

ORGANIC CHEMISTRY

FATS, OILS AND DETERGENTS

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Introduction

Description of Fats, Oils and Detergents:

Chemical Structure of Fats and Oils

Sources of Fats and Oils

Chemical Composition of Fats and Oils

Functions of Triglycerides

Monoglycerides and Diglycerides

Free Fatty Acids

Physical Properties of Fats and Oils

Factors Affecting Characteristics of Fats and Oils

Trans Fat

Production of Fats and Oils in Plants and Animals

Metabolism of Fats and Oils

Isomerism in Fats and Oils

Analysis of Fats and Oils

Adulterants in Fats and Oils

Nutritional Aspects of Fats and Oils

Triglycerides for Indication of Health

Cholesterol

Importance of Saturated Fats

Estimation of Fat Content

Importance of Fats and Oils

Industrial Applications of Fats and Oils

Deterioration Factors of Fats and Oils

Essential Fatty Acids

Functions of Essential Fatty Acids

Processing of Fatty Acids

Biosynthesis of Fatty Acids

Biodegradation of Fatty Acids

Detergents

Action of Detergents

Differences between Soaps and Detergents

Characterization of Detergents

Introduction

Fats, oils and detergents are materials of great industrial as well as household applications. Even though there exists little similarity as far as the chemistry of oils and fats (on the one hand) and the detergents (on the other hand) are concerned, they are often discussed together in the textbooks and articles. How the products are named and defined depends on the criteria adopted for it; products may have different meanings to different people and different applications to different users; unless defined with scientific criteria.

As the word suggests, 'fat' stands for anything that is bulky and rigid. There is a range of chemicals, which are bulky, rigid and solid at ambient conditions, but should all of them be termed as fats? Certainly not and in fact they are not. We all know that large sized molecules with compact structures would behave like bulky and rigid they don't flow easily and in fact behave more like solids. But all of them cannot be termed as fats. Generally speaking, organic substances that are either solids or get solidified at lower temperatures (for example, at ambient temperatures) are termed as fats, provided they are meant for edible purposes. That is how one can differentiate fats from waxes in spite of the fact that fats are also waxy and waxes do have the basic physical characteristics such as solidification at lower temperatures, a behavior similar to fats. What are oils then? Can coconut oil, which solidifies at lower temperature, be considered as fats? The biggest question is are fats and oils the same?

Dealing with food products and taking it further from just the criteria of solidification at lower temperature, one will have to really look into it, in a little more detail, in order to explain the difference between fats and oils. In India, the cream separated from milk is known as "ghee". The same product is popularly called "Butter Oil" in the western countries. How do we explain this difference in perception about a given product? Let us take an example of hydrogenated fat. In India, we call the hydrogenated fat also as "ghee" whereas in Europe, it is called mostly as hydrogenated fat and rarely as hydrogenated oil.

Let us take the example of kerosene, which is commonly known as oil. The organic can easily be put into two major categories:

- a) Those soluble in water are non-oily and b) Those insoluble in water are oily. Because kerosene is oily, people started calling it as oil.

Now, the question arises, whether kerosene can be put in the same category as soybean, groundnut, and mustard oils. Certainly not!

The oily substances would obviously include fats, (which includes the organic substances solidifying at lower temperatures and which are edible) as well as oils (which includes butter oil, vegetable oils and also kerosene oil) and hence, it should be the criteria to define or name substances.

It is always better to define substances based on their chemical structure. It is only the triglycerides which are defined as oils and fats.

The other category of substances covered under this chapter is detergents. One would wonder as to why detergents have been placed along with fats and oils in this chapter like any other textbook of chemistry.

Detergents are basically the substances, which have the tendency to exist equally (or partially) in both – the oil medium as well as in the water medium, and such substances are exploited for their use to stabilize multiphase systems. Both the hydrophilic and hydrophobic moieties coexist in the molecule of a detergent. As a result, such substances can reorient themselves in the multiphase systems depending upon the polarity of different phases.

The surface tension or interfacial tension between the two different phases i.e. polar (water-loving) and non-polar (oil loving) leads to immiscibility of the phases. Here it may be understood that it is called surface tension when the liquid is in equilibrium with air and interfacial tension when liquid is in equilibrium with another liquid. When the interfacial tension is high, the possibility of existence of the two different surfaces as one phase becomes very low. Likewise, as the interfacial tension decreases, the miscibility of two different phases becomes possible. Incidentally, in all the systems that we encounter (**Table I**), there is always more than one phase and in order to stabilize such systems, one needs to use detergents.

Table I: Different multiphase systems and the detergents used for converting them into single phase.

Phases	System	Surface Active Agents or Detergents
Liquid:Liquid	Emulsion, Microemulsion	Emulsifier, Solubliser, Co-surfactant.
Liquid: Gas	Foam, Mist	Foaming Agents
Liquid: Solid	Dispersion	Dispersant, Deflocculant,
Solid: Gas	Dust	Detergent, Rinsing aid Dispersant, Dust depressant

Detergents are substances which can homogenize two completely different phases. The special structural features responsible for this unique property of detergents are due to the presence of totally opposite functional groups; one having affinity for water and the other having affinity for oil in the same molecule. As a result, detergents can solubilize oil in water or water in oil. Infact, one can design substances that have the capability of solubilizing oil in water or water in oil to a substantially significant degree.

Because of their unique structural attributes, detergents have become one of the most important substances for various industrial applications. Substances that are completely water soluble, and non-oily when dissolved in water, would exist as a single phase system even if the solute is of a different phase. For example, a solid substance like sugar or salt dissolved in water result in a

single phase i.e. liquid. On the other hand, a liquid insoluble in water when added or mixed with water, would separate from water and there would be two distinct phases: both liquids. The different phases like solid, liquid and gas can co-exist either as one phase or two phases depending upon the inter-particle interactions or interfacial tension between the phases involved. In our day to day life and even in the industry, one often needs to mix two different phases to have one due to one reason or the other. Here, the example of mixing water with diesel or petrol as an adulterant, would perhaps be funny! Let us take the example of Several pesticides are oily and have to be mixed in water before they can be sprayed on crops. They cannot be sprayed uniformly and their objective of crop protection can hardly be achieved.

Similarly, the formulations of vitamins D and K, which are completely insoluble in water, require the use of detergents to make sure that the formulation remains stable for a long time.

Similarly, strange it may appear though, the detergents are needed even when one needs to destabilize the stable single phase systems consisting of multi-phases. There is no dearth of examples of this application of detergents in the industry as listed in **Table II**.

Hence, it is evident that whenever one needs to maneuver the interfacial tensions of multi-phase systems whether for stabilization or for destabilization, detergents always come handy.

Table II: Destabilization of homogeneous multiphase systems by using detergents

Stable System	Destabilization	Role of Detergents	Remarks
Emulsion	De-emulsification	Demulsifier	Petroleum from crude emulsions Purification of dirty water. Suppressing dust from air in mining areas. Breaking of foam in industrial systems.
Dispersion	Coagulation	Flocculant, Coagulant	
Dust	Precipitation	Dust depressant	
Foam	Air removal	Anti foaming agent, Defoaming agent.	

Description of fats, oils and detergents:

Fats and Oils

There are basically three types of products that are called fats:

- Animal fat; meat, poultry, fish, etc.
- Vegetable fat; extracts from the oil containing seeds
- Milk fat; from domestic animals.

The fats from all the three sources are known to have the basic structure of a triglyceride but with varying degree of unsaturation (estimated by determination of iodine value) and the hydrocarbon chain length attached to the fatty acid part of the triglyceride.

Similarly, oils are derived from different origins such as:

- Animal origin: Tall oil, fish oil, etc.
- Vegetable origin: Groundnut oil, Coconut oil, Soya oil, Palm oil, etc.
- Mineral origin: Kerosene oil and series of liquid hydrocarbons.

As presented in **Table III**, all the oils except the mineral oil are similar to fats as they are basically triglycerides. The mineral oils are, on the other hand, hydrocarbons.

Table III: Nature and structure of fats and oils from different sources

Source	Nature	Structure	Carbon Chain length	Iodine value
Animal Fat	Solid and/or Semi solid	Tiglycerides; mainly saturated	$C_4 - C_{30}$	Lard: 46-70 Beef: 34-46 Mutton: 38-44 Goat: 30-38
Vegetable Fat	Liquid and/or Semi-solid	Triglycerides; mainly unsaturated	$C - C_{30}$	Cocoa: 32-40 Borneo: 28-36 Shea: 56-62 Mowrah: 60-68
Milk Fat	Semi-solid and/or Solid	Triglycerides; mainly saturated	$C_4 - C_{22}$	Goat: 24-32 Sheep: 32-40 Buffalo: 30-36
Mineral Oil	Liquid	Saturated hydrocarbons	$C_4 - C_{30}$	Camel: 36-44 Not of significance

Note: The mineral oils, hydrocarbons, is even though commonly known as oils, are not taken along with the fats and oils simply because only the triglycerides are defined as fats and oils.

From this discussion, it can be stated that:

- Fats and oils derived from the animals, plants and milk are composed of “triglycerides”. The difference is mainly due to the degree of unsaturation and the carbon chain length of the fatty acid in the triglyceride, otherwise all of them can be easily understood as triglycerides and

- b) Oils from mineral (petroleum) sources are completely different from the oils from vegetable sources. The mineral oils are basically mixture of long chain hydrocarbons and have no triglycerides.

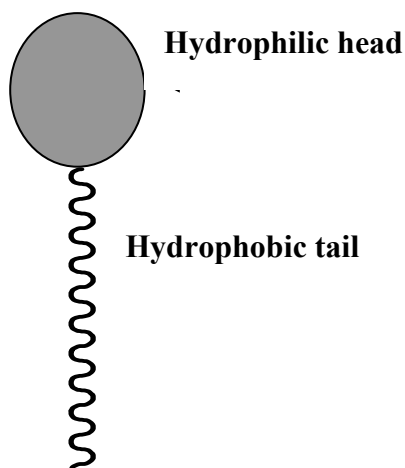


Fig 1: Description of the structure of a detergent molecule as a unit consisting of the hydrophilic part commonly referred as ‘head’ and a hydrophobic part referred as ‘tail’.

From the above conclusions, one can easily understand that oils and fats are the same as far as their basic chemistry is concerned. Since, the mineral oils are nothing but hydrocarbons, their chemistry and properties are generally discussed and described under the petroleum products. This is why in this chapter only the oils and fats of animal and vegetable origins including the ones derived from milk would be described in detail.

Detergents

As we have known, detergents possess (a) significantly high degree of liking for both the oily as well as the non-oily phases mainly because the detergents consist of two completely different moieties. Thus, the description of detergent structure as “two molecules in one molecule” needs to be appreciated while understanding the behavior of detergents as speciality chemicals or performance chemicals.

For the purpose of understanding the structure (**Fig 1**) the moiety which likes water is referred as the “head” and the moiety which doesn’t like water is assumed as “tail” of the molecule of detergent. To elaborate it further, the head has the hydrophilic nature and likes to stay with non-oily phase while the tail has the hydrophobic nature which means it likes to stay with the oily phase. Now, depending upon the size, shape and nature of the head and tail, as also on the balance between the two that a given detergent can be designed as per the requirements.

Of the same molecule, if the head stays with water keeping itself away from oil and the tail does the same with the oil keeping itself away from water, it can be easily predicted that the oil and water phases can co-exist as one phase in the presence of a detergent. This can be possible because the interfacial tension between the two phases is brought down. The detergent molecules reorient themselves in such a way that they exist more at the interface than in the bulk of the two

phases. In other words, detergent becomes active at the interface of two opposing phases. That is why, they are also called as “surface active” agents or “surfactants”.

One can classify detergents into two basic categories:

- a) Synthetic detergents and
- b) Natural detergents

Further the detergents can be put into different groups based on their nature e.g. ionic (cationic and anionic), non-ionic and zwitter ionic. The detergents of different classes can be designed using different moieties as per the requirements. More often than not, fats and oils are the major raw materials for producing different types of detergents. Perhaps that could be the reason as to why fats, oils and detergents are often discussed together.

For better understanding, it would be useful if the fats and oils are discussed together first and then the detergents.

Chemical Structure Of Fats And Oils

Fats

As stated earlier, we can now say that fats are naturally occurring esters (tri) of the higher alkyl (paraffinic or olefinic) monocarboxylic acids and the trihydric alcohol, i.e. glycerol; that is why they are also called triglycerides.

However, fats do occur, in sizeable quantities as esters with complex structures involving:

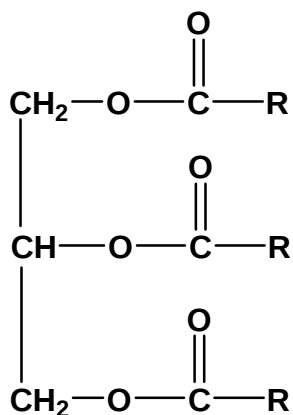
- a) Alkyl monocarboxylic acid of relatively large alkyl chain and an alcohol with the alkyl chain as big as that of the monocarboxylic acid and
- b) Alkyl monocarboxylic acid with large alkyl chain and an alcohol of complex structure.

Fats are one of the important classes of food as they contain the most concentrated form of metabolic energy available to humans. This can be understood from the fact that fats top the list of data about the energy available from 1g of various materials: Fats 38KJ/g; Ethanol 29KJ/g and sugar 17KJ/g.

Since fats are esters, their structure would therefore consist of:

- An acid: monocarboxylic acids of varying carbon chain lengths and varying degree of unsaturation: in the case of triglycerides there would be three molecules of monocarboxylic acid.
- An alcohol: glycerol (triglycerides); alcohol with longer alkyl chain and alcohols of complex structure.

The general structure of fats and oils has been shown in **Fig II and Figs III a and b**. The fatty acids are generally with saturated alkyl chain which is why fats are solid at room temperature. Further, the triglycerides can have all the three carboxylic acid of the same structure or of different structures. Accordingly their properties will differ from each other.



R= Hydrocarbon chain with varying carbon chain length and degree of saturation. In the case of saturated fats and oils the chain has no unsaturation.

Fig II: General structure of a simple saturated fats and oils.

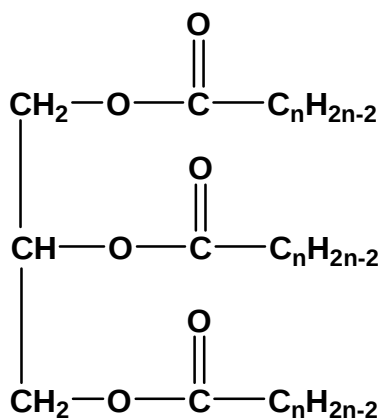
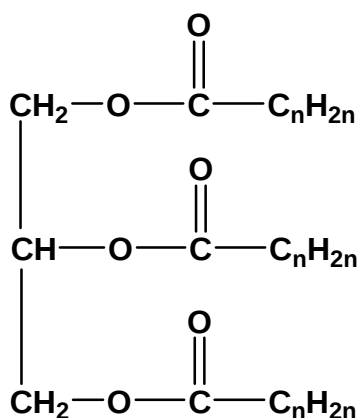


Fig III: General structure of simple unsaturated fats and oils with hydrocarbon having a) one double bond in each chain b) two double bonds in each chain

Oils

As said earlier generally, the term oil is used to indicate a variety of greasy, fluid substances that are: (i) viscous fluids at ordinary temperatures (ii) lighter than water (iii) insoluble in water but soluble in organic solvents such as aliphatic alcohols, ethers, etc. and are (iv) flammable.

At the same time, the distinction between oils and fats is only due to their form at lower temperature, one can say, without doubt, that all the oils are fats but all the fats are not oils. So, from the point of view of their structure and their chemistry, fats and oils are the same and however, the difference between oils and fats due to their form at lower temperature is because of the type of fatty acids present in the triglycerides that oils and fats are composed of.

Thus, it can be said that

- a) both fats and oils are esters of fatty acids; triglycerides and
- b) if they are liquid at ordinary temperature they are called oils and those which solidify at lower temperatures are fats.

The difference in their forms at low temperature is attributed largely to the degree of saturation or unsaturation in the alkyl chain of fatty acid. Oils have high degree of unsaturation instead of the saturation in the alkyl chain length of the fatty acid in their structure.

To appreciate the distinction between fats and oils, let us understand the properties of various fatty acids with varying degree of unsaturation. It is the inherent liquid form of unsaturated fatty acids that is responsible for the liquid form of oils at lower temperature and like-wise, the solid form of saturated fatty acids is responsible for the solid form of fats at lower temperature.

Sources of Fats and Oils

◆ *Vegetable Source*

Oils can be categorized as both edible and non-edible. While the edible oils have been well studied and their advantages as well as disadvantages for health are fairly understood, the non-edible ones have always been the subject of research for their exploitation for industrial applications.

The largest source of oils is the seeds of annual plants, such as flax, soybean, mustard, sesame, and the peanut. Soybeans and peanuts produce seeds, which are not only a source of oil, but are also widely utilized as protein-rich foods.

Second large source of vegetable oils comprises of certain oil-bearing trees, of which the coconut, palm, olive, and tung are the most important ones. All these sources are being exploited for meeting the requirements of food and nutrition. The large scale plantation of palm trees in, several South East Asian countries (especially Indonesia and Malaysia) has contributed in growth of their economy is an established fact by now; both Indonesia and Malaysia being the

major exporters of palm oil earn a significant amount of their foreign exchange from palm oil exports.

The non-edible oils are also obtained from the seeds of the annual crops like cottonseed, castor seeds, jatropha, rice bran etc. Some of these oil seeds are already being used either as a food source for cattle or for medicinal purposes. There are also oil-bearing trees, which produce non-edible oils with unique features and the most notable amongst them is “Neem”. For several industrial applications, non-edible oils have been found to be the sustainable materials. Recently, the non-edible oils are being explored as the source for biodiesel. The whole world has started preparing to deal with the crisis due to the phenomenal rise (in recent times) in petroleum prices by putting emphasis on the development of non-edible oils as a sustainable source of biodiesel.

♦ *Animal Source*

The animal fats of technical importance are derived from domestic animals such as Pigs, Oxen, Hogs, Cattle and Sheep. The body fat of Pigs is also known as Lard; Ox and Sheep body fats are known as beef and mutton Tallow respectively. Greases are low-grade inedible fats of softer consistency. These fats are characterized by a high content of fatty acids of the carbon chain length of C_{16} and C_{18} and a comparatively low percentage of unsaturated acids in their structure.

Other animals such as Fowl are raised in large numbers, but their carcasses are so small in quantity that they are usually consumed without the fatty proportions being separated and processed to yield pure fat from the body mass.

A considerable volume of oils is derived from marine animals, (such oils are derived from oily fish,) for example sardines, herring, etc. Fish oils are usually not the byproducts like in the case of the preparation of carcasses for meat.

Chemical Composition of Fats and Oils

Triglyceride is the major component of most fats and oils especially those of edible grade. The minor components of fats and oils include mono- and diglycerides, free fatty acids, phosphatides, sterols, fatty alcohols, and fat soluble vitamins. Many of these minor components have to be removed from the edible grade fats and oils. Let us now discuss the major and minor components of fats and oils, in order to understand the chemical composition of fats and oils in a little more detail.

♦ *The Major Component: Triglycerides.*

A glyceride is an ester formed by the reaction of fatty acids with glycerol (**Fig IV**). Since glycerol has 3 hydroxyl ($-OH$) groups, it can combine with three, two or one carboxylic acid ($-COOH$) group depending upon the quantity of the fatty acid as also on the conditions of the reaction.

If only one of the OH groups of glycerol has combined with a fatty acid, the ester is called a monoglyceride. If two molecules of fatty acids combine with two OH groups in one molecule of

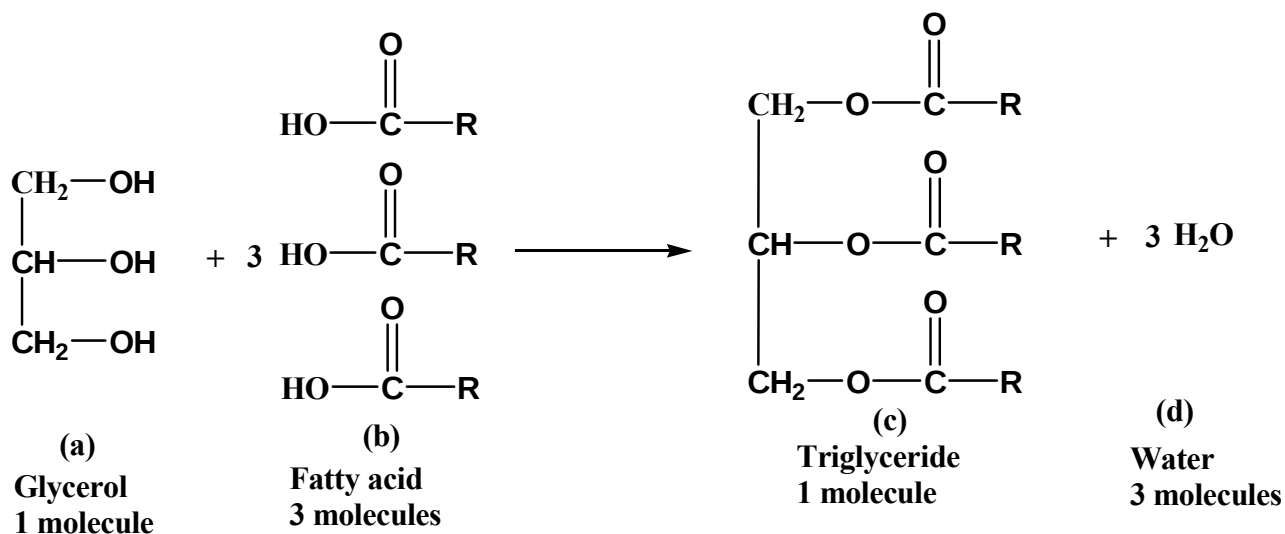
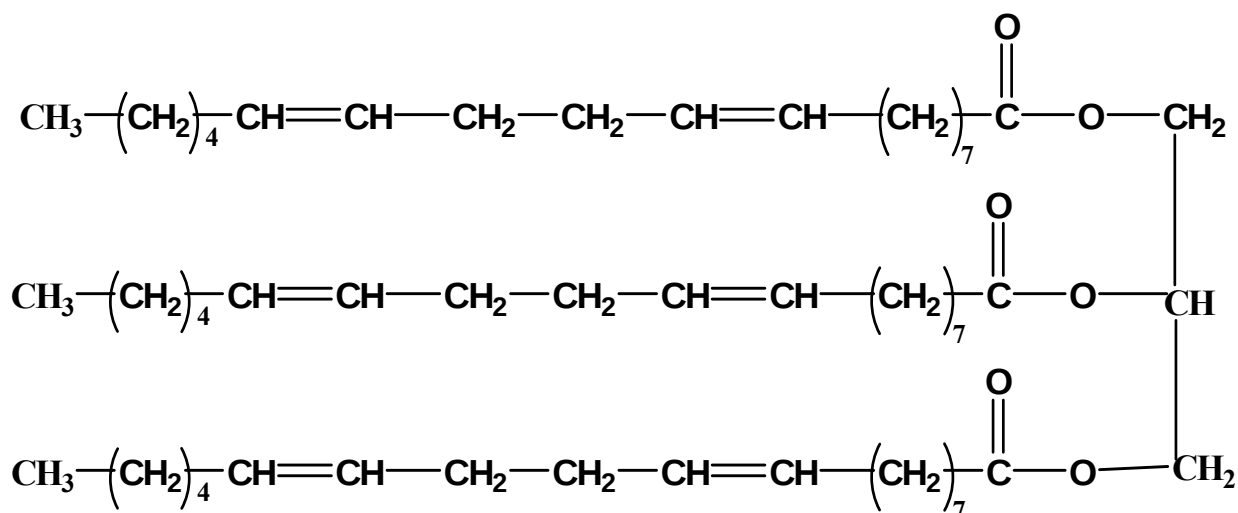


Fig IV: Formation of a triglyceride (c) by condensation of one molecule of glycerol (a) with three moles of fatty acids (b), with the evolution of water (d).

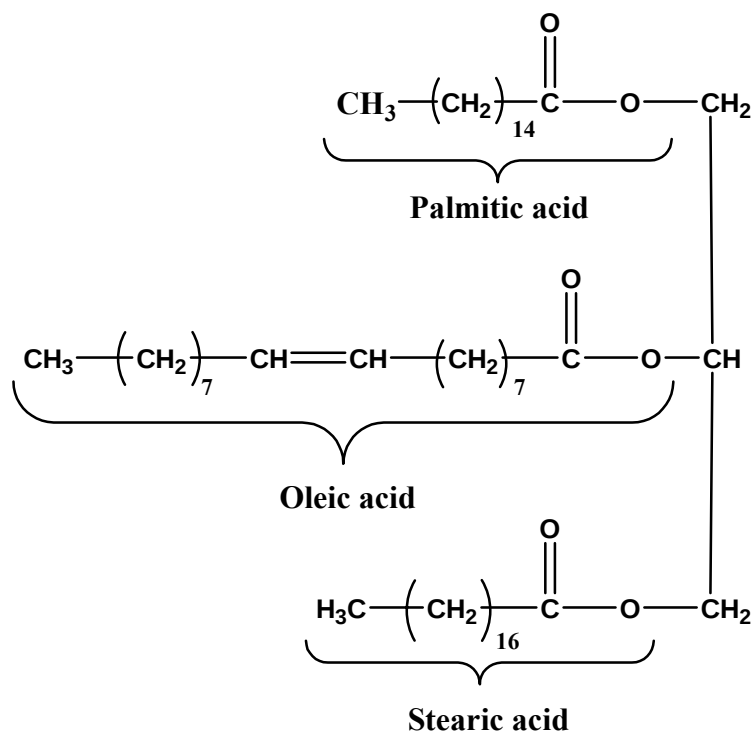
glycerol, the ester is called diglyceride. Similarly, if all the three OH groups of glycerol combine with three molecules of fatty acids, it will be called triglyceride. In other words, in triglycerides, all the three-hydroxyl groups of glycerol are combined with three molecules of fatty acids to form three ester linkages in the same molecule and for the di and mono, there are two and one ester linkages present respectively in the same molecule. The chemistry of glycerides therefore would be determined by the nature of the fatty acid present and would show the characteristics of an ester.

Thus, structurally, one molecule of triglyceride is a condensation product of one molecule of glycerol and three molecules of fatty acids, the by product is water (three molecules). (**Fig V**). When all the fatty acids in a triglyceride are identical, it is called a ‘Simple’ triglyceride (**Fig V a**) but if the acids are different, it is known as a ‘Mixed’ triglyceride. The more common forms, however, are the ‘Mixed’ triglycerides in which two or three kinds of fatty acids are present in the same molecule of triglyceride. An example of mixed triglyceride is shown in **Fig V b**. Here, the three hydroxyls of glycerol are combined with three different types of fatty acids e.g. palmitic, stearic and oleic. In the mixed triglycerides, one may have acids of different degree of saturation besides the varying chain length in the same molecule. In the present example, the molecule contains saturated fatty acids: Palmitic (C₁₆ chain length), Stearic (C₁₈ chain length) and unsaturated fatty acid such as Oleic acid (C₁₈ chain length) in the same molecule.

Triglycerides are a common form of fat found in both our food and our body. They make up a major portion of the fat in the food that a person eats. They are also found in blood plasma and along with cholesterol, they make up the plasma lipids. The liver also makes them from carbohydrates when calories are not needed right away. They are stored in the body’s fat tissues. Certain hormones control the release of triglycerides from the body’s fat tissue, as more energy is needed between meals.



a) Simple Triglyceride



b) Complex Triglyceride

Fig V: a) Structure of trilinolein (a simple triglyceride) having all the three hydroxyls of glycerol involved in esterification with three molecules of linoleic acid. The double bond at 9 and 12 position of the fatty acid indicates the diunsaturation in the triglyceride. b) Depiction of a mixed triglyceride where the three hydroxyls of glycerol are involved in forming the ester bond with three different fatty acids (for example palmitic acid, oleic acid and stearic acid)

We must remember that while triglycerides are present naturally in all foods that contain fat, whether derived from animals or plants. They are also added to some foods during food processing.

Functions of Triglycerides

Triglycerides circulate constantly in all the subtypes of lipoproteins carrier in the blood, carrying fat-soluble vitamins A, D, E and K to locations where they are needed; aiding in the synthesis of certain hormones and protecting cell membranes. In fact they play a key role in the metabolic process and the growth of humans etc.

The fat tissues in which triglycerides are stored also serve as fluid cushions around organs, such as the kidneys and the abdomen, protecting the organs from injury. They also act as thermal cushions and play a very important function in the well being of the body organs.

Triglycerides of naturally occurring oils and fats of vegetable origin are of “mixed” type and contain at least two different fatty acid groups. Since chemical, physical, and biological properties of fats and oils are determined mainly by the type of fatty acids and their distribution over the triglyceride molecules, one can easily determine the right type and source of the fats and oils for growth and better health of human beings.

Minor Components

In addition to the major component i.e. triglycerides, fats and oils also contain certain minor components which are mainly the glycerides other than the triglycerides, free fatty acids, phosphatides, sterols, fatty alcohols and fatty esters as described in the following sections.

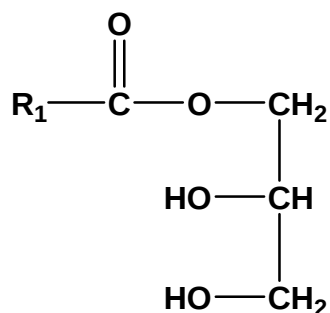
Monoglycerides and Diglycerides

As said earlier, monoglycerides (**Fig VI**) are those in which only one of the hydroxyl groups of glycerol is combined with one fatty acid whereas in diglycerides, there are two hydroxyl groups combined with two fatty acids. In other words, monoglycerides will have two and diglyceride will have one free hydroxyl groups respectively. They do not occur naturally in appreciable quantities except in fats that have undergone partial hydrolysis.

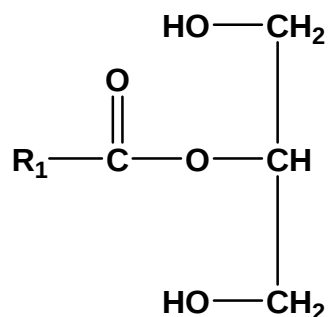
From the point of view of health, the fats and oils must be made free of both these glycerides. However, for certain industrial applications, one may find the mono and diglycerides quite useful as the free hydroxyl groups serve the purpose of the base for producing the derivatives with unique properties.

Free Fatty Acids

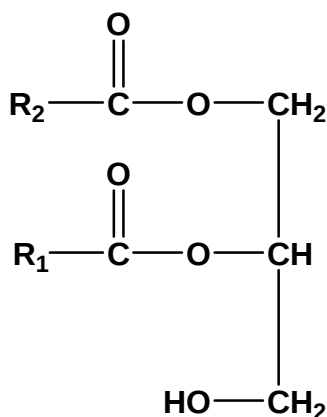
Free fatty acids are the ones remaining unattached or non-esterified fatty acids present in fats and oils. The fatty acids that form the triglycerides of naturally occurring oils and fats are



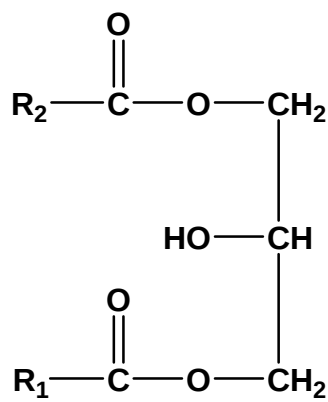
1-monoglyceride
or α -monoglyceride



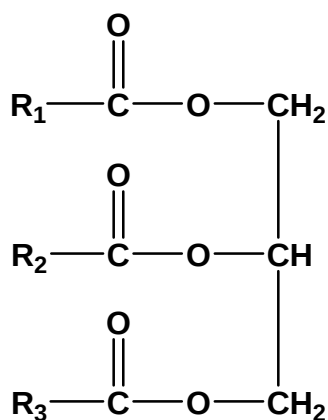
2-monoglyceride
or β -monoglyceride



1, 2-diglyceride



1, 3-diglyceride



Triglyceride

Fig VI: Structure of various glycerides: a) Monoglyceride where only one of the hydroxyl groups of glycerol is involved in the formation of an ester, the other two hydroxyls are free. b) Diglyceride where two of the hydroxyl groups of glycerol are involved in the formation of ester bonds whereas one hydroxyl is free and c) Triglyceride where all the three hydroxyls of glycerol are combined with three fatty acids to form three ester bonds.

predominantly even-numbered, straight chain, aliphatic monocarboxylic acids with chain lengths ranging from C_4 to C_{24} . Therefore, the free fatty acids from natural fats and oils would have the chain length of even numbered carbon. When oils are extracted from plant seeds, the crude oil contains significant amount of free fatty acid. At times, the free fatty acid content increases with time due to certain biochemical reactions. Most vegetable fats and oils consist predominantly of palmitic, oleic, and linoleic acids as free fatty acids. The fatty acids of land-animal fats mainly have a chain length of C_{16} or C_{18} .

Phosphatides.

Phosphatides consist of alcohols (usually glycerol), combined with fatty acids, phosphoric acid, and a nitrogen-containing compound. For all practical purposes, during the refining of the crude oil the phosphatides from the fat or oil are removed. Lecithin is the common phosphatides generally found in edible fats.

The fats and oils meant for human consumption must be free from fatty acids. As a quality criteria, the content of free fatty acids in edible fats and oils is kept at as minimum as possible. The fatty acids separated from the fats and oils have numerous industrial applications though.

Sterols

Sterols are a class of substances that contain a common steroid nucleus plus 8 to 10 carbon side chain and an alcohol group. Cholesterol (**Fig VII**) is the popularly known sterol present in the fats and oils derived from animals.

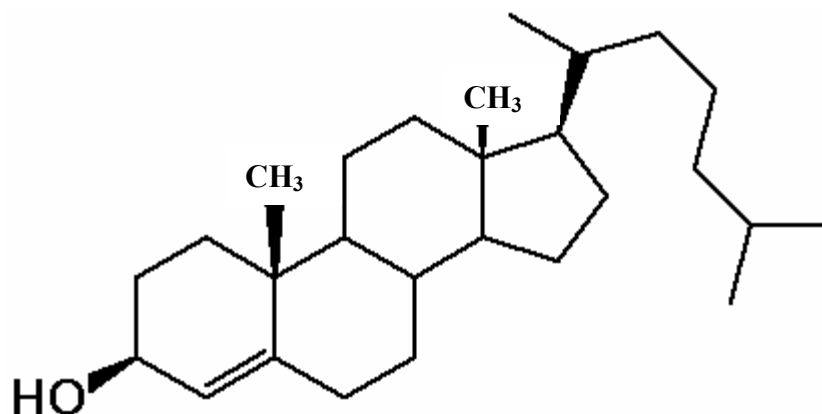


Fig VII: Structure of cholesterol, consisting of 4 rings making the molecule rigid. There are two angular methyl groups and a side chain containing 8 carbon atoms. The hydroxyl group, two angular methyl groups and side chain have β -configuration i.e. they are all above the plane. Cholesterol is synthesized in the cell membranes to impart rigidity.

The advantages and disadvantages of cholesterol are very well known even to the common public as the health experts always advice to restrict the consumption of fats that raise the level of bad (low density lipoprotein type) cholesterol in the body and to consume the fats that help

build the levels of good (high density lipoprotein type) cholesterol in the body. Because the vegetable oils do not contain the cholesterol, they are recommended over the animal fat for better health.

The vegetable oils consist of various types of sterols known commonly as phytosterols. Certain phytosterols are known for their anti-oxidative as well as anti-cancerous properties. That is why the vegetable oils are considered more advantageous than the animal fat. Efforts are also being made to separate out phytosterols from plants for their exploitation for medicinal uses.

Fatty alcohols

Alcohols with long carbon chain length called as fatty alcohols are also found present as the minor component of the fats and oils. In marine oils, the presence of fatty alcohols can be considerably high. Since fatty alcohols are non-edible, the fats and oils meant for edible purposes must be processed to remove the fatty alcohols.

Fatty alcohols find preference in numerous industrial applications. Various derivatives of fatty alcohols have been in use in different industries for quite some time; mainly for cosmetic and personal care industry. The bio-degradability of products based on fatty alcohols is the main reason for the rising preference and hence, demands for fatty alcohols replacing the base materials, which are biodegradable. Most of the vegetable oils are being used for manufacture of fatty alcohols.

Fatty esters

Some times, the fats and oils are also found to contain small quantity of fatty esters which are nothing but the condensation product of long chain fatty acids with long chain fatty alcohols. The waxes found present in certain vegetable oils are the example of fatty esters and like other unwanted impurities, they must be removed from edible fats and oils.

Physical Properties of Fats and Oils

♦ Melting and freezing points

The melting point and freezing point of fatty acids increases with increasing degree of saturation as well as with increasing the carbon chain length. As a result, the triglycerides based on fatty acids also follow a similar trend of melting point. From the melting behavior of the fats and oils, one can make an idea of their type as well as their source.

The melting point also depends upon the polymorphic form of the glycerides. The solidification point is generally lower than the melting point and the solidification behavior can also be used for characterization of fats and oils.

Since the naturally occurring fats and oils are a mixture of glycerides, they melt over a wide range of temperatures

♦ Thermal property

The specific heat of oils and fats increases with the increase in chain length and degree of saturation in the carbon chain of the fatty acid. It also increases with temperature. Oils and

fats are relatively poor thermal conductors. The smoke, flash and fire points are measures for their thermal stability when heated in air.

◆ Density

The density of fatty acids and hence, of the triglycerides decreases with increasing molecular mass and degree of saturation. Oxidation of the triglycerides generally leads to higher densities. A high free fatty acid content lowers the density of a crude oil and hence, density can be a criteria for quality of fats and oils.

◆ Viscosity

Oils tend to have a relatively higher viscosity because of intermolecular hydrophobic attraction between their fatty acid chains. Generally, viscosity tends to increase slightly with increasing carbon chain length. (**Table V**)

Table V: Viscosity of certain oils at different temperatures

Fats/Oils	Viscosity (mPa s ⁻¹) at Different Temperatures			
	20 ⁰ C	30 ⁰ C	40 ⁰ C	50 ⁰ C
Castor Oil	1000	454	232	128
Coconut Oil*	Solid	39	26	19
Lard*	Solid	Solid	35	25
Fish Oil	60	43	32	22
Soybean Oil.	65	45	33	25

* At lower temperatures, these oils exist in the form of solids and hence, their viscosity cannot be determined.

◆ Solubility and miscibility

Nearly all fats and oils are easily soluble in common organic solvents such as hydrocarbons, chlorinated hydrocarbons, ethers, and acetone. However, the solubility of fatty acid is greater than that of their corresponding triglycerides. The water solubility of fats is low and decreases with increase in carbon chain length and with the increase in the degree of saturation.

Factors affecting Characteristics of Fats and Oils

The characteristics of fats and oils depend upon the degree of saturation, the length of the carbon chain, isomeric form of the fatty acids, molecular configuration, and the type and extent of processing.

Degree of unsaturation of fatty acids

Degree of unsaturation of fatty acids forming the triglycerides plays an important role in deciding the characteristics of fats and oils. That is why, the fats and oils are also classified based on the number of double bonds present in the carbon chain of the fatty acid; mono-, di- and tri-unsaturated fats for the presence of one, two and three double bonds in the chain respectively. Fats with higher number of double bonds (unsaturation) are also called as poly unsaturated fats or PUFA fats. From the health point of view, the consumption of PUFA fats are recommended over the others, for example, MUFA fats (mono unsaturated fats). For the determination of degree of unsaturation, fats and oils are checked for their capacity to absorb the quantity of iodine per unit weight of the fats. The average iodine value (amount of iodine absorbed per unit weight) of natural fats and oils is 125-140.

Length of carbon chain in fatty acids.

The length of the carbon chain of the fatty acid has the bearing on most properties of fats and oils. For detailed characterization of fats and oils, it is important to study the distribution of carbon chain length of their fatty acids.

Isomeric forms of fatty acids.

Isomeric form of the fatty acid also affects the behavior of triglycerides. For example, oleic acid is liquid even at temperature lower than room temperature whereas its isomeric form elaidic acid is solid at temperatures much higher than room temperature.

Polymorphism

Solidified fats exhibit polymorphism, i.e., they exist in several different crystalline forms, depending on the manner in which molecules orient themselves in the solid state. The crystal form of fats can be transformed from lower to higher melting modifications. The rate of transformation and the extent to which it proceeds are governed by the molecular configuration and composition of the fat, crystallization conditions, and the temperature and duration of storage. The crystal form of the fat has a marked effect on various properties of fats.

Classification of Fats and Oils

On the basis of applications

There are various ways in which the fats and oils have been classified. The first criteria of classification has been the edible nature; edible fat and non-edible fat. . Fats in the diet are also referred to as visible or invisible; visible fats are those added to the diet in foods such as dressings, spreads, whereas invisible fats are those which occur naturally in foods such as meat and dairy products. While the classification of fats and oils is done based on their chemistry and

chemical composition, they are also known by several names, depending on their applications as drying oils, non-drying oils, semi-drying oils, etc.

Drying Oils: The fats having a large proportion of unsaturated acids have the tendency to get solidified on exposure to air. This property is also known as drying behavior. The oils, e.g., linseed, hemseed, and poppy seed oil, are the prominent drying oils and they are used in making paints and varnishes.

Non-drying Oils: Vegetable oils such as olive, rapeseed, and castor oil and animal oils such as lard oil and neat's foot oil do not possess this property of drying oils and are classified as non-drying .

Semi-drying oils: Those which can neither be termed as completely drying nor as completely non-drying are called as semi-drying oils. This type of classification, however, fails to take into account a number of important distinctions within the three broad classes.

There is another well recognized criteria for classification of fats and oils that deals with the degree of unsaturation of the fatty acid chain and fats are categorized as saturated, monounsaturated and polyunsaturated.

On the basis of saturation.

Saturated: A fat or oil is saturated when all available carbon bonds are occupied by hydrogen atom. They are highly stable, because all the carbon-atom linkages are filled or saturated with hydrogen and hence they do not normally go rancid, even when heated for cooking purposes. They are straight in form and hence, pack together easily, so that they form solid or semisolid fat at room temperature.

Butyric acid is an example of saturated fat found in the fat derived from milk.

Monounsaturated: Monounsaturated fatty acids have one double bond which means that such acids lack two hydrogen atoms in comparison to the saturated acid on each of the two carbon atoms of the fatty chain. The human body can make monounsaturated fatty acids (MUFA) from saturated fatty acids and use them in a number of ways. Such fats have a kink at the position of the double bond so that they do not pack together as easily as saturated fats and, therefore, tend to be liquid at room temperature.

Polyunsaturated: Such fats have two or more pairs of double bonds, as Trilinolein, therefore, lack four or more hydrogen atoms. Such fats have a kink at more positions than in MUFA so that they do not pack together. They are

liquid even when refrigerated. The unpaired electrons at the double bond make these oils highly reactive. They go rancid easily and should not be used for cooking. Polyunsaturated fatty acids are usually found in cis form.

All fats and oils, whether of vegetable or animal origin, are combinations of triglycerides based on saturated fatty acid, monounsaturated and polyunsaturated fatty acids. Vegetable oils from the

plants grown in hot climates are more of saturated type because the increased saturation helps maintain stiffness in plant leaves.

Besides the above mentioned ways of classifying fats and oils, there is yet another widely accepted basis of classification which primarily deals with the origin or source, carbon chain length and some unique feature of fats and oils.

According to recent survey, the Asia Pacific omega-3 PUFA market earned revenues of US\$279.6 mn in 2005, which is expected to reach US\$596.6mn in 2012. Omega-3 consumption in Asia is growing stronger. Omega-3 consumption advised for women is 430 mg and 610 mg for men to reduce the risk of chronic disease.

On the basis of carbon chain length

Short Chain fatty acids, generally, mean four to six carbon atoms and they are always saturated. These fatty acids have anti-microbial properties. They do not need to be acted upon by the bile salts but are directly absorbed for quick energy. For this reason they are less likely to cause weight gain and also contribute to the health of the immune system.

Butyric acid is an example of short chain fatty acid, which is found present for example, in the fats from milk. The fats and oils based on short chain fatty acids are known for their health benefits.

Medium Chain fatty acids have eight to twelve carbon atoms and are found mostly in butter fat and oils produced from plants grown in tropical regions. They too have antimicrobial properties and they; are absorbed directly for quick energy; and contribute to the health of the immune system.

Lauric acid, the main component of the triglyceride in coconut oil is an example of medium chain fatty acid with 12 carbon atoms. For several advantageous attributes of coconut oil, it is a preferred cooking medium in many parts of the world.

Long Chain fatty acids have 14 to 18 carbon atoms and can be different types such as saturated, monounsaturated or polyunsaturated. For e.g. Palmitic acid with 16 carbon atoms, stearic acid and oleic acid with 18 carbon atoms are the examples of long chain fats with different degrees of saturation.

From the standpoint of their Industrial production as well as their utilization, fats and oils are more rationally divided into the following groups.

Milk fat : The fats of this group are derived from the milk of domesticated land animals for example, cow, buffalo, goat, etc. Principal fatty acids in such fats are palmitic, stearic and oleic acids with minor presence of butyric acid.

Vegetable butter: They are obtained from the seeds of various tropical trees. They all contain mostly the saturated C₁₂ to C₁₈ acids. The representative fat of this group is cocoa butter.

Animal fat : This group consists of the body fats of mainly the domestic land animals (lard, tallow, etc.). These fats have high content of C₁₆ and C₁₈ fatty acids and a low degree of unsaturation. They contain considerable proportions of fully saturated triglycerides, which give them an extended plastic range. They are important edible fats but because they are derived from animals and parts of carcasses, in some cases, when they are considered as unfit for human consumption, they are used in the manufacture of industrial products such as soap, for which they are considered as an important ingredient.

Lauric acid group: The fats of this group are derived from the seeds of species of plants such as the coconut and babassu. They contain smaller amounts of saturated acids with carbon chain length of 8 to 14. The content of unsaturated acids is very less; they are the least unsaturated of all the industrially important fats.

Oleic- Linoleic acid group – The oils of this group are mainly of vegetable origin. They consist predominantly of unsaturated fatty acids which consist of oleic and linoleic acids. Most members of this group are liquids except at

quite low temperatures. They are not sufficiently unsaturated to have more than weakly drying properties, so they are not used to any great extent in paints and other protective coatings. They are excellent edible oils. These oils may also be considered as medium priced fats. More important members of the oleic-linoleic acid group include cottonseed, peanut, sesame, corn, palm, olive, sunflower and safflower.

Erucic acid group: The members of this group, of which only mustard, ravison, and rapeseed oil are commercially important, are distinguished by a high content(40-50%) of erucic acid. In comparison with other vegetable oils, these oils are normally cheap and thus ,become the preferred choice for common people as edible oils. There have been studies which show that the mustard oil is very good for health. The efforts to develop the mustard oil with minimum possible content of Erucic acid have always found support from all the stake holders.

Linolenic acid group: The oils of this group are distinguished by a significant amount of linolenic acid, in addition to oleic and linoleic acid. The most important members are derived from the seeds of annual plants. These oils have drying properties and hence, are used in paints and similar products. Because they tend to revert in flavor with slight oxidation, these oils are not considered as desirable for edible purposes for which only the oleic-linoleic acid oils are suitable. They are cheaper than oleic-linoleic acid oils. The most important members of this group are linseed, perilla and hempseed oil.

Conjugated acid group: The oils of this group are differentiated from others by the presence of fatty acids with conjugated double bond. The commercially important members are tung oil and oiticica oil which are derived from seeds of trees grown in a mild climate. Because of conjugated double bonds, which favor oxidation and polymerization, these oils dry more rapidly than ordinary drying oils. They are unsuitable for edible purposes but can be used for industrial applications such as paints, varnishes etc.

Marine oil group: These oils are distinguished by the diversity of their unsaturated fatty acids. They contain large proportions of unsaturated acids mainly of 16 to 18 carbon atoms but with significant amount of the carbon chain longer than 18 carbons. The group comprises of fish oils and marine mammal oils, such as whale oil. These are the cheapest of all fats and oils. They are used in edible fat products but can also be used, in soap, and in protective coatings. Fish liver oils constitute a special class of oils, which are highly valuable as a source of vitamins A and D, and are used for edible as well as industrial purposes.

Hydroxy acid group: The sole representative of this group used commercially is castor oil which is unique as it consists largely of triglycerides of ricinoleic-2-hydroxyoctadecenoic acid. It is not an edible oil but it is used in several industrial applications such as lubricants, surfactants, oil for sulphonation, a fluid for hydraulic systems etc.

From the above discussion, it may be noted that the same fat or oil may be classified under the different categories depending upon the basis of classification. Of course, there are only two basic categories of fats and oils; edible and non-edible.

Trans fat

Trans fat, as its name suggests consists of trans fatty acid which is an unsaturated fatty acid containing trans double bond between carbon atoms. The trans double bond of fatty acids are less kinked compared to those with cis double bond. A majority of trans fats are formed during the manufacture of processed foods. In unprocessed foods, most unsaturated bonds in fatty acids are in the cis configuration. Though some trans fats are found to be present naturally such as conjugated linoleic acid or CLA, these conjugated systems with trans linkages are not counted as trans fats for the purpose of nutritional regulations and labeling.

Partial hydrogenation increases the shelf life and flavor stability of foods containing these fats. Partial hydrogenation also raises the melting point, producing a semi-solid material, which is much more desirable for use in baking than liquid oils. Partially hydrogenated vegetable oils are much less expensive than the fats originally favored by bakers, such as lard or butter.

Saturated and trans fats can be found together in some foods such as vegetable, shortenings, some margarines (specially margarines that are harder), crackers, candies, cookies, snack foods, fried foods, baked foods and other processed foods made with partially hydrogenated vegetable oils. High amounts of saturated fats are found present in animal products, such as beef and pork, chicken skin, butter, whole milk and cheese. Foods high in cholesterol include egg yolks and dairy fats.

Trans fat is an artery clogging fat that is formed when vegetable oils are hardened for example into margarine or shortening. It is found in many foods including fried foods.

Trans fat is known to increase levels of low density lipoprotein (LDL) or bad cholesterol, while lowering levels of high density lipoproteins (HDL) or good cholesterol in blood. It causes clogging of arteries and it is believed to be responsible for type-2 diabetes and other serious health problems. It has been found to increase the risk of heart diseases because the trans fat is not recognized by the body's metabolism, causing it to deposit in the blood vessels.

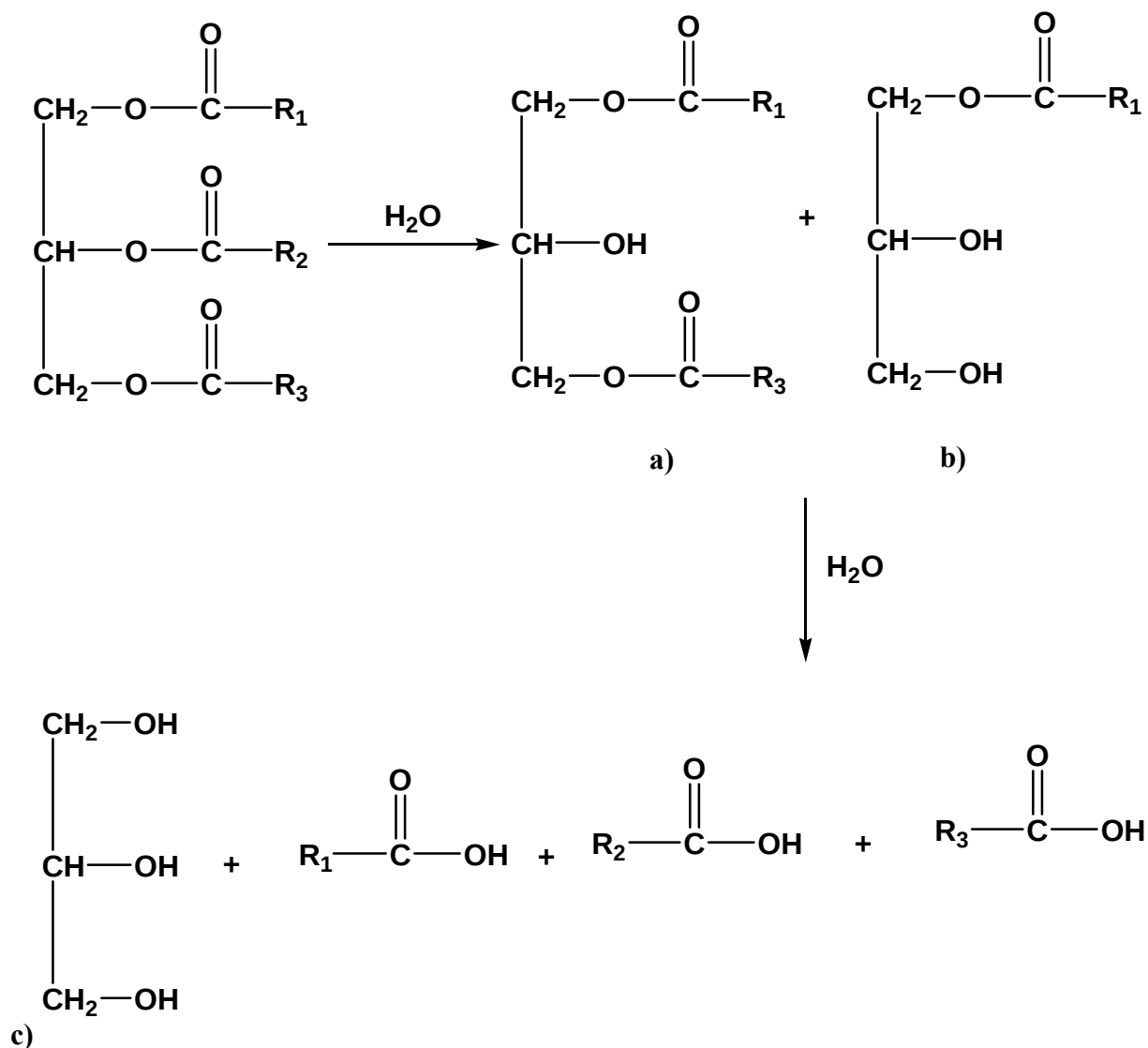


Fig VIII: All the three ester groups have the equal possibility of hydrolysis. However, depending upon the pH, catalyst and enzymes, one or more of the ester groups get hydrolyzed. For example, a) in the case of only one ester getting hydrolyzed, it results in the formation of a diglyceride; b) in the case of two ester groups getting hydrolyzed, the end result is a monoglyceride and c) in the case of three ester groups getting hydrolyzed, formation of glycerol takes place.

Trans fats should not be completely eliminated from the diet because of the fact that it may require extraordinary dietary changes that eliminate trans fats and cause inadequate intake of some nutrients which could create health risks..

Trans fats are always compared with saturated fats in terms of their affect on blood cholesterol levels. Trans fats raise LDL blood cholesterol as much as saturated fat does. However, trans fats have lesser effect on total blood cholesterol than saturated fats.

Chemistry of trans fatty acids.

Trans fatty acids are made when manufacturers add hydrogen to vegetable oil, in the presence of small amounts of catalyst such as nickel, palladium, platinum or cobalt in a process called partial hydrogenation. If the hydrogenation process was allowed to go to completion, there would be no trans fatty acids. The resulting material would be too solid for practical use. However, partial hydrogenation reconfigures most of the double bonds that do not become chemically saturated, so that the hydrogen atoms end up on different sides of the chain. This type of configuration is called “trans”.

Increasing the pressure at which oil is hydrogenated reduces trans fat formation. Blended with pure soybean oil, the high pressure processed oil produce margarine containing 5-6 percent of trans fat which could qualify for a label of zero grams of trans fat.

Chemical Properties of Fats and Oils

Hydrolysis of fats and oils:

Like all esters, glycerides can also be easily hydrolyzed yielding mono and diglycerides (on partial hydrolysis) and glycerol and fatty acid (on complete hydrolysis) (**Fig VIII**). With sodium hydroxide, glycerol and sodium salt of fatty acid (soaps) are formed. The hydrolysis can also become possible through enzymes. In the digestive systems of animals and humans, fats are hydrolyzed by the enzyme (lipases).

Oxidation of fats and oils:

Autoxidation: Oxidation at room temperature is referred to as autoxidation and this is also referred to as rancidity of fats and oils. This is a slow process, which occurs only to a limited degree if fats and oils are left for storage. In this process, oxygen reacts with unsaturated fatty acid chains. Initially, peroxides are formed which in turn breakdown the chain of fatty acids into hydrocarbons, ketones, aldehydes, and small amounts of epoxides and alcohols. The result is objectionable flavor and odor. The fats and oils after autoxidation, therefore, become unsuitable for human consumption if the extent of oxidation is very high.

Oxidation at higher temperature: Differences in the stability of fats and oils often become more apparent when the fats are used for frying and baking. The more unsaturated the fat or oil is the greater will be its susceptibility to oxidative rancidity. It is precisely due to this reason that the re-use of the frying oils is not good for health, especially after the oil has been in the frying pan for a long time. Generally, the peroxide content is the criteria for checking the autoxidation or rancidity of fats and oils.

Polymerization of fats and oils:

Fats, particularly those with, high content of polyunsaturated fatty acids tend to form larger molecules (known as polymers) when heated under extreme conditions of temperature and for an extended time period. Under normal processing and cooking conditions, polymers are formed in

insignificant quantities. Polymerization takes place through the double bonds between the carbon atoms or by oxygen bridges between molecules. When polymerization takes place there is a marked increase in viscosity of the oils.

In any case, polymer, present in the fat or oil are absorbed poorly by the intestinal tract and removed as such from the body.

Hydrogenation of fats and oils:

The fats which are liquid at room temperature preponderate in nature over those which are solid. To meet the demand of solid fats, therefore, one has to make an effort. Taking advantage of the experience where the ethylenic organic compounds when exposed in the vapor state to hydrogen in the presence of nickel formed the corresponding saturated derivatives, the unsaturation in fats were also subjected to the hydrogenation. Liquid fats and fatty acids having unsaturated bonds could also be hydrogenated in a similar way using nickel, palladium, copper, or platinum and the liquid oil was converted into solid form.

Hydrogenation is the single largest chemical reaction in the fatty oil processing industry. Since each double bond may be either isomerized or hydrogenated at different rates depending on its position or environment in the molecule, the overall reaction becomes quite complex. The partial hydrogenation of soybean oil would result in at least 4000 different triglycerides.

Primarily, hydrogenation is a means of converting liquid oils to semisolid fats suitable for shortening or margarine manufacture. It also accomplishes various other desirable purposes, including enhancement of the stability and the improvement of the color of the fat. However, the hydrogenation of fats and oils is also associated with some disadvantages. If fats are subjected to the action of hydrogen in the presence of an appropriate catalyst at relatively higher temperature and at a very high pressure during the hydrogenation, fatty alcohols are also formed. Higher fatty alcohols are in demand nowadays because their sulphates and phosphates possess very valuable properties as detergents, emulsifiers, wetting out agents, etc.

Since the ethylenic linkages in a highly unsaturated fatty acid occurs at different points in the chain of carbon atoms, there is a formation of iso- acids in the glycerides of partially hydrogenated oils. The most objectionable properties of these acids are connected with their behavior as soaps. For example, whereas the oleic acid is an almost ideal constituent of soap by virtue of the relative solubility and low surface tension of solutions of its sodium salts, the lower solubility and much higher surface tension of the sodium salt of the iso-oleic acid does not allow it to exhibit the similar behavior. The iso-acid based soaps are inferior in lathering and detergent power to soap made from natural fatty acids of same degree of unsaturation and hydrogenation causes the formation of iso-oleic acid..

As regards color, hydrogenated fats are usually superior to much natural fat and objections were raised to a specific color associated with soaps or fats containing hydrogenated material.

Production of Fats and Oils in Plants and Animals

The primary seat of the production of fats is in the vegetable kingdom; here, the carbohydrate material produced in the plant from carbonic acid and water by the agency of enzymes and sunlight are converted into fatty compounds, mainly during the period of ripening of fruits and seeds. The fats are deposited, in general, either in the tissues, which surround the embryo or germ of the seed, or in the external fleshy covering, in which the seed-capsule is enclosed.

In plants and animals, the fats are normally a form of reserve or storage of organic matter, which, at a later stage in the life cycle may be required for purpose of nutrition.

In animals, fats are produced by assimilation of either the fats consumed as food or of the fats produced in the body through vital synthesis (enzymatically driven) involving various types of organic matter, such as carbohydrates, proteins, etc.

The formation of fats in the animal body is believed to take place mainly in the liver and related organs. The primary organic materials are converted into fatty acids and their esters, whilst fat already present as such may be hydrolyzed and re-built into esters with or without alteration in the constitution of the fatty acids originally ingested. The synthesized fat passes via the blood stream into various parts of the body-notably the flesh tissues near the skin in which it is stored.

In vegetable oils and fats, unsaturated fatty acids are linked to the 2- position of the glycerol group, whereas in animal fats they appear in 1 – and 3- positions

Metabolism of Fats and Oils

As stated above, the primary role of fats and oils in the diet is to be a source of energy. Before the fat can be utilized for the desired purpose it must first be absorbed from the intestine. The fat must be hydrolyzed to free fatty acids, for the absorption to take place. While the hydrolysis occurs, there is also some direct absorption of triglycerides, which is influenced by the solubilising effect of the bile. When absorption of fatty acids takes place, esterification takes place in the intestinal wall. That is how the fat gets stored in the body.

When the body needs to use its fat supplies as a source of energy, the fat is broken down to simpler units by a chain of enzymatic reactions. The first step in the process is through the action of lipase which hydrolyses the glycerides, liberating fatty acids and glycerol. The glycerol is converted to glycerol phosphate which is then oxidized to dihydroxyacetone phosphate and thus enters the same sequence of reactions by which glucose is oxidized to carbon dioxide and water. These oxidation processes generate energy.

Isomerism in Fats and Oils

Isomers are two or more forms of a substance composed of the same elements combined in the same proportions but differing in molecular structure. In other words, a given substance having a fixed composition and functionality may exist in different forms, which are called as its isomers.

The two important types of isomerism among fats and oils ascribed to the isomeric forms of fatty acids are

1. *Geometric Isomerism*: Unsaturated fatty acids can exist either in cis or in trans form depending on the configuration of the hydrogen atoms attached to the carbon atoms joined by the double bonds. If the hydrogen atoms are on the same side of the carbon chain, the arrangement is known as cis. If the hydrogen atoms are on the opposite sides of the carbon chain, the arrangement is called trans. Conversion of cis to trans form increases the melting point. Elaidic and oleic acids are the example of geometric isomers; in the former, the double bond is in the trans configuration and in the latter, it is in cis configuration. Cis isomers are those occurring in natural fats and oils. Trans isomers occur naturally in ruminant animals such as cows, sheep, and goats and also result from the partial hydrogenation of fats and oils.
2. *Positional Isomerism*: In this case, the location of the double bond differs among the isomers. The position of the double bond affects the melting point of the fatty acid to a limited extent. Shifts in the location of the double bond in the fatty chain as well as cis-trans isomerization may also occur during hydrogenation. Petroselinic acid is cis-6-octadecenoic acid and it is a positional isomer of (oleic acid), cis-9-octadecenoic acid

Analysis of Fats and Oils

As stated above, the fats and oils consist of a major component (triglyceride) and various types of minor components. For any application, the processing of the crude fats and oils is essential. For using fats and oils as food, it is not only important to process them but also to check their quality by analyzing them thoroughly. Analysis and characterization of fats and oils is done by using simple methods as well as sophisticated techniques such as HPLC, GLC, TLC etc. as depicted in. Standard methods of analysis of fats and oils to be used as food are listed out in the. Codex Standard-19 Codex Standard-210. (Annexure 1 and 2).

Saponification value

It is also a measure of the mean molecular weight of the fatty acid present in the fat. The process of saponification is the hydrolysis of triglycerides into glycerol and the potassium salt of the fatty acid, using an alcoholic solution of potassium hydroxide. The amount of alkali required to combine with the fatty acids liberated by the hydrolysis of the fat on saponification gives the equivalent weight as well as molecular weight of the fatty acids. The saponification value is expressed in milligrams of the potassium hydroxide required to saponify one gram of fat. For all the fats and oils, the limits for the saponification value are fixed and based on this one can easily identify the fat. For given fat, this can be a useful tool to check quality of fats.

Iodine value

Iodine number is the number of grams of iodine absorbed by 100g of the sample. It is a measure of the degree of unsaturation in the fatty acid chain. The test measures the amount of iodine which can be absorbed by the fats. As the addition of iodine takes place at the double bond,

measurement of the quantity of iodine absorbed gives the idea about the number of the double bonds present.

Unsaponifiable matter

Since the fats are triglycerides, they would saponify in the presence of alkali. But the fats and oils contain certain fraction which cannot be saponified; called as unsaponifiable matter. During this process, all the triglycerides are broken down to form glycerol and potassium salts of the fatty acids. Both of these products are water-soluble. But there is a third component which is water insoluble. The water insoluble component may consist of hydrocarbons, sterols and fatty alcohols, which are all unsaponifiable. The amount of unsaponifiable matter found in eatables, fats, is supposed to be absent; high unsaponifiable may indicate contamination or adulteration.

Refractive index

It is a physical attribute of triglycerides, measured by the angle through which a beam of light is bent when passing through a thin film of melted fat. The index of each type of fat falls within a narrow range and it can be used as a characteristic of the fat in checking purity or searching for components of a mixture. It is temperature dependent and is usually measured at 40°C, a temperature at which most fats are liquid. A correction factor can be used if it is not possible to work at a selected temperature for which reference data are available.

Melting and solidification temperature

As fats are a mixture of a number of different triglycerides, the melting point becomes difficult to measure. It is therefore necessary to impose an empirical test procedure, which will allow reproducible results to be achieved, but which cannot be used to identify components of a mixture. The two common measurements generally adopted are “slip point” and “titre”.

The slip point measures the temperature at which a carefully prepared sample will move or slip in a capillary tube when heated slowly in a water bath.

The titre is not really a characteristic of fat itself, but is the solidifying point of the fatty acids prepared from the fat. It has some significance in soap-making technology but is of little importance in the examination of eatable fats.

The sample is melted and filtered to remove impurities. The molten product is taken in a melting point tube, placed in a beaker, which is then placed in a refrigerator for 16 hrs. The sample is removed and heated in a water bath till the liquid becomes completely clear. The temperature at which the sample becomes completely clear is noted as the melting point or titre value of the fat.

Impurities

Determination of impurities present is not as simple as it may appear. In principal, it is the measurement of solid matter, which is not soluble in fat. This is complicated because some insoluble materials may get dispersed in the fat. Such materials precipitate out when a suitable solvent is added during the estimation of impurities.

Acid value

It is a measure of the amount of free fatty acid present in fat. Some of the deterioration that takes place during storage of either the raw material from which the fat is obtained or in the fat itself after isolation results in hydrolysis of triglycerides to yield free fatty acids. As these free fatty acids must be removed in the preparation of eatable fats, the commercial yield will be reduced by an amount proportional to (but greater than) the amount of free fatty acid present.

Peroxide value

It is usually used as an indicator of deterioration (rancidity) of fats. As oxidation takes place, the double bonds in the unsaturated fatty acids are attacked resulting in peroxides. These break down to produce secondary oxidation products, which indicate a condition known as rancidity. The peroxide value can therefore be used to estimate oxidation but as the compound formed is unstable and oxidation proceeds further, it is not a complete measure of oxidation and if taken in isolation may give rise to misleading conclusions. In any case, peroxide value is one parameter based on which one can reject or approve the fats and oils for human consumption.

Adulterants in Fats and Oils

The cases of adulterants in oils and fats are generally related to the mixing of cheaper material into the costlier one. Distinction between milk fat (desi ghee) and hydrogenated vegetable oil (vanaspati ghee) is a very common case of adulteration in fats in India. Vanaspati ghee contains 5% sesame oil, which is added during its manufacture. Pure desi ghee does not contain sesame oil and thus the presence of sesame oil is detected by Baudouin test to check adulteration.

Shake 2cm³ of melted ghee with equal amount of HCl acid and 1 cm³ of 1% w/v sucrose and allow it to stand for 5 minutes. Appearance of rose red color indicates the presence of sesame oil.

Baudouin test is also used to detect the presence of sesame oil in butter. Sometimes, butter is colored with certain aniline-azo dyes to mask the adulteration, gives a pink to violet coloration with hydrochloric acid. In such a case, heat the mixture of butter and hydrochloric acid until it becomes colorless otherwise the dye gives pink or violet color with the acid and then add the solution of furfural. Rose red color is formed in the presence of sesame oil.

Halphen test for cottonseed oil. Dissolve 5cm³ of butter in 5cm³ of amyl alcohol and add 1 cm³ of a solution of sulfur in CS₂. Heat the mixture in a boiling water bath for 15-20 minutes. A red coloration will confirm the presence of cottonseed oil in butter.

Aniline azo dyes. Take two clean test tubes. Place about 2 g of the melted fat in each of the test tube and add light petroleum. To one test tube add 1cm³ of dil. HCl and to other 1cm³ of 10% potassium hydroxide solution. Shake the test tubes thoroughly. A pink color in the lower layer in the HCl tube and no color in the potassium hydroxide tube is seen if an azo-dye is present.

Paraffin wax in vegetable ghee. Place a small amount of vegetable ghee in a test tube. Add 1cm³ of acetic anhydride and heat gently. An oil drop floating in unused acetic anhydride indicates paraffin wax in the vegetable ghee.

Argemone oil in eatable oils. Place one cm³ edible oil in a test tube. Add few drops of conc. HNO₃ and shake well. A red color in the acid layer indicates the presence of argemone oil.

Tests for preservatives in butter.

There are limits specified for the preservatives used to increase the shelf life of butter. The commonly used preservatives which, must not be presented in butter are tested as per the methods described below.

Formaldehyde Hahner's test. To one cm³ of melted butter or butter milk add a trace of ferric chloride and then conc. H₂SO₄. A violet ring is formed due to the presence of formaldehyde.

Boric acid. To 1 cm³ of melted fat add one drop of dil. HCl and 10 drops of turmeric solution. Evaporate to dryness. A purple red color changes to indigo by the addition of a drop of concentrated solution of ammonia.

Even though the above mentioned tests can serve as an easy tool to detect adulteration, it is suggested that for quantitative estimation as well as for confirmatory results, one will have to use the sophisticated instrumental techniques for adulteration as well as characterization.

Nutritional Aspects of Fats and Oils

Fats are the most important constituents of our diet contributing about 38 J/g of energy as compared to 17 J/g provided by carbohydrates and proteins. The nutritive value of fats is dependent upon the number of carbon and hydrogen atoms, and on the ability to be absorbed in the body. If the fats are liquid at body temperature they are much more readily digested and absorbed than the ones which are solid. The ease of emulsification of fat is the important factor for its absorption. The nutritional value of fat also depends upon the presence of certain fatty acids, which were at first called vitamin F, and later as essential fatty acids.

Triglycerides for Indication of Health

The normal range of triglycerides in the blood depends upon the age and gender of the patients. Women naturally have high levels of triglycerides than men. Pregnancy also increases triglyceride level in women. As people age and gain weight, triglyceride levels generally increase. For adults, a normal level is considered to be less than 200 mg/dl. Levels from 200-400 mg/dl are considered borderline high. Triglyceride level ranging from 400-1000 mg/dl are considered high and levels greater than 1000 mg/dl are considered very high.

Extremely low triglycerides levels (less than 10 mg/dl) indicate malnutrition, malabsorption, a diet too low in fats, or an overactive thyroid problem.

A triglyceride count in the 250-750 range indicates a high risk of heart disease. Because of the close relationship between triglycerides and cholesterol, the higher risk is from elevated blood/serum cholesterol levels. AIDS patients usually have low cholesterol levels, so a sudden increase may be related to triglyceride problem.

High blood levels of triglycerides result in the following cases :-

- 1) Carbohydrate sensitive people whose bodies have trouble breaking down fats or carbohydrates.
- 2) Obesity
- 3) Diabetes
- 4) Heavy alcohol drinkers

Many people with high triglycerides levels have low levels of high density lipoproteins, called HDL or good cholesterol as it acts like a removal system for cholesterol. Low level of HDL is another risk factor for heart disease.

Triglyceride levels can be affected by any or all of the following factors:

- 1) Alcohol intake
- 2) Medicine
- 3) Hormones
- 4) Diet
- 5) Menstrual cycle
- 6) Time of day
- 7) Recent exercise

While there are several reasons for high triglyceride levels in the blood of humans, it is not in the scope of this chapter to elaborate on all those and their effects on the health of humans. However, the subject of interest is whether the high level of triglycerides in food products has any direct relationship with the high triglyceride levels in blood. The diet certainly plays an important role in keeping the triglyceride levels in blood under control. What should be eaten and what should not be eaten again depends on the metabolic system, exercise and the general health condition of the consumer. However, the following basic facts must be kept as the ground rule for controlling the glyceride levels in blood:

1. Use of fats and oils of different types, in varying proportions and in a controlled way.
2. Use of more of unsaturated fats than the saturated fats.
3. Avoid the trans fats as much as possible.

Cholesterol

Fat travels in the blood in two forms. One is **Cholesterol**, which is a structural fat. It glues cells together, insulates nerves and provides raw material for making hormones. Fat also travels in small energy packets, called triglycerides, which are further, coated with cholesterol.

Cholesterol is a waxy substance that occurs naturally in the tissues of all animals. The human body needs cholesterol to function properly, such as producing vitamin D, bile acids (to digest fat) and many hormones. Given the capability of all tissues to synthesize sufficient amounts of cholesterol for their needs, there is no evidence for a biological requirement for dietary cholesterol.

Importance of Saturated Fats

One of the most important organs of our body is kidney. Both cholesterol and saturated fats are important in maintaining the function of kidney. The kidneys need stable fats both for their cushioning and also as their source of energy. The kidney fat normally has a higher concentration of the important saturated fatty acids than are found in any other fat depots. These saturated fats are based on myristic acid, palmitic acid, and stearic acid. When we consume various polyunsaturated fats in large amounts, they are incorporated in the kidney tissues, usually at the expense of oleic acid, because the normal high level of saturated fat in the kidney fat does not change.

Adding the saturated fats, especially like coconut oil, improves the body's use of omega -3 fatty acids. This is because it supplies myristic acid; the 14 carbon saturated fatty acid. Myristic acid is involved in the signaling from cell membrane receptors through G proteins and their attachment to membranes.

When it comes to lungs the very important class of phospholipids is lung surfactant, which is a special phospholipid with 100% saturated fatty acids. On consumption of a lot of partially hydrogenated fats and oils, the trans fat are put into the phospholipids whereas the body normally wants to have saturated fats and this prevents the lungs from working properly. Having enough saturated fats prevents stroke, and protects our kidney from disease. We need certain kinds of saturated fatty acids which are found only in the natural fats such as animal fats and coconut and palm kernel oils.

The saturated fatty acids that play an important role in the body processes are palmitic acid, myristic acid, and the lauric acid. When these important saturated fatty acids are not available, certain growth factors in the cells and organs will not be properly aligned. This is because; the various receptors such as G-protein receptors need to be coupled with lipids in order to provide localization of function. The messages that are sent from the outside of the cell to the inner part of the cell control many functions including those activated by adrenaline in the primitive mammalian fight reactions. When the adrenal gland produces adrenaline and the adrenaline receptor communicates with the G-protein and its signal cascade, the parts beat faster, the blood flow to guts decreases while the blood flow to muscle increases and the production of glucose is stimulated.

A loss of saturated fatty acids in the lymphocytes is responsible for age-related declines in white blood cell function. They could correct cellular deficiencies in palmitic acid and myristic acid by adding these saturated fatty acids. Myristic acid is a very important acid, which the body uses to stabilize many different proteins, including proteins used in the immune system and to fight tumors.

The diet should contain at least 25% of fats as saturated fat. Food with best proportion of saturated fat was lard as per the nutrition experts. Those who are vegetarians should eat a mixture of different fats and oils including the milk fat to ensure the desired quantity of different fats and fatty acids in the body.

Estimation of Fat Content

One useful measure of fat is the percentage of calories as fats in a diet. To compute this percentage, one needs to know both- the total calories and the grams of fat:

$$\% \text{ CFF} = \frac{\text{grams of fats} \times 9}{\text{total calories}} \times 100$$

%CFF= Calories from fat

Fat content of oils

All oils are 100% fats. These include olive oil, sesame oil, chilli oil, fish oil, avocado oil, walnut oil, etc. Oils and fats have been studied thoroughly and they are found to have 9 kilocalories per gram.

Dietary need for fat

It is absolutely true that we need fat in our diet to function properly. It would be unhealthy to eliminate all fat. All foods have fats but with varying content and of different types. A diet consisting only of beans, fruits, vegetable, and grains will naturally obtain about 6-10%CFF. Foods labeled “fat free” can contain anywhere up to 0.5g of fats per serving and this shows that all foods contain some fat: even the skimmed milk!

How much fat do we need?

A diet with at least 10g of fats per day will result in normal vitamin absorption. However, it depends on the status of the health of the consumer.

Disadvantages of unsaturated fat

Unsaturated fats can exhibit different 3-D structures, notably a structural difference called cis-trans isomerism. Natural fatty acids have a cis form but on hydrogenation their form changes from cis to trans, which are known for their disadvantages as described earlier.

Importance of Fats and Oils

Fats and oils are recognized as essential nutrients in both human and animal diets due to the following reasons:

1. They provide the most concentrated source of energy than any foodstuff.
2. They supply essential fatty acids (which are precursors for important hormones, the prostoglandins),
3. They contribute greatly to the feeling of satiety after eating,
4. They are carriers for fat-soluble vitamins, and serve to make food more palatable.
5. Fats play a vital role in maintaining healthy skin and hair,
6. Fats insulate body organs against shock,
7. Fats help in maintaining body temperature and healthy cell function.
8. Fats also serve as the stock of energy stored in the body.

Fats are broken down in the body to release glycerol and free fatty acids. The glycerol can be converted to glucose by the liver and is thus used as a source of energy. The fatty acids are a good source of energy for many tissues, especially the heart, kidney and skeletal muscle.

Industrial Applications of Fats and Oils

The potential for commercial exploitation of fats and oils for industrial applications has also been rated very high not less than their use for food.

1. **Paints:** As drying oils as well as the specialty chemicals.
2. **Cosmetics:** As basic raw material for nail polish, lipstick, creams and lotions.
3. **Polymers:** Epoxides of oils are used as plasticizers applications in the polymer industry.
4. **Energy:** As a base material for biodiesel
5. **Lubricants:** A range of lubricants (biodegradable) based on oils and their derivatives.
6. **Surfactants** A range of **surfactants** is made from derivatives of fats and oils.

Deterioration Factors of Fats and Oils

Several forms of deterioration occur in fats and oils.

- ◆ **Flavor reversion-** flavor and odor may develop after deodorization of a product to complete blandness. The flavor is generally characteristic of the oil source and is therefore acceptable. Reversion is apparently caused by changes in substances, which have been oxidized by deodorization. Ordinary chemical tests do not indicate any change in the oil; it is strictly an organoleptic observation.
- ◆ **Oxidative rancidity-** A serious flavor defect and it is objectionable. Peroxides are formed at the double bond of the fatty acids, which then decompose to form aldehydes, which have a pungent, disagreeable flavor and odor. It is chemically tested by peroxide value and one of the many methods of aldehyde detection. Retardation of oxidation is brought about by using opaque, airtight containers, or nitrogen blanketing if clear bottles are used.

- ◆ Hydrolytic rancidity- This type of rancidity results from the liberation of free fatty acids by the reaction of fats and oils with water. While most fats show no detectable off flavors, coconut and other lauric acid oils develop a soapy flavor, and butter develops the strong characteristic odor of butyric acid. In some foods, active lipase catalyses the hydrolysis of fats and oils.
- ◆ Deep Frying- Fats and oils used in deep fat frying can break down under adverse conditions. This results in the low fat turnover rate. Further deterioration results in the oil becoming very dark in color, foul smell, viscous and foaming during frying. The oil gets oxidized and then polymerized.

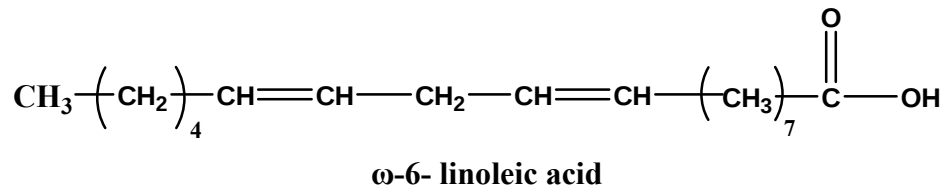
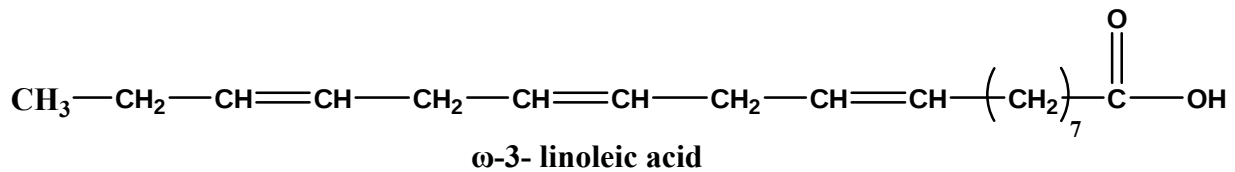


Fig IX: Structure of essential fatty acids; a) ω -3 linoleic acid b) ω -6 linoleic acid

- ◆ Crystal transformation- Crystal structure transformation of packaged shortening results in formation of a grainy, soft product, which, on loss of incorporated gas may take the appearance of petroleum jelly. It is caused by improper hydrogenation, poor formulation, unstable hard fat used for texturing, or the wrong chilling conditions.

Essential Fatty Acids

Certain fats are called essential because the body cannot synthesize them and they must be provided from outside the body through food or supplements. Such fats are required for the normal cell, tissue, gland, and organ function, for health, and for life. Deficiency of such fats results in the progressive deterioration of the body and ultimately leads to death.

There are two essential fats (**Fig IX**)

- Omega 3- alpha linolenic acid
- Omega 6- linoleic acid

Functions of Essential Fatty Acids

Essential fatty acids have many functions in the body, as listed below:

- energy production,
- brain function,
- healthy skin, hair and nails,
- lowering the risk of cancer,
- decrease in cardiovascular disease risk
- reduced diabetes,
- weight management,
- improved gut integrity,
- reduced symptoms of allergy, etc.

Processing of Fatty Acids

Food fats and oils are derived from oil seed and animal sources. Vegetable fats are obtained by the extraction of the oil from the oilseeds source. Instead of mechanically extracting the oils from the seeds, it is always advised to opt for solvent extraction as the latter method gives a better oil yield.

The fats and oils obtained directly from extractions of the oilseeds are termed “crude” fats and oils. They contain small amount of naturally occurring non glyceride materials, some of them may be undesirable and hence, the oils have to be purified by removing such impurities.

Degumming

Crude oils having high level of phosphatides may be degummed prior to refining to retain the majority of phospholipid compounds. The process generally involves treating the crude oils with limited amount of water to hydrate the phosphatides and make them separable by centrifugation. Soybean oil is the most common oil to be degummed.

Refining

The process of refining is performed on vegetable oil to reduce the free fatty acid content and to remove other impurities such as phosphatides, proteinaceous, and mucilaginous substances. The most important and wide spread method of refining is the treatment of the oil or fat with an alkali solution. This results in the reduction of free fatty acid through their conversion into water-soluble soaps. Most phosphatides and mucilaginous substances are soluble in the oil only in an anhydrous form and upon hydration with the caustic or other refining solution are readily separated. Oil low in phosphatides content may be physically refined to remove free fatty acid. After alkali refining, the fat or oil is water washed to remove residual soap.

Bleaching

It is a process of removing color-producing substances and for further purifying the oil or fat. It is done by adsorption of the color producing substances on an adsorbent material. Acid activated bleaching earth or clay, also called Bentonite, is the adsorbent material that has been used most extensively. This substance consists of hydrated aluminum silicate. Anhydrous silica gel and activated carbon also are used as bleaching adsorbent materials.

Deodorization

It is a vacuum steam distillation process for the purpose of removing trace constituents that give rise to undesirable flavors, colors and odors in fats and oils. Normally this process is accomplished after refining and bleaching.

The deodorization of fats and oils is simply a removal of volatile components from the fat or oil using steam. It is feasible because of the great differences in volatility between the substances that give flavors, colors and odor to the fats and the triglycerides. It is carried out under vacuum to facilitate the removal of volatile substances to avoid hydrolysis of the fat and to make the most efficient use of the steam.

Deodorization does not have any significant effect upon the fatty acid composition of most oil and fats. In the case of vegetable oil sufficient tocopherols remain in the finished oils after deodorization to provide stability.

Fractionation

It is the removal of solids by controlled crystallization and separation techniques involving the use of solvent or dry processing. Dry fractionation encompasses both winterization and pressing techniques and is the most widely practiced form of fractionation. It relies upon the differences in melting point and triglyceride solubility for separation of the oil fractions.

Biosynthesis of Fatty Acids

Synthesis of fatty acid takes place in cytosol of the cell. Fatty acid synthesis starts from acetyl CoA. AcetylCoA has 2 carbon atoms. It is carboxylated by acetyl CoA carboxylase, which has a biotin prosthetic group.

Reduction, dehydration and a second reduction convert $C_6 \beta$ keto acyl ACP into C_6 acyl ACP. C_6 acyl ACP undergoes a third cycle of elongation by condensation with monoacyl ACP followed by reduction, dehydration and a second reduction. Thus, every elongation cycle adds 2 carbons to the chain. When the chain has 16 carbon atoms, it is a good substrate for thioesterase which hydrolyses the C_{16} acyl ACP to give palmitate and ACP. Thus further elongation stops. Fatty acids longer than C_{16} are formed by enzymes in the endoplasmic reticulum membrane.

The synthesis of fatty acids in plants and animals generally starts with “activated” acetic acid i.e. with acetyl coenzyme A, which is derived from carbohydrates via pyruvic acid (glycolysis). Animals also synthesize acetyl coenzyme A from amino acids.

Biodegradation of Fatty Acids

Fatty acids are acylated by coenzyme CoASH; the acyl CoA formed as a result is a active form. The double bond generated at position ' α ' to the $\text{O}=\text{CSCoA}$ group is hydrated by enzyme enoylCoA hydratase in a stereospecific manner. Hydration is followed by a second oxidation reaction where the β carbon is oxidized to the keto group. The 3-keto acyl CoA is then cleaved by a molecule of CoASH; this step is called thiolysis and is catalyzed by β - keto thiolase. Since there is a loss of 2 carbon atoms from fatty acid chain, the reaction is called β -oxidation. The cycle repeats and in the case of even chain fatty acid, the last cycle yields two molecules of acetyl CoA while in case of odd chain fatty acid, the last step yields propionyl CoA and acetyl CoA.

During digestion and absorption of fats, triglycerides are successively split into diglycerides and monoglycerides, glycerol, and fatty acids by lipases. The products are absorbed by the epithelial cells of the intestines either as water-soluble complexes or as micelles. The fatty acids are biodegraded by β - oxidation.

Biodegradation of fatty acid takes place in mitochondrial matrix of cells. This is also why mitochondria is called "powerhouse" of the cell.

Note: Synthesis of fatty acid involves addition of 2 carbon atoms in one cycle; biodegradation involves removal of 2 carbon in one cycle.

Detergents

Detergents are the unique substances, which always prefer stay at the interface of the two different phases. The molecular structure of detergents has attributes like two different moieties (polar and non polar) in the same molecule by which one part of the detergent molecule prefers to stay in the polar phase while the other one stays in the non polar phase. This way, a sort of bridge is built between the two different types of phases.

It is because of the fact that the detergents are active at interfaces, they are also called as "surfactants".

Surfactants or detergents, thus are very useful chemicals because in our day – to- day activities at all levels, we encounter problems associated with the interfaces as also due to the fact that either we need to make two different phases miscible or we need to separate homogeneous and stable systems consisting of different phases. In all such cases, Surfactants or detergents are found useful in negotiating the two different phases for both the stabilization as well as destabilization of the systems.

For example, detergents can act as a link between water and the dirt particles, on any surface like fabrics that need to be cleaned. The detergent molecules can perform this function because one end is hydrophobic. The hydrophilic end is similar in structure to compounds that get hydrated. The hydrophobic part of the molecule frequently consists of a hydrocarbon chain that is similar to the structure of dirt, grease, oil, fat and hydrophobic solids. The net result of this peculiar

structure permits detergent to reduce the surface tension of water and dirt to affect cleaning of surfaces.

When detergent is used, the dirt particles on the surfaces detach from the dirty surface and go into the solution of detergent, the earliest known detergents are the soaps which are made from animal and vegetable fats and oils. Chemically, it is the sodium or potassium salt of a fatty acid, formed by the reaction fatty acid group with an alkali.

To start with, Europeans produced soap from the tallow of goats reacting it with beech ash furnishing the alkali. Boiling olive oil with lead oxide produced a sweet tasting substance called glycerin along with the soap. Thus fats did not combine with alkali to form soap but were first decomposed to form fatty acid and glycerol.

In the present times for manufacturing soaps, oils or fats are treated with an aqueous solution of an alkali such as sodium hydroxide- a process called saponification to form glycerin and soap (sodium salt of fatty acid).

Hard soaps are made from oils and fats that contain a high percentage of saturated acids, which are saponified with sodium hydroxide. Soft soaps are semi fluid soaps made from linseed oil, cottonseed oil, and fish oils, which are saponified with potassium hydroxide.

Transparent soaps usually contain castor oil, high-grade coconut oil, and tallow. A fine toilet soap made of high grade olive oil is known as castile soap. Shaving soap is a potassium-sodium soft soap, containing stearic acid, which gives a lasting lather. Shaving cream is a paste that is a combination of shaving soap and coconut oil.

Soap powder is a hydrated mixture of soap and sodium carbonate. Powdered soap, which is used in dispensers, is a dry soap that has been pulverized to a fine powder. Liquid soap is a solution of soft potassium soap dissolved in water.

Here, it may be noted that there are several other types of detergents which have been developed over the years and the dependence on soaps for such applications is minimal.

Chemical structure of Detergents

All the detergents or surfactants have one basic feature in their structure and that is the presence of two moieties of different nature: one being hydrophilic whereas the other one being hydrophobic. Depending upon the nature of the hydrophilic group, the detergents can be nonionic, anionic, cationic, amphoteric. For better understanding, let us discuss the structure of ionic and non-ionic detergents separately. The hydrophobic part is generally a long chain hydrocarbon in the case of most of the detergents. Detergents with the hydrophobic part consisting of the long chain compounds with little affinity for aqueous media. The hydrophilic part is small in size (especially for ionic detergents) but it has a strong affinity for water because either it is charged positively or negatively or it consists of groups with high degree of solvation in water through H-bonding.

Let us take the case of linear alkyl benzene sulphonate which consists of linear alkyl benzene as the hydrophobic chain (which is comparatively big in size) and a sulphonate group as a hydrophile (which is comparatively small in size) with a negative charge. Similarly, the cationic detergents would have a long chain hydrophobic part attached to a cation such as a quaternary group.

The structure of non-ionic detergents is different from ionic detergents not just on the basis of the charge (nonionic being without charge) but also on the basis of the size of the hydrophobic and hydrophilic part. Here, the size of the hydrophobic part and hydrophilic part can vary in the same series of detergents. Here, “series of detergents” means that their hydrophobic part is attached with the hydrophiles of varying size resulting in the detergents with varying hydrophile content. Several detergent series with varying hydrophobes and EO as a hydrophile are possible, the prominent ones include: NP-EO; NP (PO) EO; $(EO)_n - (PO)_n - (EO)_n$; FA-EO; FA (PO) EO. All four of them are discussed here.

NP – EO Series

Let us take an example of the most popular detergent or surfactant Nonyl Phenol (NP) series, which will have nonyl phenol as the hydrophobic part, attached with ethylene oxide (EO) of varying number of moles as the hydrophilic part. As the number of moles of ethylene oxide increases, the size of the hydrophile also increases. This means that the detergent acquires higher hydrophilic character compared to the hydrophobic character as the number of moles of ethylene oxide increases. The whole series of NP-EO can be grouped in three categories: NP-1 to 5 EO; NP – 6 to 15 EO and NP – more than 15 EO

Hydrophobe : Nonyl Phenol

Hydrophile : Ethylene Oxide chain with varying number of ethylene oxide.

NP-1 mole EO to NP-5 moles EO

With around 5 moles of the ethylene oxide in the hydrophilic chain, the hydrophobic part almost matches with the hydrophilic part; in size. It is due to this reason that NP with 5 moles of EO is used for water- in - oil emulsion because the detergent is:

- Water miscible.
- Oil soluble.

NP-More than 15 EO

When the number of moles of EO increase beyond 15, the detergent acquires the capability to solubilise the most hydrophobic substances into water. The thermodynamically stable formulations such as micro-emulsions become possible mainly because of such a type of detergents. Even the nano-dispersions could be prepared by using the highly hydrophilic detergent with a long-chain of EO.

NP-6 moles EO to NP-15 moles EO

With increasing number of moles of EO in the molecule, the detergent becomes more and more soluble in water and less soluble in non-aqueous media.

True the oil solubility decreases as the number of moles of ethylene oxide increases but that enables the detergent to form oil-in-water emulsion.

Hydrophobic part becomes much smaller in size compared to the ethylene oxide chain; for example in the case of NP-15 EO. While NP-15 EO is a very useful detergent for oil -in-water emulsion, the most versatile detergent with varied applications.

Similarly, there can be several series based on different types of hydrophobes from alkyl phenol category; octyl phenol, amyl phenol, cumyl phenol, styrene phenol etc. In all of them, the hydrophile is always ethylene oxide (EO) with varying number of moles in the same way like NP-EO and NP-PO.-EO series.

NP - (PO)_m - (EO)_n Series

Under this category, not just the number of EO moles but even the hydrophobe NP changes its size by addition of propylene oxide (PO). The famous series under this type of nonionics is that of ethylene oxide-propylene oxide block copolymers adduct of NP. Here, the hydrophobic part PO chain with varying number of moles is attached to NP to enlarge the size of effective hydrophobe which is then attached to the ethylene oxide chain with varying number of moles of EO. There can be numerous possibilities because each of the NP-(PO)_m having the propylene oxide chain of fixed molecular weight with varying content of ethylene oxide. For example, if the number of propylene oxide moles on NP can be 10,20,30, 40, etc and for each, ethylene oxide chain can be varied from 5 moles to 50 moles. Accordingly, there can be detergents with different properties varying with ethylene oxide [NP (PO)_m – (EO)_n] content on the NP-(PO)_m.

(EO)_n – (PO)_m – (EO)_n

Under this category of detergents, first the long chain of PO is prepared by addition of m number of moles of PO followed by the addition of n moles of EO. Similarly, other alkyl phenoles (AP) can also be modified by attaching m number of PO moles and then each of AP – (PO)_m can be attached with n number of EO moles to obtain AP – (PO)_m – (EO)_n. All of this is not just a possibility, in fact, there are a number of detergents being regularly designed as per requirements in addition to large number of them already in use.

There can be, therefore, a series of detergents for each chain of poly propylene oxide (PO)_m. For example one can have the hydrophobe with varying number of PO moles with molecular weights, 1000, 2000, 4000, 6000 and 8000. On each of these PO chains then, a varying number of EO moles (EO)_n can be attached and the EO content can be varied from 10% by weight to 80% by weight. With 10% by weight of EO, the detergent would be relatively more soluble in non-aqueous solvents where as with 80% by weight of EO, the detergent would be highly water soluble with great strength of solubilisation of hydrophobic materials in water. Thus, both PO

and EO can be used to design detergents of desired characteristics. This would provide us with detergents of different behaviour as per requirement.

FA – (EO)_n Series

Just like the alkyl phenols, there are other hydrophobic materials having the functional group that can make the free hydrogen available for the addition of EO or PO. The epoxide ring of EO or PO can easily be opened up by the hydrogen catalysed by alkali and this way the EO and PO get attached to such hydrophobes. The most popular ones include fatty alcohols, fatty amines and fatty amides. Here, all of them are denoted as FA-(EO)_n. With the increase in number of moles of EO, the detergents of varying behaviour can be designed.

FA – (PO)_m – (EO)_n

Here again, like NP, the m moles of PO can be attached to the different FA_s and for each of FA – (PO)_m, varying no of EO can be attached to obtain FA – (PO)_m – (EO)_n series of detergents.

There is yet another category of nonionic detergents, which have very poor water solubility; all of them have relatively strong affinity for non-polar solvents. This class of detergents are chemically known as esters consisting of an alcohol with varying hydrophilic nature and carboxylic acid with varying hydrophobic nature. The important range of detergents of this type are based on polyhydric alcohols such as ethylene glycol, glycerol, pentaerythritol and sorbitol reacted with various types of fatty acids. Since the esters have relatively poor solubility in water, they are the preferred emulsifiers for water in oil emulsions.

Here, it may be noted that the esters can be subjected to ethoxylation to create the solubility in water. Under this category there are several ethoxylates of esters of glycerol and sorbitol.

Properties of Detergents

All the detergents exhibit the following two basic properties, which enable them to be used in various industrial applications:

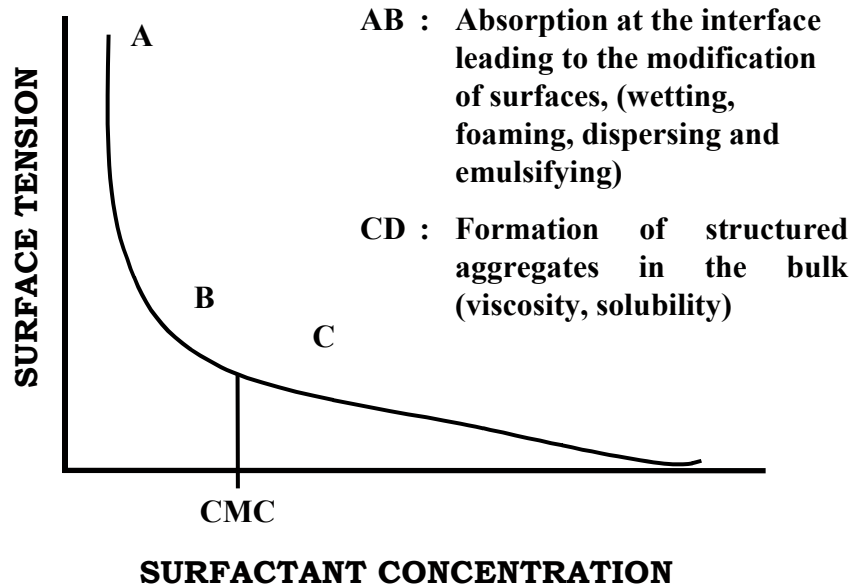
- a) Modifications of surfaces
- b) Adsorption
- c) Micellisation
- d) Solubilization

Modification of surfaces

All detergents have the basic feature of modifying the surfaces or interfaces and thereby creating compatibility between different types of surfaces. The modification of surface is always accompanied by the reduction in surface tension. When detergents are added to water, the surface tension of water is gradually reduced with the increase in concentration of the detergents. However, it reaches a minimum at a particular concentration of detergent, beyond which there is no change in the surface tension. The point at which the surface tension is minimum is also called the critical micelle concentration (CMC) of the detergent on surfactants.

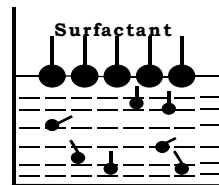
Adsorption

EFFECT OF CONCENTRATION ON THE SURFACE TENSION WHEN SURFACTANTS ARE DISSOLVED IN WATER



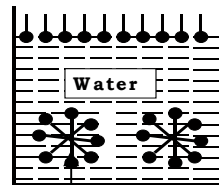
AB PORTION OF THE ABOVE CURVE

IN THE PREVIOUS GRAPH AB REPRESENTS THE HIGHER SURFACTANT CONCENTRATION AT INTERFACE THAN IN THE BULK



CD PORTION OF THE ABOVE CURVE

IN THE PREVIOUS GRAPH CD REPRESENTS THE FORMATION OF STRUCTURED AGGREGATES IN THE BULK



Micelles

Fig X: Surfactants (detergents) in water at different concentration levels. The surface tension decreases with the increase in the concentration of the detergent. Beyond the CMC, the micelle formation takes place.

The fact that the surface tension decreases with increase in the concentration of the detergent, it is expected that the detergent at lower concentration acts at the surface (interfaces) more than in the bulk. At low concentrations therefore, detergents reorient themselves in a manner that they stay at interface. This is why they are also called as surfactants or detergents. As the concentration increases, the detergents progressively accumulate on the interface. However,

beyond certain concentration, the detergents can no more be accommodated at the interface. This type of behaviour of the detergents in solution in water can be understood from the fact that upto certain concentration, the detergents preferentially adsorb at the interface as can be seen from the **Fig X**. Once the interface becomes crowded, the detergent molecules start dissolving in the bulk. Adsorption, till the surface tension decreases and self dissolution of detergents in the bulk beyond the critical micelle concentration are the two basic characteristics of detergents. In a way therefore, one would need a greater degree of adsorption at the interface to modify the surfaces.

The adsorption of detergents on the surface (interface) depends mainly on the type of the hydrophobe (besides its size and shape) and the balance in the hydrophobic and hydrophilic nature of detergents. The more the hydrophobicity, the higher would be the adsorption and greater would be the reduction in surface tension. Similarly, the higher the surface coverage, better would be the surface modification and greater would be the reduction in surface tension. Non-ionics, generally produce lower surface tension than anionics due to their better adsorption behavior at the interface. By varying the hydrophilic and hydrophobic behavior of detergents, one can alter the adsorption behavior.

Micellisation

As the concentration of detergents in water increases beyond CMC, the detergent molecules will have to start getting into the bulk rather than on the surface. This, however, is not an easy situation for detergents mainly due to the fact that the hydrophobic part of the detergent has a strong dislike for water. The situation where the hydrophobic part remains oriented away from the water surface at lower concentration, cannot remain the same once they are in the bulk. At higher concentrations, therefore, all hydrophobic parts of detergent molecules associate with each other leading to such strong hydrophobic interactions that detergent molecules dissolve into themselves.

This results in the formation of an aggregated form of detergents. This is also called “micellisation” taking place at concentrations beyond CMC.

Micellisation is one unique property of detergents or surfactants which has not been exhibited by any other chemical. For understanding the phenomenon of micellisation, it is essential that the basic factors responsible for formation of micelles are understood, first. After the initial stage of overcrowding of surfactants at the interface, the surfactant molecules will have no option but to look for space in the bulk. Obviously the bulk here means largely of aqueous medium in the case of oil-in-water systems and nonaqueous medium in the case of water-on-oil systems.

The surfactant would be more of hydrophilic character in the case of oil-in-water systems where as it would be more of hydrophobic character in the case of water-in-oil systems. In other words, the surfactant molecules have to reorient themselves in such a manner that the hydrophilic part remains with, and hydrophobic part remains away from the aqueous medium.

For the oil-in-water system the highly hydrophilic head of surfactant come close to each other in the manner that a spherical structure is formed. All the hydrophobic tails will get into the core of the sphere keeping themselves away from the aqueous medium. Since there also exists the repulsion amongst the hydrophobic tail, micellisation is quite a complex phenomenon. The size

SURFACTANT STRUCTURAL ATTRIBUTES AND CMC

HYDROPHOBIC		
Chain length	↑	CMC ↓ ➤ Strong hydrophobic interactions
Unsaturation	↑	CMC ↑ ➤ Steric hindrance
HYDROPHILIC		
Electrical charge	↑	CMC ↑ ➤ Higher electrostatic repulsion and higher dehydration free energy
Ethoxylation	↑	CMC ↑ ➤ Higher steric hindrance

Please note

- CMC of non-ionic <<< CMC of ionic
- To increase the adsorption, the CMC should be increased by using above relations.

Fig XI: Factors affecting CMC. Increase in chain length of hydrophobe reduces concentration & increase in unsaturation of the hydrophobic chain results in the increase in the CMC. On the hydrophilic front, the increase in the electric charge as well as in the hydrophilic chain (ethoxylation), result in the increase in CMC.

and shape of the tail is important but the charge, shape and size of hydrophile are also important factors for micellisation.

The concentration at which micellisation starts and the size and structure of micelles are altogether two different things. Low CMC means that the detergent saturates the interface at lower concentrations and hence, detergents would be more efficient (**Fig XI**). However the size and structure of micelles involving the hydrophobic core would determine the effectiveness of the detergents.

While certain applications such as dispersion, foaming and emulsification are due to adsorption, applications such as solubilisation and rheology are due to micellisation.

When we need to develop detergents for cleaning surfaces (including fabrics etc) we have to rely on detergents with high degree of adsorption. At the same time, when we need to prepare a homogeneous mixture, such as vitamin D in water, we would have to look for detergents with a high tendency of micellisation.

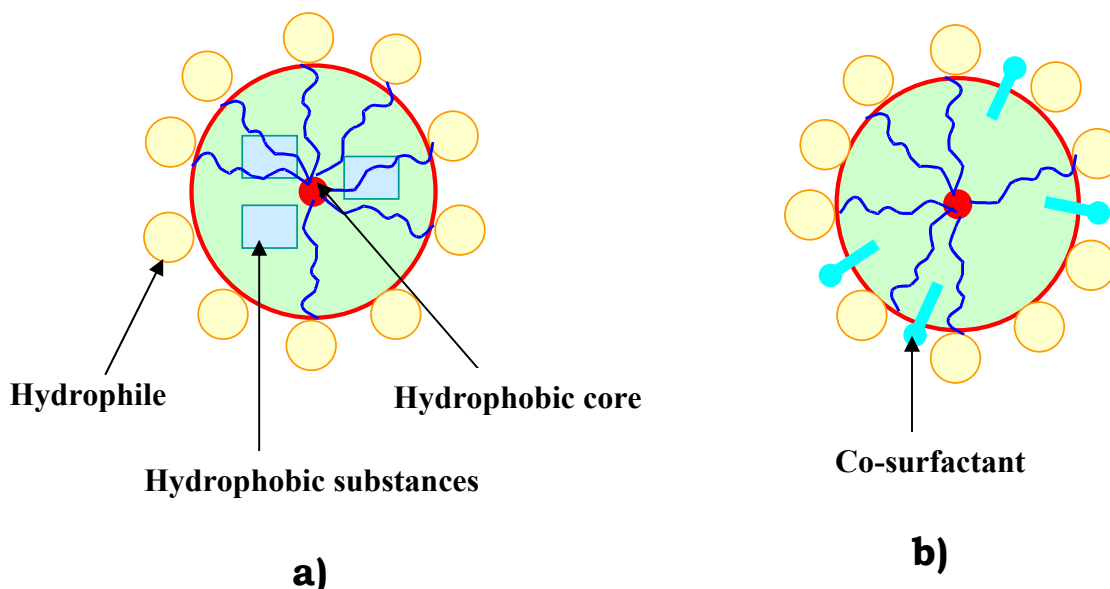


Fig XII: Micelles and solubilization a) The hydrophobic core of micelles can solubilize the hydrophobic substances in water b) Addition of a co-surfactant enables the system to solubilize the hydrophobic substances in water with great ease. Such systems are also called microemulsions, which are thermodynamically stable.

The hydrophobic core in micelles can further be enlarged by addition of smaller hydrophobic molecules known as co-surfactants (**Fig XII**). Such systems are capable of producing thermodynamically stable systems called microemulsions or permanently solubilized systems.

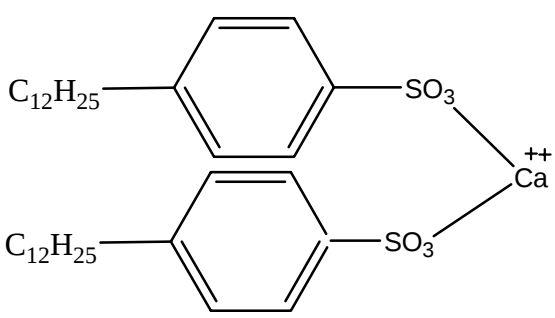
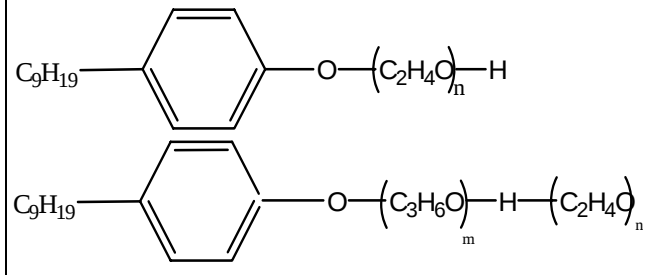
Action of Detergents

Once detergent has dissolved in water, its molecules will surround any patch of dirt on fabric, forming a ring around it called a micelle. Detergents have a hydrophilic and a hydrophobic part. Micelle formation allows the hydrophobic chain to avoid water and hydrophilic head to avoid dirt. Micelle formation makes the dirt soluble in water and thus it helps remove stain from the cloth. Cleaning action is the absorption of dirt and grease into the center of soap micelles, which transforms a stain into a soluble substance that can be, rinsed away.

Types of detergents

A large number of detergents are available for scientific use (**Table VI**). They are usually categorized according to the type of hydrophilic group they contain- anionic, cationic, amphoteric or nonionic.

Table VI: Types of surfactants (detergents) and their applications

SURFACTANT	CHEMISTRY	NATURE	APPLICATIONS
CABS	 $\begin{array}{c} \text{C}_{12}\text{H}_{25}-\text{C}_6\text{H}_4-\text{SO}_3 \\ \text{C}_{12}\text{H}_{25}-\text{C}_6\text{H}_4-\text{SO}_3 \end{array} \text{Ca}^{++}$	Anionic	◆ Emulsifier ◆ Dispersing agents ◆ Thickening agents ◆ Foaming agents
Ethoxylates ◆ NP-EO ◆ NP-PO/EO	 $\begin{array}{c} \text{C}_9\text{H}_{19}-\text{C}_6\text{H}_4-\text{O}-(\text{C}_2\text{H}_4\text{O})_n-\text{H} \\ \text{C}_9\text{H}_{19}-\text{C}_6\text{H}_4-\text{O}-(\text{C}_3\text{H}_6\text{O})_m-\text{H}-(\text{C}_2\text{H}_4\text{O})_n \end{array}$	Nonionic Nonionic	◆ Wetting agents ◆ Dispersing agents

Ethoxylates Castor Oil-EO and other	$ \begin{array}{c} \text{R}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{R}_1-\left(\text{OCH}_2\text{CH}_2\right)_n \\ \\ \text{R}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{R}_1-\left(\text{OCH}_2\text{CH}_2\right)_n \\ \\ \text{R}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{R}_1-\left(\text{OCH}_2\text{CH}_2\right)_n \end{array} $	Nonionic	♦ Emulsifying agents
Ethoxylates Vegetable oil-EO ♦ Fatty Alcohol-EO ♦ Fatty Alcohol-EO/PO	$ \begin{array}{l} \text{R}-\left(\text{OCH}_2\text{CH}_2\right)_n\text{OH} \\ \text{R}-\left(\text{OCH}_2\text{CH}_2\right)_n\left(\text{OC}_3\text{H}_7\right)_m\text{OH} \end{array} $	Nonionic	♦ Solubilising agents ♦ Low foam surfactants
Ester/Ester-EO	$ \begin{array}{ccccccc} & \text{OH} & \text{H} & \text{H} & \text{OH} & & \text{O} \\ & & & & & & \\ \text{CH}_2 & -\text{CH} & -\text{C} & -\text{C} & -\text{C} & -\text{CH}_2 & -\text{O}-\text{C}-\text{R} \\ & & & & & & \\ & \text{H} & \text{OH} & \text{O} & \text{H} & & \end{array} $	Nonionic	♦ Emulsifier ♦ Anti foaming agent
Ethoxylates Quaternary Ammonium Compound	$ \left[\begin{array}{c} \text{R}_1 \\ \\ \text{R}_2-\text{N}-\text{R}_4 \\ \\ \text{R}_3 \end{array} \right]^+ \text{Cl}^- $	Cationic	♦ Adjuvant ♦ Antibacterial

There are four main types of detergents.

Anionic detergents

Anion is a negatively charged molecule. The detergency of an anionic detergent is vested in the anion. The anion is neutralized with an alkaline or basic material to produce full detergency. Anionic detergent can belong to the following groups: -

Alkyl Aryl sulphonates

Linear alkyl benzene sulphonates are the largest used detergents in the world, and the alkyl aryl sulphonates as a group would represent more than 40% of all the detergent used. They are cheap to manufacture, very efficient and the petroleum industry is a starting point for the base raw material.

Long chain fatty alcohol sulphates

Made from fatty alcohols, which are sulphated, these are used extensively in laundry detergents. They can be produced with varying carbon chain lengths, but a C₁₂-C₁₈ alcohol sulphate is a good choice.

Other groups are the olefinic sulphates and sulphonates, alpha olefin sulphates and sulphonates, sulphated monoglycerides, sulphated ethers, sulphosuccinates, alkane sulphonates, phosphate esters, alkyl isethionates, sucrose esters.

The anionic detergents are used extensively in most detergent systems, such as dish wash liquids, laundry liquid detergents, laundry powdered detergents, car wash detergents, shampoo's, etc.

Cationic detergents.

Cation means positively charged. The detergency is in the Cation which can be a substantially sized molecule. Strong acids are used to produce a Cl⁻ anion as the "neutralizing agent", although no neutralization takes place in the manufacturing process.

These have poor detergency and can be used as germicides, fabric softeners, and special emulsifiers.

Cationic and anionic detergents cannot be mixed together as it causes precipitation. The cationic detergents invariably contain amino compounds. The most widely used are the quaternary ammonium salts.

Non-ionic detergents

As the name implies, no ionic constituents are present. They are ionically inert. The vast majority of all nonionic detergents are condensation products of ethylene oxide with a hydrophobe. This group of detergents is enormous and the permutations are endless.

Amphoteric detergents

These contain both acidic and basic groups in their molecule, and can act as cationic and anionic detergents, depending on the pH of the solution. These have the characteristics of both anionic and cationic detergent. They tend to work the best at neutral pH and they are found in shampoos, skin cleaners and carpet shampoo. They are very stable in strong acidic conditions and have found favor for use with hydrofluoric acid.

Two properties of detergents are very important in their consideration for biological studies: the critical micelle concentration (CMC) and the micelle molecular weight. The CMC is the concentration at which monomers of detergents join together to form micelles. Each detergent micelle has a characteristic molecular weight. Detergents with a high micelle molecular weight are difficult to remove from samples by dialysis. The CMC and the micelle molecular weight vary depending on the buffer, salt concentration, pH and temperature. Adding salt will lower the CMC and raise the micelle size.

The following detergents have detrimental properties for some procedures:

1. Phenol containing detergents have a high absorbance at 280nm and thus interfere with protein monitoring. They also induce protein at the Lowry protein assay.
2. High micellar molecular weight interferes with gel filtration and they are not easily removed by dialysis.
3. Sodium cholate and sodium deoxycholate are insoluble at pH 7.5. Above an ionic strength of 0.1% SDS they will often crystallize.
4. Ionic detergents interfere with nondenaturing electrophoresis and isoelectric focusing.

Ionic detergents are very good solubilizing agents, but they tend to denature proteins by destroying the three dimensional structure. Nonionic and mildly ionic detergents are less denaturing and can be often used to solubilize membrane proteins while retaining protein-protein interactions.

Differences between Soaps and Detergents

Both soaps and detergents are used for washing purposes. They form an emulsion with water and oil which washes dirt away.

Soaps are made by the action of sodium hydroxide on fats. This process is called hydrolysis or saponification. It gives soap and glycerol (as a by-product). The soaps are sodium salt of fatty acids and are useful only in soft water as they form an insoluble precipitate in hard water. This

precipitate consists of calcium and magnesium salts of higher fatty acids. No lather or emulsion is formed and washing is not possible.

Detergents on the other hand are sodium salts of alkyl or aryl sulphonic acids or sulphonates of aliphatic alcohols. Detergents can be used for washing purposes even in hard water, as the calcium salts of sulphonic acids are water-soluble.

Characterization of Detergents

Since detergents exhibit unique properties when dissolved in water, for characterisation of detergents, therefore, various characteristics of detergent solution in water are studied. The commonly used methods for characterisation of detergents are as given below :

- (a) Cloud point
- (b) Kraft point
- (c) Surface tension and interfacial tension
- (d) Critical micelle concentration

The details of each of the methods are described here.

Cloud Point

As described above, all the detergents when dissolved in water undergo two basic phenomena. Adsorption and micellisation, both of them are due to the hydrophobic interactions where in the detergent molecules reorient themselves in such a way that the hydrophilic part remains with the water molecules whereas the hydrophobic part remains away from them. With the increase in concentration of detergent, the aggregation micellisation of molecules begins with all the hydrophobic chains joined together.

The solution of detergents in water however undergo changes with the rise in temperature. In the case of nonionics, the rise in temperature causes the dehydration of the hydrophile resulting in the precipitation of the detergent manifested as the solution turning cloudy. The temperature at which this change of phase from homogenous and clear solution to hazy and cloudy form takes place is called as the cloud point of the detergent. The cloud point increases with the increase in the number of moles of EO in the nonionic. In other words, one can understand the hydrophilic character of the detergent from the measurement of cloud point. Detergents which don't turn cloudy even on temperature at which water boils are the highly hydrophilic in nature, for example, NP with 30 moles of EO. In such cases, the cloud point is measured by dissolving the detergents in salt solution in water rather than just water. The salts (eg. NaCl, KCl etc.) in water facilitate the dehydration of detergents which otherwise don't turn cloudy on heating. Similarly the detergents which have the cloud point less than the ambient say 30°C, the measurements cannot be done with solution in water. In such cases, the hydro tropic solvent such as butyl diglycol ether, isopropyl alcohol, ethanol etc. can not be used to solubilise the detergent. The solution of detergent in water with solvent is then used for cloud point measurement.

There are a large amount of information in the literature based on which one can easily determine the type of detergent once the cloud point is known. For example, if the hydrophobe is known, one can determine the number of EO moles attached in the detergent from the result of cloud point unlike the nonionics, the anionic detergents exhibit a totally different behaviour when their solution in water are heated.

Kraft Point

In the case of anionic detergents, their solution in water when heated exhibit the increase in solubility rather than precipitation. The temperature at which the solubility increases drastically, is known as its kraft point. Based on the kraft point, not only one can determine the nature of detergent but once can also make the selection of the suitable detergent for a given application. For example, if the formulation of detergent is to be developed for the washing of fabrics the detergent to be selected would have to be based on the temperature of washing. If washing is to be done at ambient, the detergent to be selected will have to have the kraft point much lower than the ambient temperature. Generally, for washings at lower temperatures one would have to opt for nonionics where as for washings at higher temperature, the anionics would be the preferred choice. The Kraft point depends on several factors such as the hydrophobic chain, type of anionic group and the neutralizing cation.

Surface tension or interfacial tension

As the hydrophobic part remains oriented away from the surface of water, the surface tension is lowered. Based on the surface tension Vs concentration pattern, once can make an assessment of the interfacial behaviour of detergents. Those which show very low surface tension are known for high wetting as well as for solubilisation power. Based on the surface tension data, once can design the detergent formulations for a given application involving different phases.

Surface tension depends upon the way the detergent molecules stay at surface and that is directly derived from the size, shape and nature of the detergent.

Critical Micelle Concentration

Based on the CMC of detergents, one can make an assessment of the nature of the detergents. For example, nonionics exhibit much lower CMC than the anionics. For applications where one needs to solubilise the hydrophobic substances in water, one will have to look for detergents with extremely low CMC values.

ANNEXURE 1

Codex Standards for Fats and Oils from Vegetable Sources

Codex Standard for Named Vegetable Oils (CODEX-STAN 210 - 1999)

METHODS OF ANALYSIS AND SAMPLING

Determination of GLC Ranges of Fatty Acid Composition

According to IUPAC 2.301, 2.302 and 2.304 or ISO 5508: 1990 and 5509: 2000 or AOCS Ce 2-66, Ce 1e-91 or Ce 1f-96.

Determination of Slip Point

According to ISO 6321: 1991 and Amendment 1: 1998 for all oils, or AOCS Cc 3b-92 or Ce 3-25 (97) for palm oils only.

Determination of Arsenic

According to AOAC 952.13, IUPAC 3.136, AOAC 942.17, or AOAC 985.16.

Determination of Lead

According to IUPAC 2.632, AOAC 994.02 or ISO 12193: 1994 or AOCS Ca 18c-91.

Table 1: Fatty acid composition of vegetable oils as determined by gas liquid chromatography from authentic samples (expressed as percentage of total fatty acids)

Fatty acid	Arachis oil	Babassu oil	Coconut oil	Cottonseed oil	Grapeseed oil	Maize oil	Mustardseed oil	Palm oil	Palm kernel oil	Palm olein
C6:0	ND	ND	ND-0.7	ND	ND	ND	ND	ND	ND-0.8	ND
C8:0	ND	2.6-7.3	4.6-10.0	ND	ND	ND	ND	ND	2.4-6.2	ND
C10:0	ND	1.2-7.6	5.0-8.0	ND	ND	ND	ND	ND	2.6-5.0	ND
C12:0	ND-0.1	40.0-55.0	45.1-53.2	ND-0.2	ND	ND-0.3	ND	ND-0.5	45.0-55.0	0.1-0.5
C14:0	ND-0.1	11.0-27.0	16.8-21.0	0.6-1.0	ND-0.3	ND-0.3	ND-1.0	0.5-2.0	14.0-18.0	0.5-1.5
C16:0	8.0-14.0	5.2-11.0	7.5-10.2	21.4-26.4	5.5-11.0	8.6-16.5	0.5-4.5	39.3-47.5	6.5-10.0	38.0-43.5
C16:1	ND-0.2	ND	ND	ND-1.2	ND-1.2	ND-0.5	ND-0.5	ND-0.6	ND-0.2	ND-0.6
C17:0	ND-0.1	ND	ND	ND-0.1	ND-0.2	ND-0.1	ND	ND-0.2	ND	ND-0.2
C17:1	ND-0.1	ND	ND	ND-0.1	ND-0.1	ND-0.1	ND	ND	ND	ND-0.1
C18:0	1.0-4.5	1.8-7.4	2.0-4.0	2.1-3.3	3.0-6.5	ND-3.3	0.5-2.0	3.5-6.0	1.0-3.0	3.5-5.0
C18:1	35.0-69	9.0-20.0	5.0-10.0	14.7-21.7	12.0-28.0	20.0-42.2	8.0-23.0	36.0-44.0	12.0-19.0	39.8-46.0
C18:2	12.0-43.0	1.4-6.6	1.0-2.5	46.7-58.2	58.0-78.0	34.0-65.6	10.0-24.0	9.0-12.0	1.0-3.5	10.0-13.5
C18:3	ND-0.3	ND	ND-0.2	ND-0.4	ND-1.0	ND-2.0	6.0-18.0	ND-0.5	ND-0.2	ND-0.6
C20:0	1.0-2.0	ND	ND-0.2	0.2-0.5	ND-1.0	0.3-1.0	ND-1.5	ND-1.0	ND-0.2	ND-0.6
C20:1	0.7-1.7	ND	ND-0.2	ND-0.1	ND-0.3	0.2-0.6	5.0-13.0	ND-0.4	ND-0.2	ND-0.4
C20:2	ND	ND	ND	ND-0.1	ND	ND-0.1	ND-1.0	ND	ND	ND
C22:0	1.5-4.5	ND	ND	ND-0.6	ND-0.5	ND-0.5	0.2-2.5	ND-0.2	ND-0.2	ND-0.2
C22:1	ND-0.3	ND	ND	ND-0.3	ND-0.3	ND-0.3	22.0-50.0	ND	ND	ND
C22:2	ND	ND	ND	ND-0.1	ND	ND	ND-1.0	ND	ND	ND
C24:0	0.5-2.5	ND	ND	ND-0.1	ND-0.4	ND-0.5	ND-0.5	ND	ND	ND
C24:1	ND-0.3	ND	ND	ND	ND	ND	0.5-2.5	ND	ND	ND

Fatty acid	Palm stearin	Rapeseed oil	Rapeseed oil (low erucic acid)	Safflowerseed oil	Safflowerseed oil (high oleic acid)	Sesame seed oil	Soyabean oil	Sunflowerseed oil	Sunflowerseed oil (high oleic acid)
C6:0	ND	ND	ND	ND	ND	ND	ND	ND	ND
C8:0	ND	ND	ND	ND	ND	ND	ND	ND	ND
C10:0	ND	ND	ND	ND	ND	ND	ND	ND	ND
C12:0	0.1-0.5	ND	ND	ND	ND-0.2	ND	ND-0.1	ND-0.1	ND
C14:0	1.0-2.0	ND-0.2	ND-0.2	ND-0.2	ND-0.2	ND-0.1	ND-0.2	ND-0.2	ND-0.1
C16:0	48.0-74.0	1.5-6.0	2.5-7.0	5.3-8.0	3.6-6.0	7.9-12.0	8.0-13.5	5.0-7.6	2.6-5.0
C16:1	ND-0.2	ND-3.0	ND-0.6	ND-0.2	ND-0.2	0.1-0.2	ND-0.2	ND-0.3	ND-0.1

C17: 0	ND- 0.2	ND- 0.1	ND-0.3	ND-0.1	ND-0.1	ND-0.2	ND- 0.1	ND-0.2	ND-0.1
C17: 1	ND- 0.1	ND- 0.1	ND-0.3	ND-0.1	ND-0.1	ND-0.1	ND- 0.1	ND-0.1	ND-0.1
C18: 0	3.9-6.0	0.5-3.1	0.8-3.0	1.9-2.9	1.5-2.4	4.8-6.1	2.0-5.4	2.7-6.5	2.9-6.2
C18: 1	15.5- 36.0	8.0- 60.0	51.0-70.0	8.4-21.3	70.0-83.7	35.9- 42.3	17-30	14.0-39.4	75-90.7
C18: 2	3.0- 10.0	11.0- 23.0	15.0-30.0	67.8-83.2	9.0-19.9	41.5- 47.9	48.0- 59.0	48.3-74.0	2.1-17
C18: 3	ND- 0.5	5.0- 13.0	5.0-14.0	ND-0.1	ND-1.2	0.3-0.4	4.5- 11.0	ND-0.3	ND-0.3
C20: 0	ND- 1.0	ND- 3.0	0.2-1.2	0.2-0.4	0.3-0.6	0.3-0.6	0.1-0.6	0.1-0.5	0.2-0.5
C20: 1	ND- 0.4	3.0- 15.0	0.1-4.3	0.1-0.3	0.1-0.5	ND-0.3	ND- 0.5	ND-0.3	0.1-0.5
C20: 2	ND	ND- 1.0	ND-0.1	ND	ND	ND	ND- 0.1	ND	ND
C22: 0	ND- 0.2	ND- 2.0	ND-0.6	ND-1.0	ND-0.4	ND-0.3	ND- 0.7	0.3-1.5	0.5-1.6
C22: 1	ND	> 2.0- 60.0	ND-2.0	ND-1.8	ND-0.3	ND	ND- 0.3	ND-0.3	ND-0.3
C22: 2	ND	ND- 2.0	ND-0.1	ND	ND	ND	ND	ND-0.3	ND
C24: 0	ND	ND- 2.0	ND-0.3	ND-0.2	ND-0.3	ND-0.3	ND- 0.5	ND-0.5	ND-0.5
C24: 1	ND	ND- 3.0	ND-0.4	ND-0.2	ND-0.3	ND	ND	ND	ND

ND - non detectable, defined as £ 0.05%.

ANNEXURE 2

CODEX STANDARD FOR EDIBLE FATS AND OILS

NOT COVERED BY INDIVIDUAL STANDARDS

CODEX STAN 19-1981 (Rev. 2-1999)

The Appendix to this Standard is intended for voluntary application by commercial partners and not for application by governments.

1. SCOPE

This Standard applies to oils and fats and mixtures thereof in a state for human consumption. It includes oils and fats that have been subjected to processes of modification (such as trans-esterification or hydrogenation) or fractionation.

This Standard does not apply to any oil or fat which is covered by one of the following:

the Codex Standard for Named Animal Fats;

the Codex Standard for Named Vegetable Oils;

the Codex Standard for Olive Oils and Olive-pomace Oils.

2. DESCRIPTIONS

2.1 **Edible fats and oils** are foodstuffs defined in Section 1 which are composed of glycerides of fatty acids. They are of vegetable, animal or marine origin. They may contain small amounts of other lipids such as phosphatides, of unsaponifiable constituents and of free fatty acids naturally present in the fat or oil. Fats of animal origin must be produced from animals in good health at the time of slaughter and be fit for human consumption.

2.2 **Virgin fats and oils** are edible vegetable fats and oils obtained, without altering the nature of the oil, by mechanical procedures, e.g. expelling or pressing, and the application of heat only. They may be purified by washing with water, settling, filtering and centrifuging only.

2.3 **Cold pressed fats and oils** are edible vegetable fats and oils obtained, without altering the oil, by

mechanical procedures, e.g. expelling or pressing, without the application of heat. They may have been purified by washing with water, settling, filtering and centrifuging only.

3. FOOD ADDITIVES

3.1 No additives are permitted in virgin or cold pressed oils covered by this Standard.

3.2 Colours

No colours are permitted in vegetable oils covered by this Standard.

The following colours are permitted for the purpose of restoring natural colour lost in processing or for the purpose of standardizing colour, as long as the added colour does not deceive or mislead the consumer by concealing damage or inferiority or by making the product appear to be of greater than actual value:

Maximum level

100 Curcumin or Turmeric 5 mg/kg (calculated as total curcumin)

160a Beta-carotene 25 mg/kg

160b Annatto extracts 10 mg/kg (calculated as total bixin or norbixin)

3.3 Flavours

Natural flavours and their identical synthetic equivalents and other synthetic flavours, except those which are known to represent a toxic hazard.

3.4 Antioxidants

Maximum level

304 Ascorbyl palmitate) 500 mg/kg individually or in combination

305 Ascorbyl stearate)

306 Mixed tocopherols concentrate GMP

307 Alpha-tocopherol GMP

308 Synthetic gamma-tocopherol GMP

309 Synthetic delta-tocopherol GMP

310 Propyl gallate 100 mg/kg

319 Tertiary butyl hydroquinone (TBHQ) 120 mg/kg

320 Butylated hydroxyanisole (BHA) 175 mg/kg

321 Butylated hydroxytoluene (BHT) 75 mg/kg

Any combination of gallates, BHA and

BHT and/or TBHQ

200 mg/kg but limits above not to be exceeded

389 Dilauryl thiodipropionate 200 mg/kg

3.5 Antioxidant synergists

330 Citric acid GMP

331 Sodium citrates GMP

384 Isopropyl citrates) 100 mg/kg individually or in combination

Monoglyceride citrate)

3.6 Anti-foaming agents (for oils and fats for deepfrying)

900a Polydimethylsiloxane 10 mg/kg

4. CONTAMINANTS

4.1 Heavy metals

The products covered by the provisions of this Standard shall comply with maximum limits being established by the Codex Alimentarius Commission but in the meantime the following limits will apply:

Maximum permissible concentration

Lead (Pb) 0.1 mg/kg

Arsenic (As) 0.1 mg/kg

4.2 Pesticide residues

The products covered by the provisions of this Standard shall comply with those maximum residue limits established by the Codex Alimentarius Commission for these commodities.

5. HYGIENE

5.1 It is recommended that the products covered by the provisions of this Standard be prepared and handled in accordance with the appropriate sections of the Recommended International Code of Practice - General Principles of Food Hygiene (CAC/RCP 1-1969, Rev. 3-1997), and other relevant Codex texts such as Codes of Hygienic Practice and Codes of Practice.

5.2 The products should comply with any microbiological criteria established in accordance with the Principles for the Establishment and Application of Microbiological Criteria for Foods (CAC/GL 21-1997).

6. LABELLING

The product shall be labelled in accordance with the Codex General Standard for the Labelling of Prepackaged Foods (Ref. CODEX STAN 1-1985, Rev. 1-1991; Codex Alimentarius, Volume 1A).

6.1 Name of the food

6.1.1 The designation "virgin fat" or "virgin oil" may only be used for individual fats or oils conforming to the definition in Section 2.2 of this Standard.

6.1.2 The designation "cold pressed fat" or "cold pressed oil" may only be used for individual fats or oils conforming to the definition in Section 2.3 of this Standard.

6.2 Labelling of non-retail containers

Information on the above labelling requirements shall be given either on the container or in accompanying documents, except that the name of the food, lot identification and the name and address of the manufacturer or packer shall appear on the container.

However, lot identification and the name and address of the manufacturer or packer may be replaced by an identification mark, provided that such a mark is clearly identifiable with the accompanying documents.

7. METHODS OF ANALYSIS AND SAMPLING

7.1 Determination of lead

According to IUPAC 2.632, AOAC 994.02 or ISO 12193: 1994.

7.2 Determination of arsenic

According to AOAC 952.13, IUPAC 3.136, AOAC 942.17, or AOAC 985.16.

APPENDIX

OTHER QUALITY AND COMPOSITION FACTORS

This text is intended for voluntary application by commercial partners and not for application by governments.

1. QUALITY CHARACTERISTICS

1.1 Colour:

Characteristic of the designated product.

1.2 Odour and taste:

Characteristic of the designated product and free from foreign and rancid odour and taste.

Maximum level

1.3 Matter volatile at 105°C: 0.2% m/m

1.4 Insoluble impurities: 0.05 % m/m

1.5 Soap content: 0.005 % m/m

1.6 Iron (Fe):

Refined fats and oils 2.5 mg/kg

Virgin fats and oils 5.0 mg/kg

Cold pressed fats and oils 5.0 mg/kg

1.7 Copper (Cu):

Refined fats and oils 0.1 mg/kg

Virgin fats and oils 0.4 mg/kg

Cold pressed fats and oils 0.4 mg/kg

1.8 Acid value:

Refined fats and oils 0.6 mg KOH/g fat or oil

Virgin fats and oils 4.0 mg KOH/g fat or oil

Cold pressed fats and oils 4.0 mg KOH/g fat or oil

1.9 Peroxide value:

Virgin oils and cold pressed fats and oils up to 15 milliequivalents of active oxygen/kg oil

Other fats and oils up to 10 milliequivalents of active oxygen/kg oil

2. METHODS OF ANALYSIS AND SAMPLING

2.1 Determination of acid value (AV)

According to IUPAC 2.201 or ISO 660: 1996.

2.2 Determination of peroxide value (PV)

According to IUPAC 2.501 (as amended), AOCS Cd 8b - 90 (97) or ISO 3961: 1998.

2.3 Determination of matter volatile at 105°C

According to IUPAC 2.601 or ISO 662: 1998.

2.4 Determination of insoluble impurities

According to IUPAC 2.604 or ISO 663: 1999.

2.5 Determination of soap content

According to BS 684 Section 2.5.

2.6 Determination of iron

According to IUPAC 2.631, ISO 8294: 1994 or AOAC 990.05.

2.7 Determination of copper

According to IUPAC 2.631, ISO 8294: 1994 or AOAC 990.05.

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