COURSE CODE: SC202(CHEMISTRY)

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IIITG, GUWAHATI

LECTURE-LIPIDS

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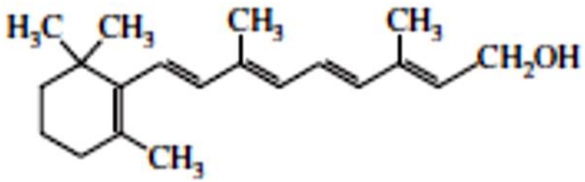
LIPIDS

Biological lipids are a chemically diverse group of compounds. The common and defining feature of them is their insolubility in water, but solubility in nonpolar solvents and solvents of low polarities, such as diethyl ether.



vitamin A

limonene

(Found in orange and lemon oils)

The biological functions of the lipids are as diverse as their chemistry. Lipids are classified in many ways:

A. Classification by Function

Lipids play three major roles in human biochemistry:

(1) They **store energy** within fat cells, e.g., fats and oils are the principal stored forms of energy in many organisms.

(2) They are parts of **membranes** that separate compartments of aqueous solutions from each other. e.g., Phospholipids and sterols are major structural elements of biological membranes.

(3) They serve as chemical **messengers**. e.g., steroid hormones, prostaglandins and thromboxanes.

LIPIDS

B. Classification by Structure

For purposes of study, we can classify lipids into four groups:

(1) Simple lipids, such as fats/oils and waxes: **Esters of fatty acid** with various **alcohol**.

(a) Fats/Oils: Alcohol part is glycerol (trihydric alcohol)

(b) Wax: Alcohol part is higher molecular weight mono-hydric alcohol.

(2) Complex lipids: **Esters of fatty acid** containing groups in addition to alcohol and a fatty acid. Alcohol can be glycerol or sphingoshine.

(a) Phospholipids : Glycerophospholipid and Sphingophospholipid

(b) Glycolipids (Glycosphingolipids)

(3) Steroids and

(4) **Prostaglandins, thromboxanes and leukotrienes.**

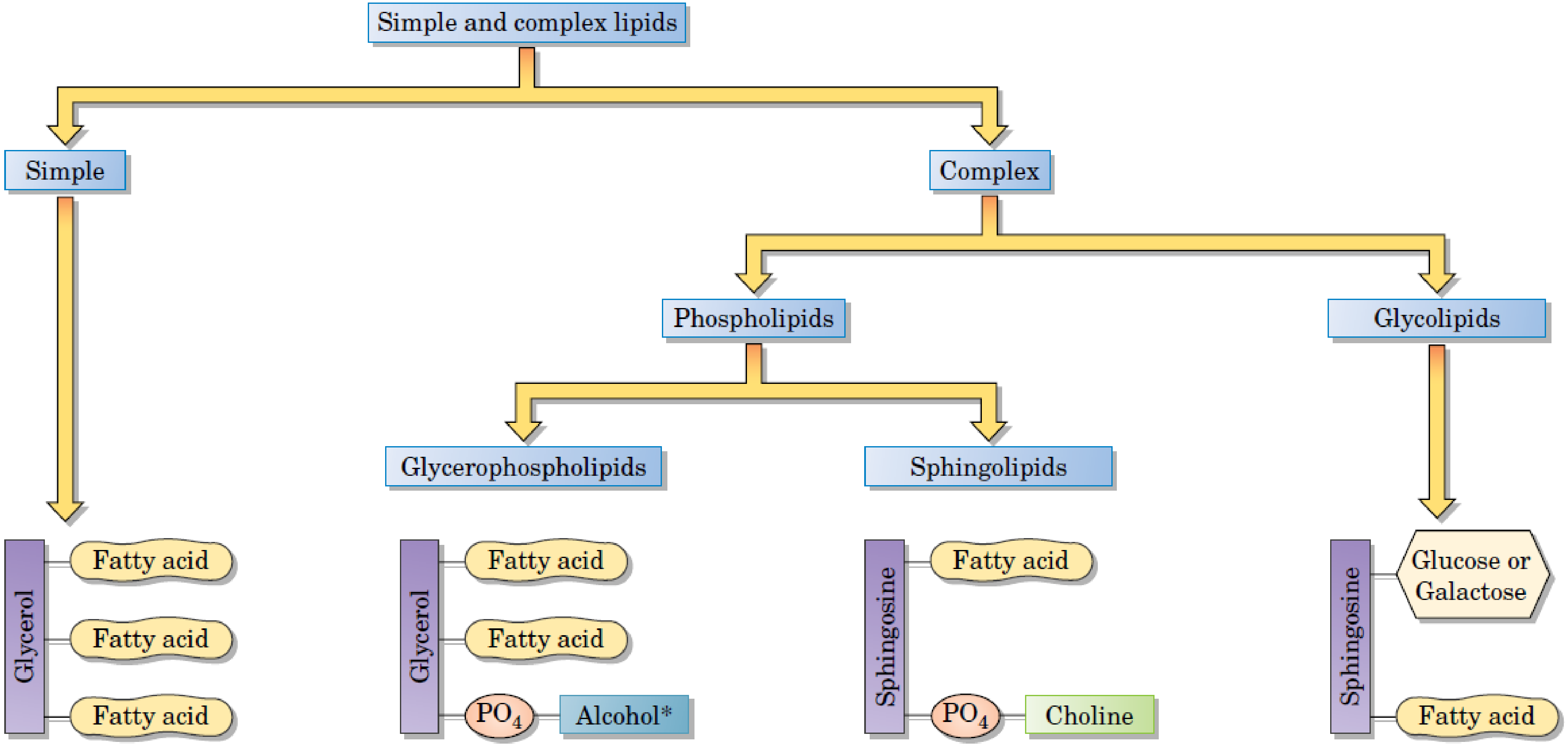
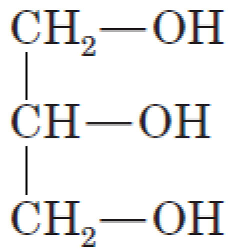
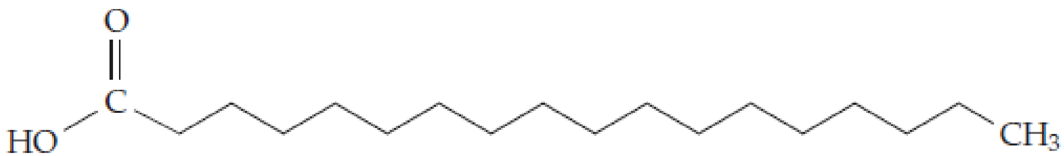


Figure Schematic diagram of simple and complex lipids.*

* The alcohol can be choline, serine, ethanolamine, inositol, or certain others.

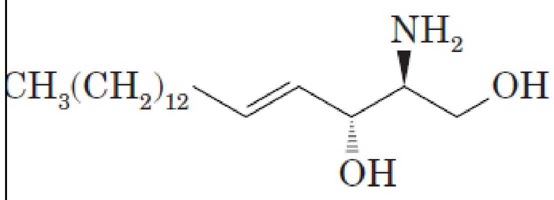


Glycerol



A fatty acid

Stearic acid, 18 carbon atoms, major component of animal triacylglycerols



Sphingosine

Fatty Acid

A fatty acid

Stearic acid, 18 carbon atoms, major component of animal triacylglycerols

- Fatty acids are carboxylic acids with hydrocarbon chains ranging from 4 to 36 carbons in length (C4 to C36). They are essential components of lipid.
- In some fatty acids, this chain is unbranched and fully saturated (contains no double bonds); in others the chain contains one or more double bonds (Table-1).
- Fatty acids with more than one double bond are called **polyunsaturated fatty acids**. Double bonds in naturally occurring unsaturated fatty acids are never conjugated—they are always separated by one methylene group.
- The physical properties of a fatty acid depend on the length of the hydrocarbon chain and the degree of unsaturation.

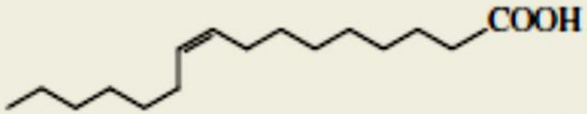
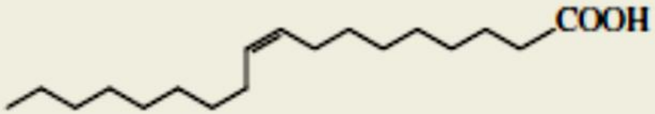
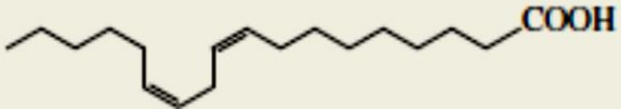
Fatty Acid

- The double bonds are in the cis configuration in nearly all naturally occurring unsaturated fatty acids. Trans fatty acids are produced by fermentation in the rumen of dairy animals and are obtained from dairy products and meat.

- They are also produced during hydrogenation of fish or vegetable oils.

- As diets high in trans fatty acids, correlate with increased blood levels of LDL (bad cholesterol) and decreased HDL (good cholesterol), it is generally recommended that one should avoid large amounts of these fatty acids. Unfortunately, French fries, doughnuts and cookies tend to be high in trans fatty acids.

Common Naturally Occurring Fatty Acids (Table-1)

Number of carbons	Common name	Systematic name	Structure	Melting point °C
Saturated				
12	lauric acid	dodecanoic acid		44
14	myristic acid	tetradecanoic acid		58
16	palmitic acid	hexadecanoic acid		63
18	stearic acid	octadecanoic acid		69
20	arachidic acid	eicosanoic acid		77
Unsaturated				
16	palmitoleic acid	(9Z)-hexadecenoic acid		0
18	oleic acid	(9Z)-octadecenoic acid		13
18	linoleic acid	(9Z,12Z)-octadecadienoic acid		−5

Ref: Organic Chemistry, Paula Y Bruice

Physical Properties of Fatty Acid

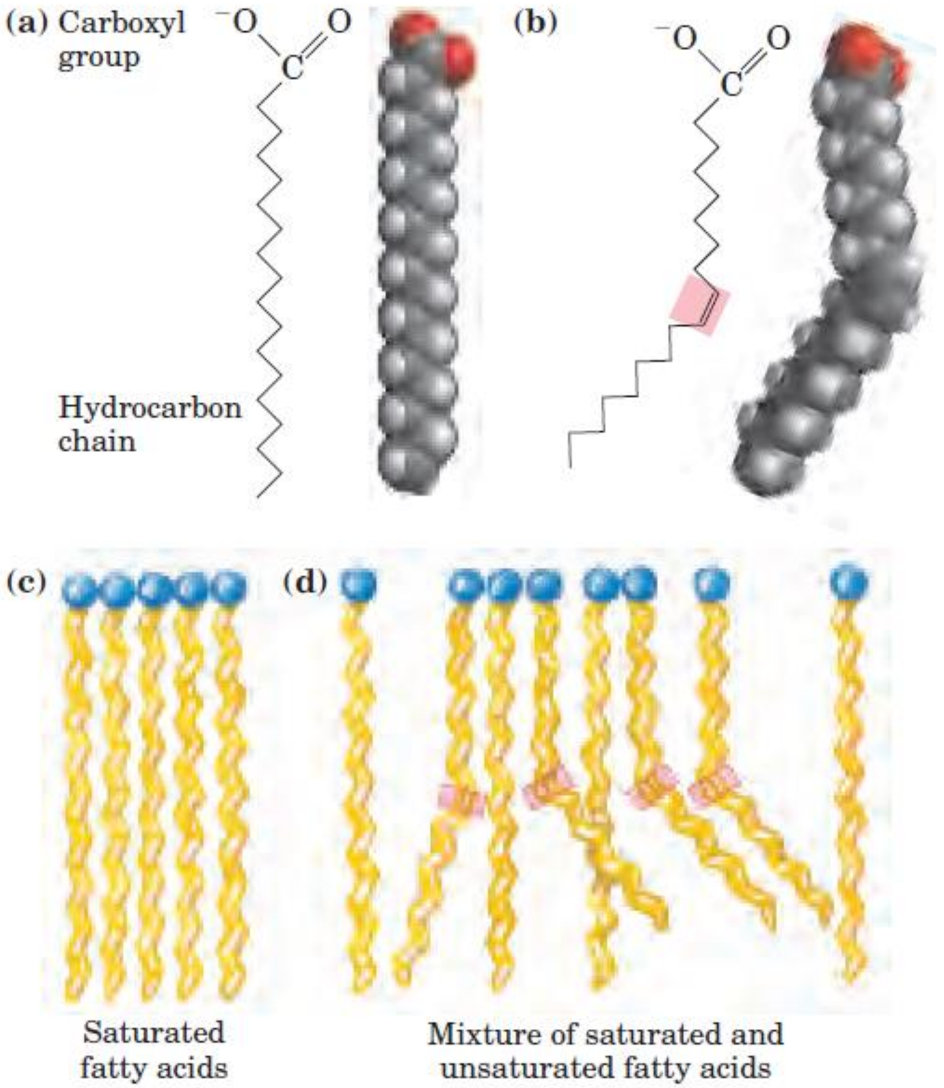
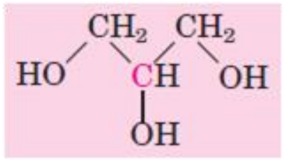


Fig: The packing of fatty acids into stable aggregates

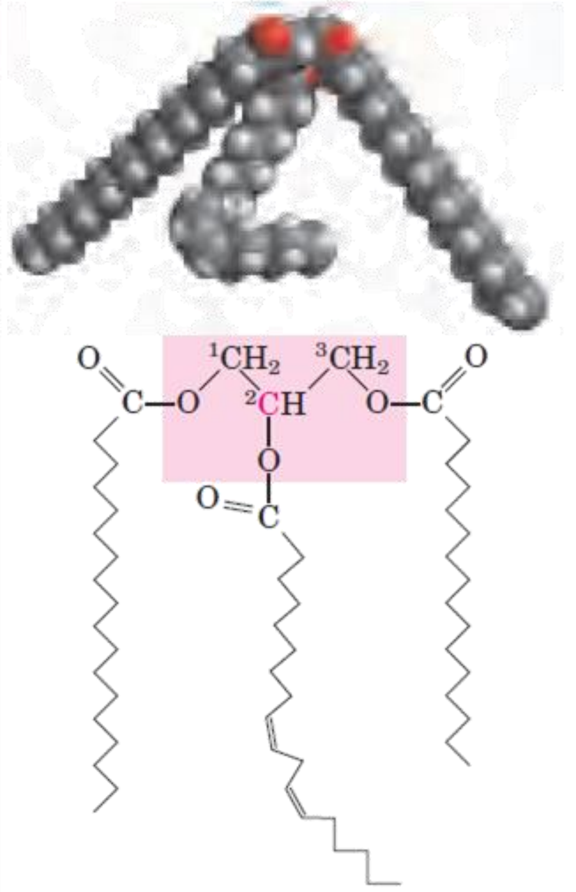
- The physical properties of the fatty acids and of compounds that contain them, are largely determined by the length and degree of unsaturation of the hydrocarbon chain.
- The melting points of saturated fatty acids increase with increasing molecular weight because of increased van der Waals interactions between the molecules.
- The double bonds in unsaturated fatty acids generally have the cis configuration. This configuration produces a bend in the molecules, which prevents them from packing together as tightly as fully saturated fatty acids. So, unsaturated fatty acids have fewer intermolecular interactions and therefore, lower melting points than saturated fatty acids with comparable molecular weights.

Introduction to Fat and Oil

The simplest lipid: Storage lipid



Glycerol



-Stearoyl, 2-linoleoyl, 3-palmitoyl glycerol, a mixed triacylglycerol

- Oils and fats are fatty esters of glycerols, also called tri-acylglycerols or triglycerides. They are composed of three fatty acids, each in ester linkage with a single glycerol.
- They have a important role for stored energy and insulation.
- Oils and fats containing the same kind of fatty acid are called simple Triacylglycerols.
- Most naturally occurring triacylglycerols, such as those in vegetable oils, dairy products and animal fat are mixed - they contain two or more different fatty acids.
- They are hydrophobic, non-polar and essentially water insoluble molecule.

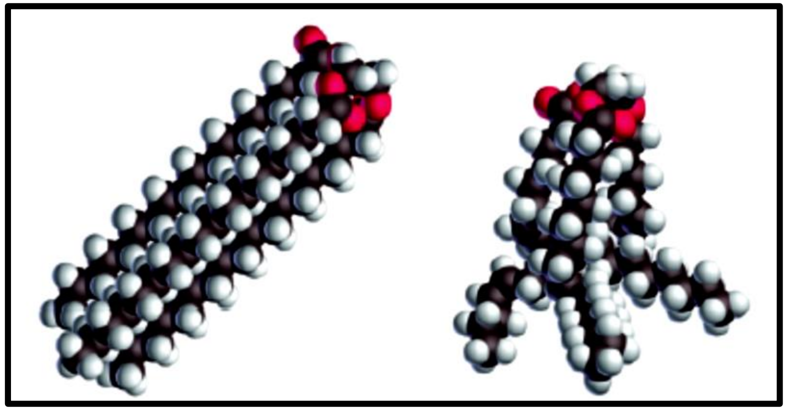
Physical State of Triglycerides

In general fats that come from animals are generally solids at room temperature, and those from plants or fish are usually liquids. Liquid fats are often called **oils.**

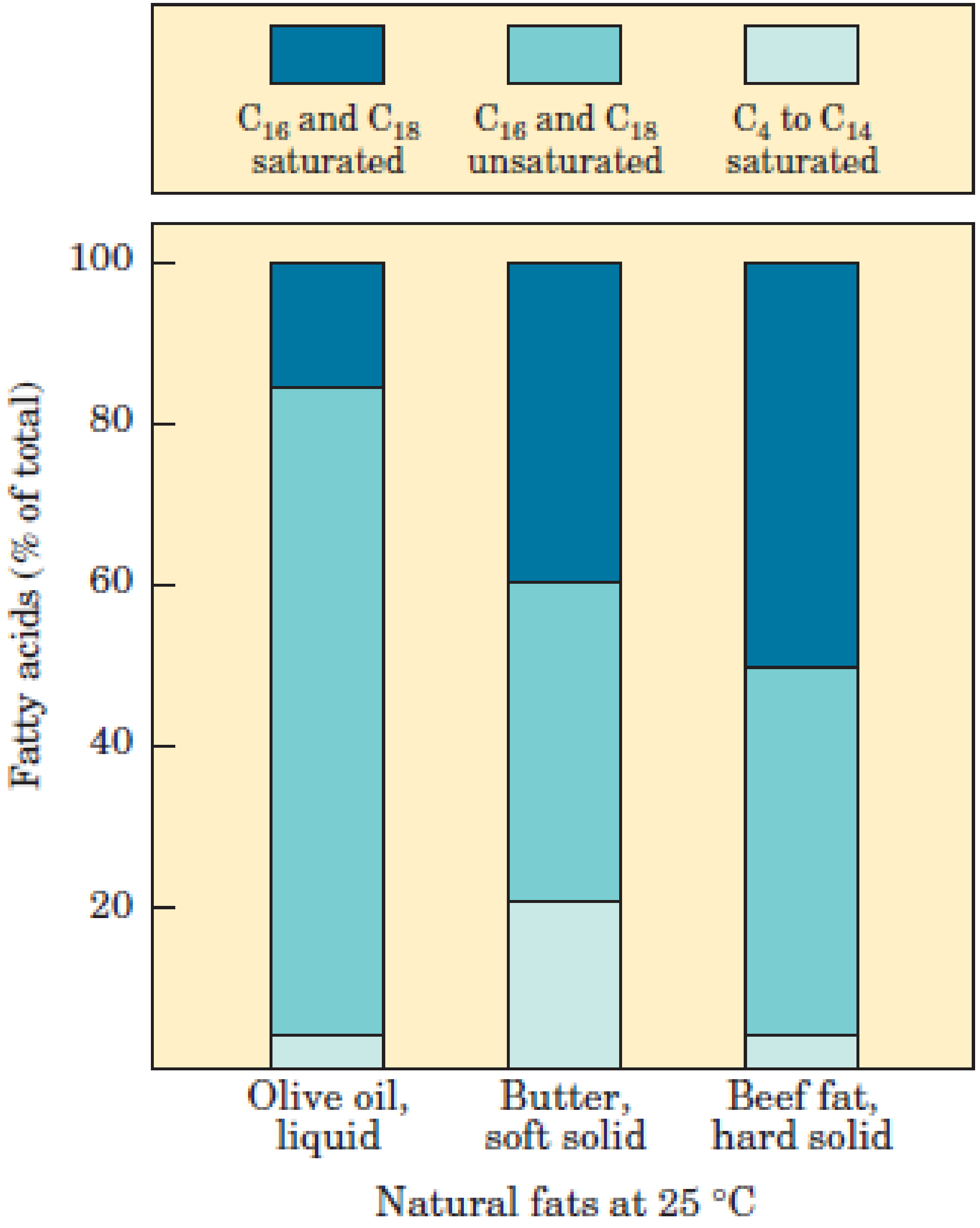
Fat: A mixture of triglycerides containing a high proportion of long-chain, saturated fatty acids (high melting points).

Oil: A mixture of triglycerides containing a high proportion of long-chain, unsaturated fatty acids (low melting points). Oils typically come from plant products such as corn, soybeans, olives and peanuts.

The higher proportion of long-chain saturated fatty acids increases its melting point.



a fat an oil

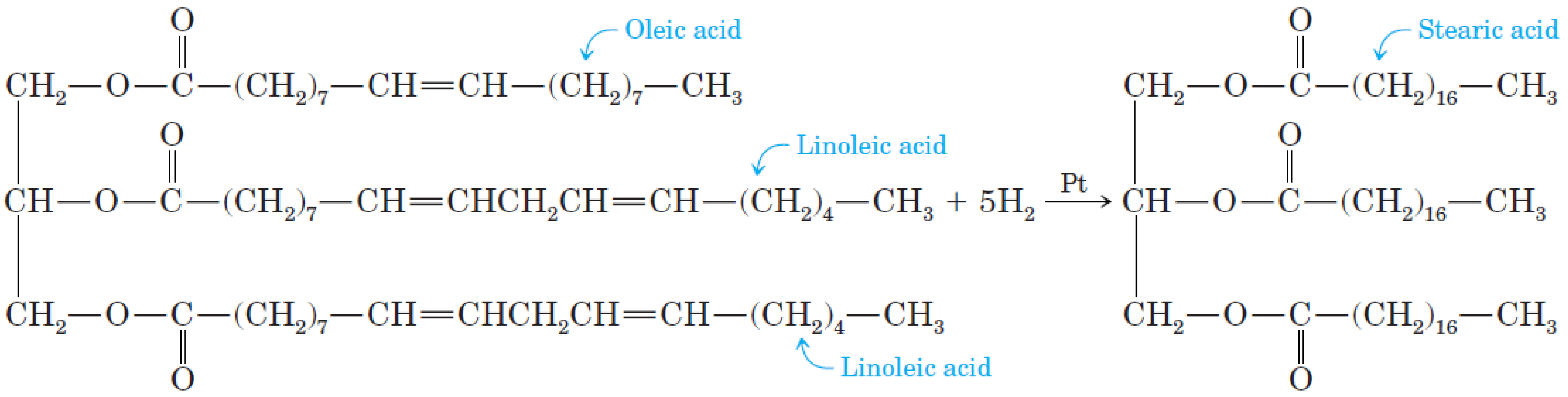


- **Olive Oil has more unsaturated fatty acid: liquid at room temp**
- **Butter has more saturated fatty acid than olive oil: soft solid at room temp**
- **Beef fat has even more saturated fatty acid than butter: Hard solid at room temp.**

Hydrogenation of Fats and Oil

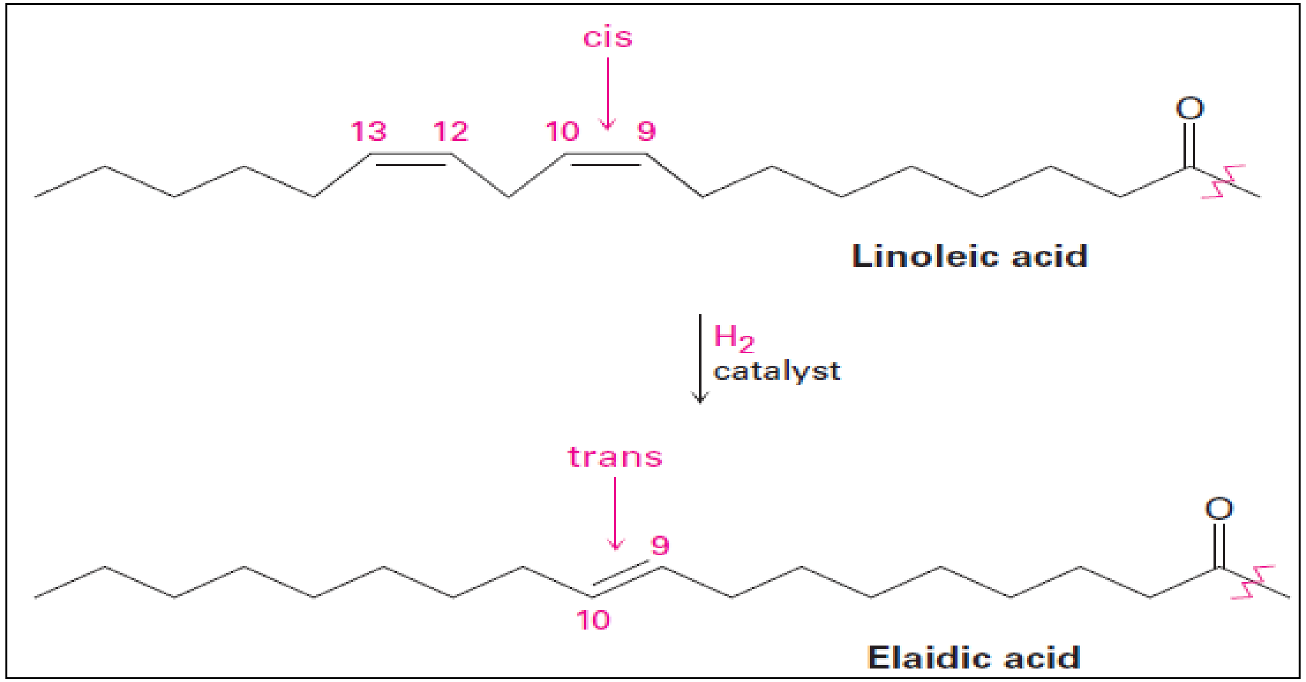
Unsaturated liquid oils can be converted to solids by hydrogenation.

- Some or all of the double bonds of polyunsaturated oils can be reduced by catalytic hydrogenation. Margarine is prepared by hydrogenating vegetable oils such as soybean oil and safflower oil, until they have the desired consistency. This process is called "hardening of oils."



Hydrogenation of Fats and Oil

- **Hydrogenation is carried out on a large scale to produce the solid shortening.**
- **The hydrogenation reaction must be carefully controlled because reducing all the carbon–carbon double bonds would produce a hard fat (Caution!! fat with no double bonds would be *too* solid).**
- **The hydrogenation reaction is accompanied by some cis–trans isomerization of the double bonds, producing fats with about 10% to 15% trans unsaturated fatty acids.**



WAXES

- Biological waxes are esters of long-chain (C14 to C36) saturated and unsaturated fatty acids, with long-chain (C16 to C30) alcohols.
- Their melting points (60 to 100 °C) are generally higher than those of triacylglycerols.
- Waxes serve as energy stores and water repellents.

$$CH_3(CH_2)_{24}\overset{\overset{O}{\|}}{C}O(CH_2)_{29}CH_3$$

a major component of beeswax

structural material of beehives

$$CH_3(CH_2)_{30}\overset{\overset{O}{\|}}{C}O(CH_2)_{33}CH_3$$

a major component of carnauba wax

coating on the leaves of a Brazilian palm

Layers of honeycomb in a beehive

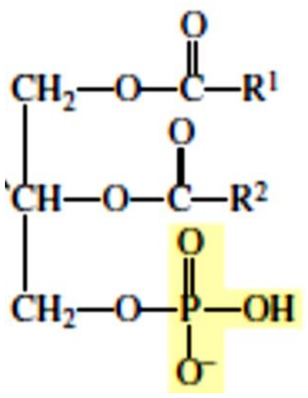
Raindrops on a feather

Membranes

For biological systems to operate, some parts of organisms must be separated from other parts, like the outside of the cell must be separated from the inside. “Greasy” lipid **membranes** serve as the barrier. In addition to isolating the cell’s contents, these membranes allow the selective transport of ions and organic molecules into and out of the cell.

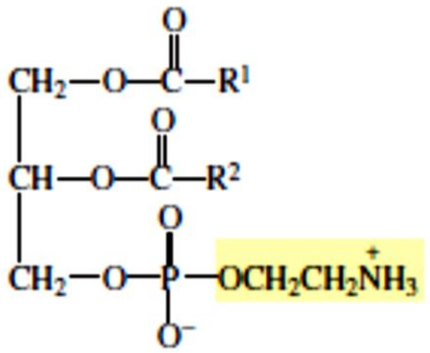
Phospholipids

Phosphoacylglycerols (also called **phosphoglycerides**) are the major components of cell membranes. They are similar to triacylglycerols except that a terminal -OH group of glycerol is esterified with phosphoric acid rather than with a fatty acid, forming a **phosphatidic acid**. Because phosphoacylglycerols are lipids that contain a phosphate group, they are classified as **phospholipids**.

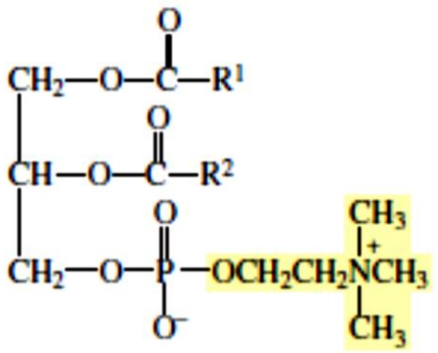


a phosphatidic acid

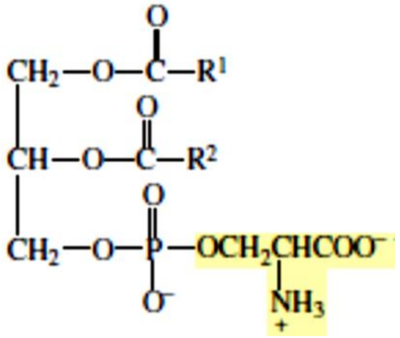
- Phosphatidic acids are the simplest phosphoacylglycerols and are present only in small amounts in membranes.
- The most common phosphoacylglycerols in membranes have a second phosphate ester linkage. The alcohols most commonly used to form this second ester group are ethanolamine, choline and serine.
- Phosphatidylethanolamines are also called **cephalins** and phosphatidylcholines are called **lecithins**.



phosphatidylethanolamine
cephalin

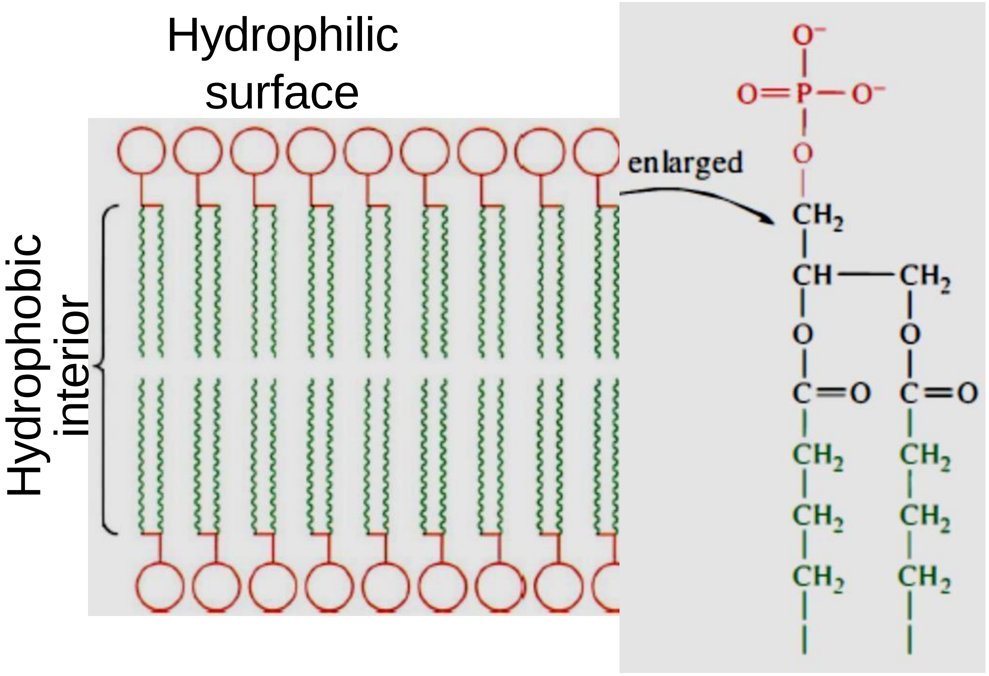


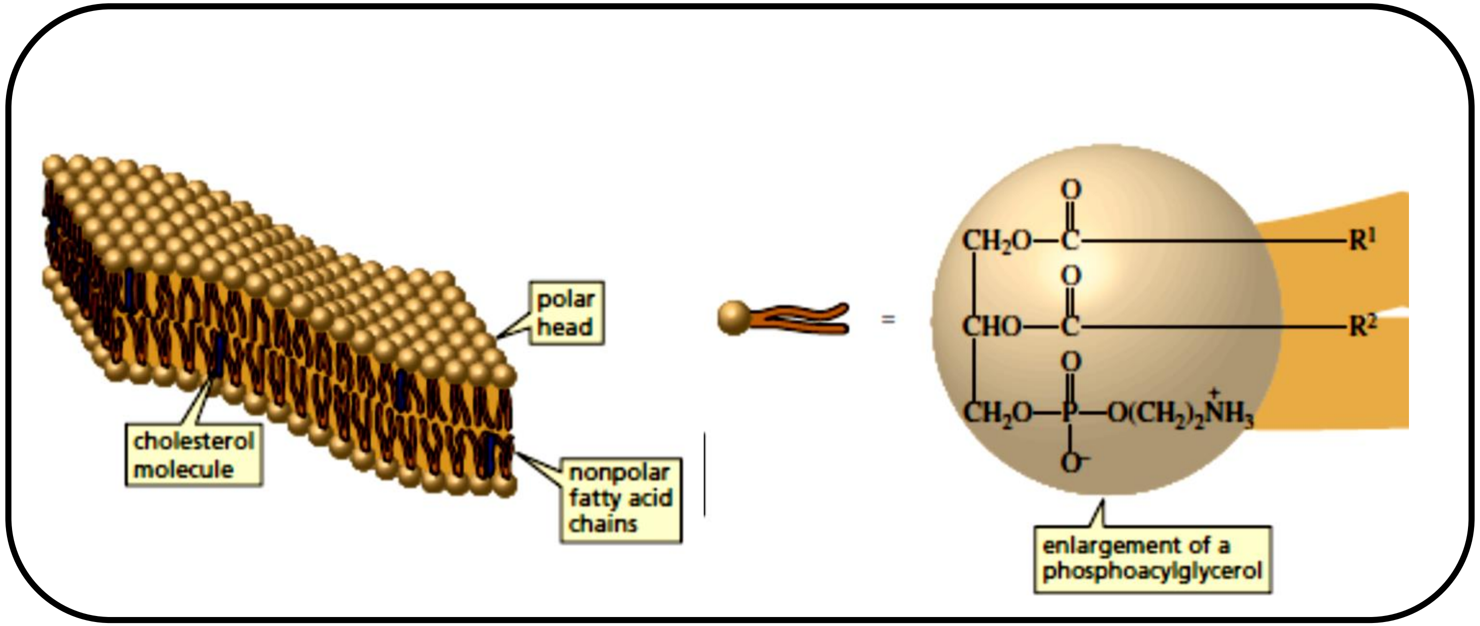
phosphatidylcholine
lecithin



phosphatidylserine

Phosphoacylglycerols form membranes by arranging themselves in a **lipid bilayer**. The polar heads of the phosphoacylglycerols are on the outside of the bilayer and the fatty acid chains form the interior of the bilayer. Cholesterol—a membrane lipid is also found in the interior of the bilayer. Atypical bilayer is about 50 Å thick.

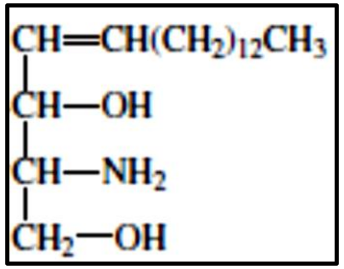




Lipid bilayer

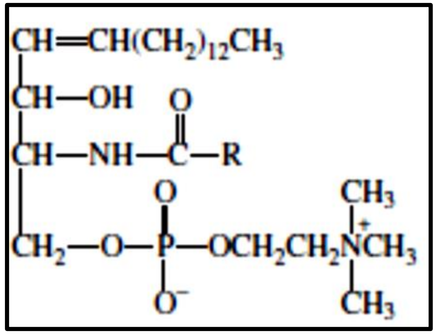
Sphingolipids

- **Sphingolipids** are also found in membranes. They are the major lipid components in the myelin sheaths of nerve fibers. Sphingolipids contain sphingosine instead of glycerol. In sphingolipids, the amino group of sphingosine is bonded to the acyl group of a fatty acid.

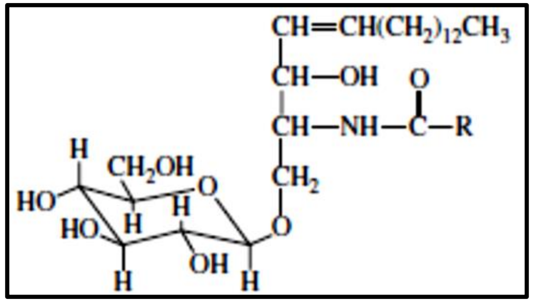


sphingosine

- Two of the most common kinds of sphingolipids are **sphingomyelins** and **cerebrosides**. In sphingomyelins, the primary -OH group of sphingosine is bonded to phosphocholine or phosphoethanolamine.
- In cerebrosides, the primary -OH group of sphingosine is bonded to a sugar residue through a β-glycosidic linkage.



sphingomyelin

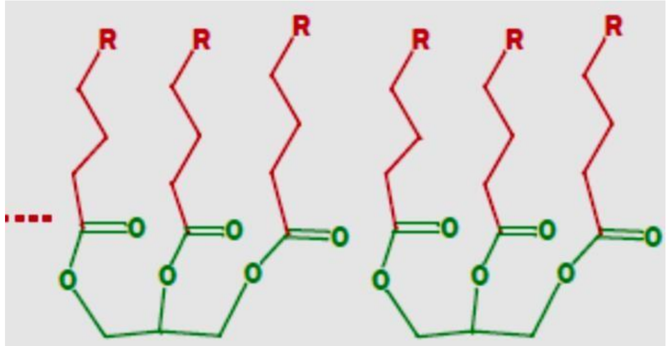


glucocerebroside

Saponification

Air

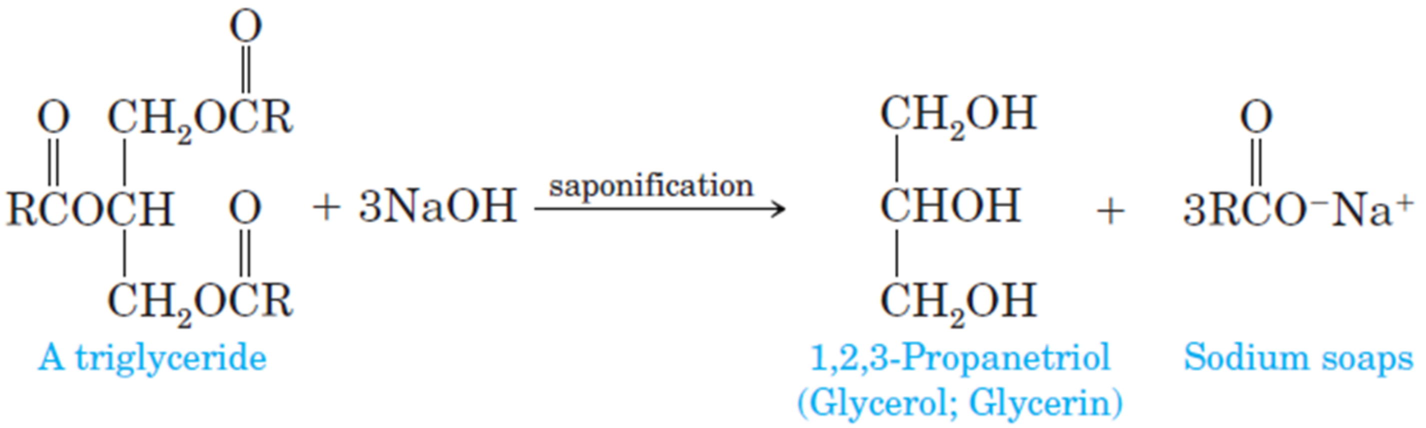
Water

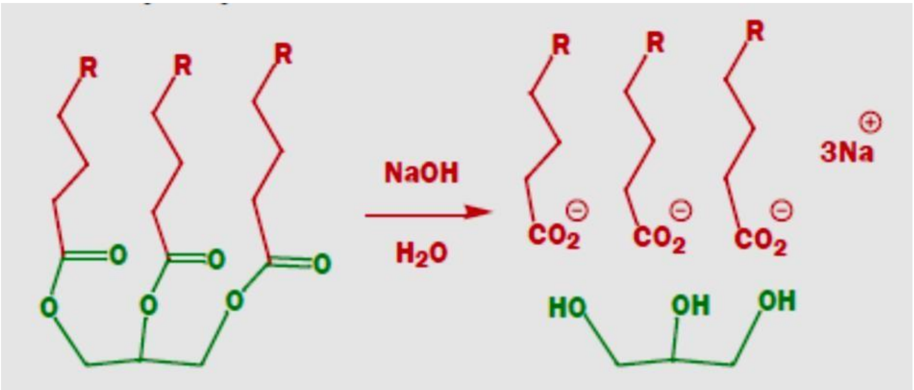


hydrocarbon
side chains
clumped together
outside the water

polar groups
inside the water

When triglycerides are boiled up with alkali, the esters are hydrolysed, and a mixture of carboxylate salts and glycerol is formed. This is how soap is made—hard soap is the sodium salt and soft soap, the potassium salt.





Thus saponification is the base-promoted hydrolysis of fats and oils producing glycerol and a mixture of fatty acid salts, called soaps.

Soaps

When a soap is suspended in water, the carboxylate groups show a strong affinity for the water and so oily globules or **micelles** are formed with the hydrocarbon side chain inside. It is these globules that remove greasy dirt from you or your clothes.

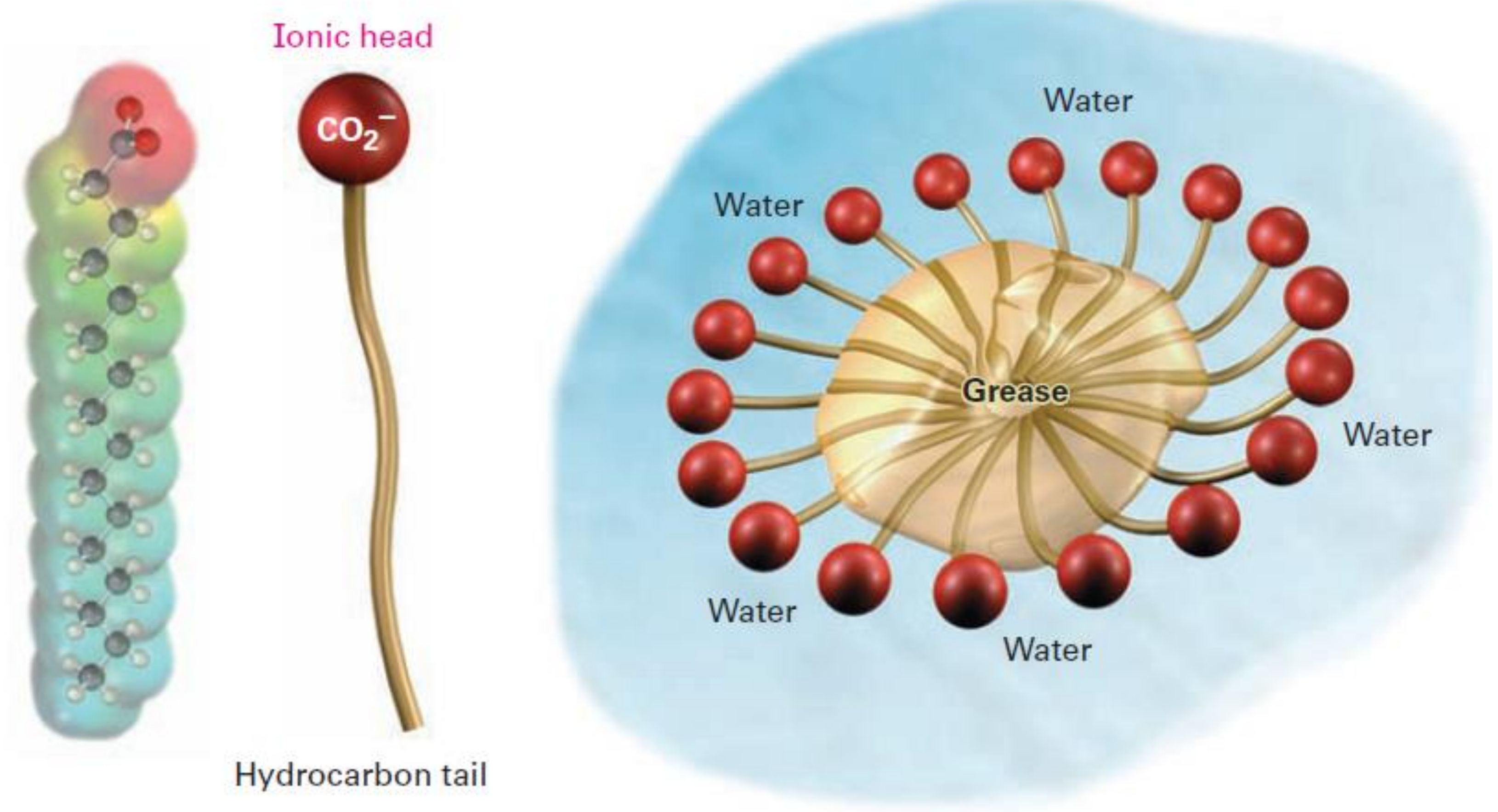
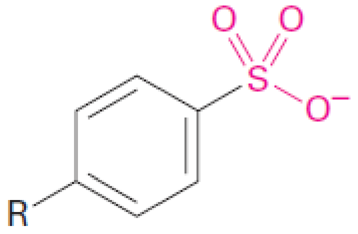


Figure A soap micelle solubilizing a grease particle in water. An electrostatic potential map of a fatty acid carboxylate shows how the negative charge is located in the head group.

Soaps and Detergents

- In hard water, which contains metal ions, soluble sodium carboxylates are converted into insoluble magnesium and calcium salts, leaving the familiar ring of scum around bathtubs and the gray tinge on white clot.
- Chemists have circumvented these problems by synthesizing a class of synthetic detergents based on salts of long chain alkylbenzenesulfonic acids.
- Unlike soaps, sulfonate detergents don't form insoluble metal salts in hard water and don't leave an unpleasant scum.



A synthetic detergent
(R = a mixture of C_{12} chains)

References

1) **Organic Chemistry by Paula. Y. Bruice**
2) **Organic chemistry by Morrison & Boyd**
3) **Organic chemistry by Jonathan Clayden, Nick Geeves, Stuart Warren, Organic Chemistry, 2nd Edition, 2012.**