, blood, wine, chocolate and coffee.

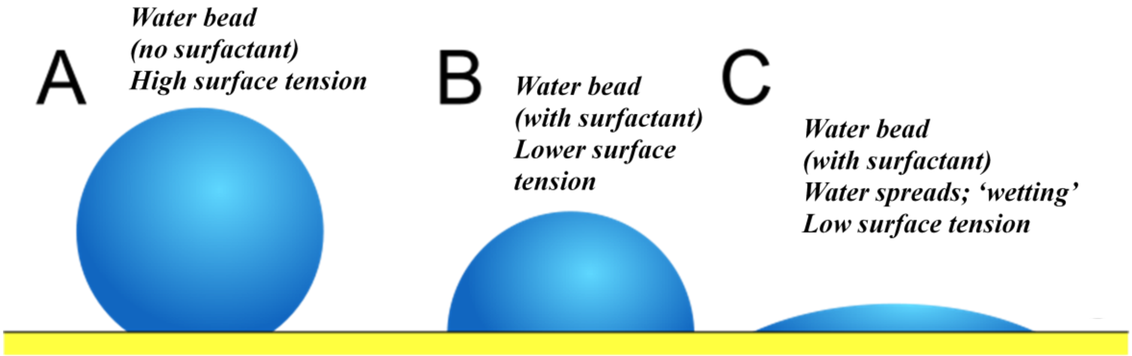
Structure and Composition

A broad definition of a surfactant is: a substance, such as soap, that possesses a hydrophobic tail and a hydrophilic head and which, on being made into a solution with water, reduces the surface tension of water and also reduces the interfacial tension between oil and water.

What is surface tension and how does a surfactant lower it?

The surface tension of water can be seen in the picture below. The cohesion between the water molecules is strong enough to allow relatively dense objects to be suspended above the water line.

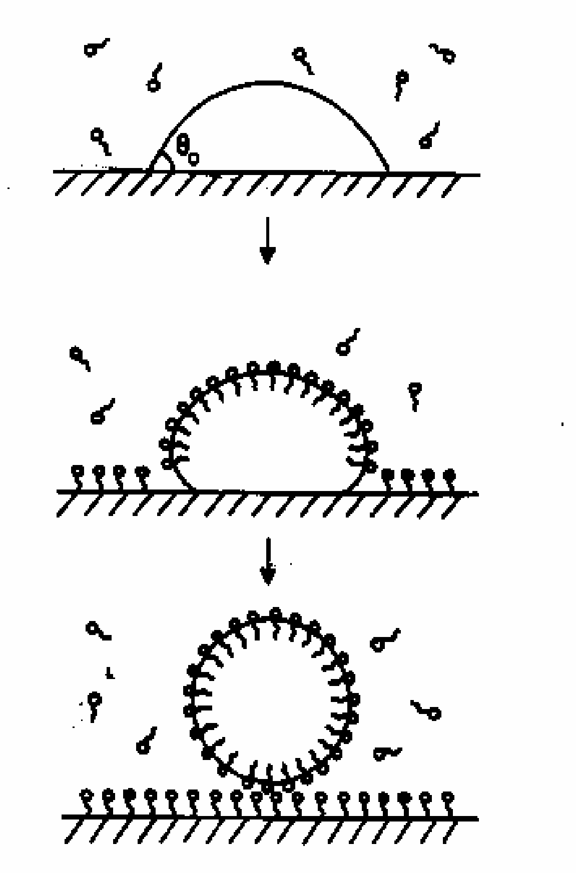
The diagram below shows how surface tension can be disrupted. In steps A-C a water bead is placed on the surface of a fabric:



The addition of a surfactant, such as soap, disrupts the cohesion between the water molecules, causing the water droplet to spread, covering a wider surface area of the fabric (a process called wetting). This maximises contact with any stains or dirt deposited on the fabric.

Mechanism of stain/dirt removal

Roll-up mechanism



The hydrophobic tails 'burrow' into the droplet of oil or grease.

The hydrophilic heads are left to face the surrounding water.

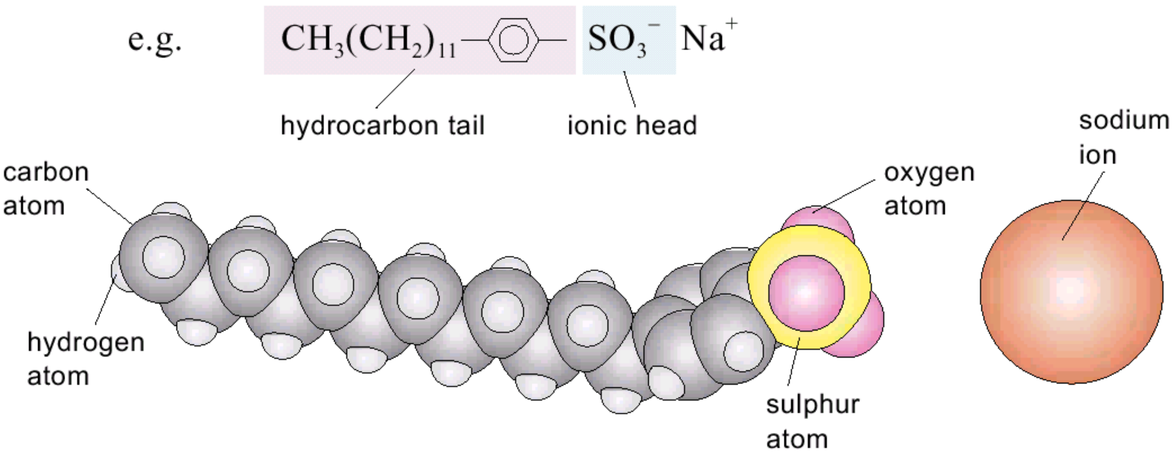
This results in the formation of a ball-like structure (a micelle).

The non-polar substances, such as oil or grease, are held inside the ball and suspended in water, to be washed away.

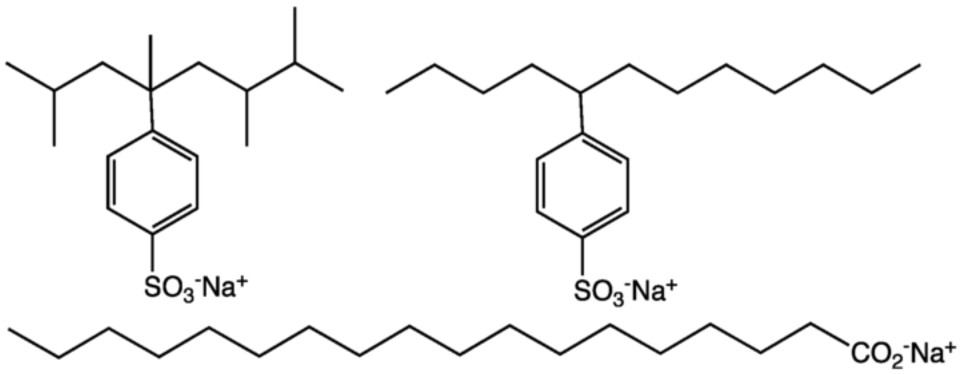
Soapless detergents

When soap is used in hard water, a white solid precipitate we call scum forms. This is because charged calcium and magnesium ions present in the hard water react with soap to form an insoluble substance. Scum builds up on clothes, baths and sinks. Soapless detergents do not form scum. **Like soap, detergent molecules have a long chain of carbon and hydrogen atoms, but at the end of the molecule there is this group -SO_3^- called sulphonate instead of the -COO^- carboxylate group present in soap.**

e.g.



Or



The calcium salt of a sulphonate is soluble in water unlike the calcium salts of the carboxylate.

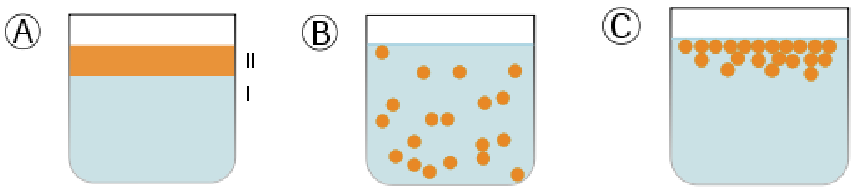
Problems with Soapless Detergents.

When a soap solution is washed away, the soap molecules break up into smaller molecules containing carbon, hydrogen and oxygen atoms. These go back into the soil and are taken up by plants and micro-organisms. Detergents break down in a similar way, but take much longer. This is why foam is sometimes seen on rivers and streams - the detergent molecules keep their properties much longer than soap.
Although detergents are good at removing grease and dirt, they can also irritate and dry out the skin. Some people are sensitive to detergents and may have skin reactions when using products which contain them.

Emulsions

An *emulsion* contains small droplets of one liquid dispersed in another liquid.
In diagram A two liquids not yet emulsified form two separate phases, a layer of oil on top of a layer of water.

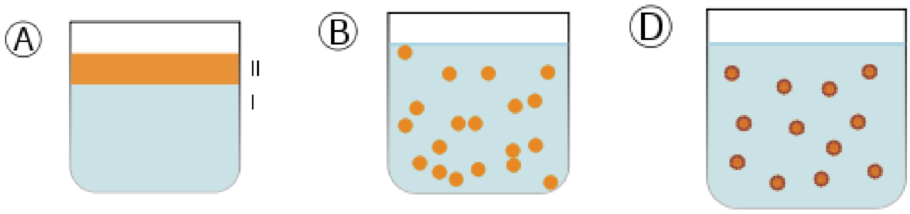
Phase II: Oil
Phase I: Water



In diagram B the liquids have been agitated (stirred vigorously), initally the water layer and oil layers have formed an emulsion. In diagram C the *unstable* emulsion progressively separates back into two distinct layers (phases).

Eventually, after some minutes, the two liquids return to form two separate phases, a layer of oil on top of a layer of water. However some substances areable to stablise an emulsion.

Phase II: Oil
Phase I: Water



With the addition of an emulsifier (dark outline around particles) the interfaces between phase II (oil) and phase I (water) create a stabilised emulsion.
This addition of an emulsifier allows two otherwise *immiscible* layers to be mixed uniformly, dispersing an equal amount of each throughout the entire volume. The mixture is able to exist as a stable (non-separating) emulsion for a reasonable time (known as shelf-life).

It is very important that we have a way of preventing the layers from separating, otherwise the majority of our consumer products, including shampoo, toothpaste, cosmetics, ice-cream, washing detergents and salad dressings, would all end up as seperated layers, with the active ingredients no longer able to work effectively.

Emulsions in Food

Emulsions in food are mixtures of oil and water. To prevent oil and water components separating into layers, a soap-like molecule known as an emulsifier is added. Emulsifiers for use in food are commonly made by reacting edible oils with glycerol to form molecules in which either one or two fatty acid groups are linked to a glycerol backbone rather than the three normally found in edible oils. The one or two hydroxyl groups present in these molecules are hydrophilic whilst the fatty acid chains are hydrophobic. This presence of this emulsifier is shown on packaging by E-number E471 and is one of the most common on food packaging. Many foods contain emulsifiers.

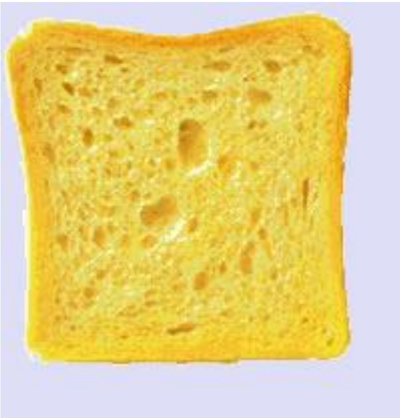
Foods that Commonly Contain Emulsifiers		
Biscuits	Toffees	Bread
Extruded snacks	Chewing gum	Margarine / low fat spreads
Breakfast cereals	Frozen desserts	Coffee whiteners
Cakes	Ice-cream	Topping powders
Desserts / mousses	Dried potato	Peanut butter
Soft drinks	Chocolate coatings	Caramels

Mayonnaise is a mixture of vegetable oil and water or vinegar or lemon juice, depending on the recipe. Egg yolk or a synthetic emulsifier can be used to keep the normally immiscible liquids evenly mixed. Without the emulsifier the two liquids would separate and would not appear appetising.

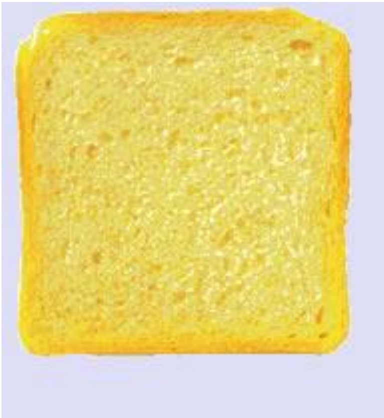
Bread making

Emulsifiers help to give consistent and high quality bread. They stabilise the dough so that it can be processed in the bakery and

reduce the rate at which bread goes stale. Emulsifiers are also used to "condition" the dough.
Wheat flour is used in the production of bread. It contains a protein, called gluten that is responsible for giving the dough made from the wheat its elastic texture. This is important in the baking process as it traps carbon dioxide produced by the yeast during fermentation and makes the bread rise evenly. Emulsifiers interact with the gluten to strengthen this gluten network and give the bread a good texture.



No emulsifier
The bread has large and uneven holes in it and will not have the correct texture.



With emulsifier
The dough has risen evenly. The holes are small and consistent. The bread will have a good texture

Practical activity

Emulsions can be investigated using 2 cm^3 each of vegetable oil and water and mixing. The layers separate. Various substances such as mustard powder, sugar, flour, salt, egg white, egg yolk and washing up liquid can be added to separate mixtures to see which act as emulsifiers.

Soaps, Detergents and Emulsions –Glossary

Word	Meaning
Soap	The sodium or potassium salts of long chain fatty acids e.g. sodium stearate or potassium oleate.
Hydrolysis	a reaction where water is used to break chemical bonds. Literally splitting a substance using water.
Glycerol	The trivial name for the alcohol propane-1,2,3-triol found in fats and oils.
Fatty acid	A carboxylic acid with between 4 and 24 (but usually 16 or 18) carbon atoms in the molecule and found in fats and oils. Only even numbers of carbon atoms are found.
Trihydric alcohol	A molecule with three -OH groups in it.
Hydrophobic	a substance which is repelled by water and so is insoluble in water. Literally - water hating.
Hydrophilic	a substance which is attracted by water and so is soluble in water. Literally - water loving.
Miscible	Describes two liquids which can dissolve completely so that only one layer exists e.g. ethanol and water are miscible
Immiscible	Describes liquids which separate into two layers, even after being mixed. e.g. oil and water are immiscible
Surfactant	a material that can greatly reduce the surface tension of water when used in very low concentrations.
Emulsion	a mixture of small droplets of one liquid such as oil dispersed in an another liquid such as water and kept there by an emulsifier.
Emulsifier	a substance which will help maintain the mixing of two immiscible liquids into a relatively stable mixture called an emulsion.