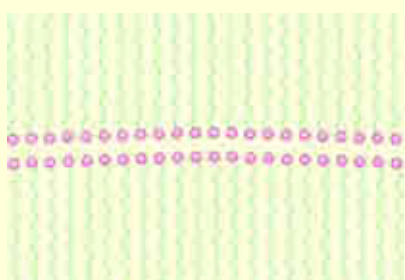
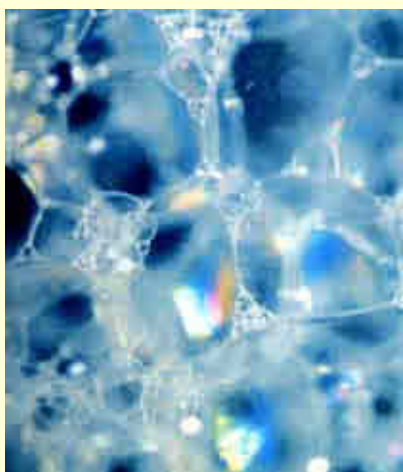


## CONTENTS

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  - Geometric Isomerism • Insulation • Emulsification • Surface Tension
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**The surface of a soap bubble is a bilayer formed by detergent molecules.**

The polar heads (red) pack together leaving the hydrophobic groups (green) in contact with air on the inside and outside of the bubble. Other bilayer structures define the boundary of a cell.

[Courtesy : (Upper) Photonica]

## CHAPTER

## 14

# Lipids–III

## Properties of Fats and Oils

The fats and oils owe the manifestation of their properties to the fatty acids and alcohols, the two component units.

### PHYSICAL PROPERTIES

**1. State.** Fats containing saturated fatty acids are solid at ordinary room temperature. The *animal fats* belong to this category. Most *plant fats*, on the contrary, possess unsaturated fatty acids and are, henceforth, liquid at room temperature.

**2. Colour, Odour and Taste.** When pure, the fats are *colourless*, virtually *odourless* and *possess* an extremely *bland taste*. They are capable of absorbing a variety of odours and hence flavour during storage. For the same reason, a housewife knows that the flavour of an onion quickly permeates butter that is stored with it in a refrigerator. In some cases, however, this absorbing property of fats is of advantage. For example, the perfumes of some flowers can be isolated by placing their petals in contact with the fat for a certain period, then extracting the fat with alcohol and concentrating the essence.

**3. Solubility.** The fats are, however, only sparingly soluble in water. These are, therefore, described as *hydrophobic* in contrast to the water-soluble or hydrophilic substances like many carbohydrates and proteins.

However, these are freely soluble in organic solvents like chloroform, ether, acetone and benzene. These solvents, as they dissolve fats in them, are also known as '*fat solvents*'. The solubility of the fatty acids in organic

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solvents, in fact, decreases with the increase of chain length. *The introduction of hydroxyl groups, however, increases solubility.*

**4. Melting point.** The melting point of fats depends on the chain length of the constituent fatty acid and the degree of unsaturation. Fats containing saturated fatty acids from C 4 to C 8 are liquid at room temperature but those containing C 10 or higher saturated fatty acids are solid and their melting points increase with increasing chain length. With the introduction of double bond in the fat molecule, the melting point lowers considerably. It may be stated, in general, that *greater the degree of unsaturation (or higher the number of double bonds) of the constituent fatty acid, the lower is the melting point of the fat.* This may be easily visualized in terms of constituent fatty acids from the Table 14–1. In fact, short chain length and unsaturation enhance the fluidity of fatty acids and of their derivatives.

**Table 14–1. Melting points of the common fatty acids\***

Fatty acid	No. of carbon atoms	No. of double bonds	M.P. (in °C)
<b>Saturated</b>			
Caprylic	8	0	16.0
Capric	10	0	31.0
Lauric	12	0	44.2
Myristic	14	0	53.9
Palmitic	16	0	63.1
Stearic	18	0	69.6
Arachidic	20	0	76.5
Behenic	22	0	79.9
Lignoceric	24	0	86.0
<b>Unsaturated</b>			
Palmitoleic	16	1	11.0
Oleic	18	1	13.4
Linoleic	18	2	– 5.0
Linolenic	18	3	–11.0
Arachidonic	20	4	– 49.5

\* Here mention has been made only of even numbered fatty acids as they alone are one of the two constituents of the saturated fats. If, however, the entire homologous series of the saturated fatty acids is taken into consideration, the fact emerges that this series shows an alternation or oscillation of melting points, *i.e.*, the melting point of an ‘even’ acid is higher than that of the ‘odd’ acid immediately below and above it. Thus, the fatty acid series follows what is known as the **saw-tooth rule**. However, in many other homologous series the melting points of the n-members rise continuously, tending towards a maximum value.

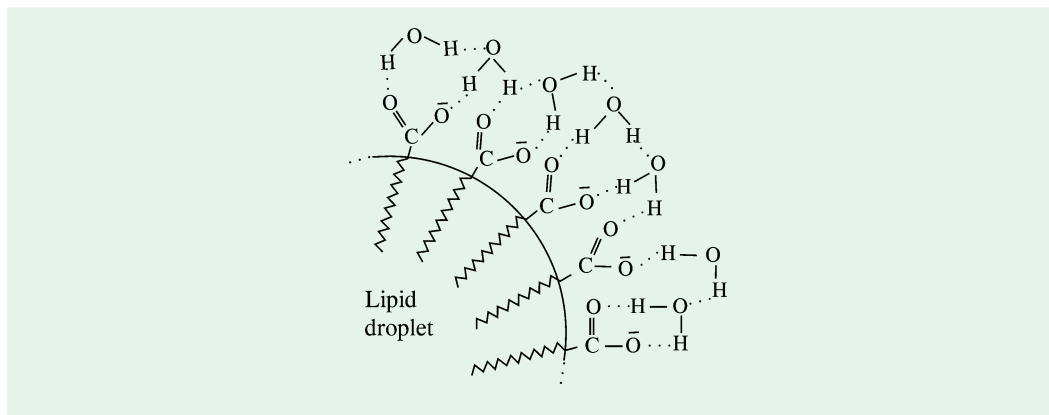
**5. Specific gravity.** The specific gravity of the fats is less than 1 (about 0.86) and, therefore, they float on water surface. Solid fats are lighter than the liquid fats. Oils spread on water to form thin monomolecular layers. In general, either unsaturation of the fatty acid chains increase or increase in chain length of the fatty acid residues tend to increase the specific gravity.

**6. Geometric isomerism.** As stated earlier, the presence of double bond (s) in the unsaturated fatty acid part of the fat molecule produces geometric (or *cis-trans*) isomerism.

**7. Insulation.** The fats possess *high insulating power*, *i.e.*, they are bad conductor of heat. A layer of fat below the skin provides a sort of blanket for warm-blooded animals (or *homoiotherms*). This is especially important for whales and seals which have to maintain a high temperature in cold waters. The fishes are cold-blooded animals (or *poikilotherms*) and, therefore, do not require maintenance of high temperature and so have very little subcutaneous fat.

**8. Emulsification.** It is the process by which a lipid mass is converted into a number of small lipid droplets. The fats may be emulsified by shaking either with water or with emulsifying agents like soaps, gums, proteins etc. An emulsifying agent helps in the production of a finely divided suspension of a fat in an aqueous medium. The hydrocarbon portions of the two (the emulsifier and the fat) tend to aggregate. This leaves the water-soluble group of the emulsifier projecting into the aqueous phase. A fat droplet will associate with a number of molecules of the emulsifier, thus producing a new water-soluble surface. Water molecules, henceforth, tend to be held in a layer or 'cloud' around each droplet, thus disallowing the aggregation of the fat droplets (Fig. 14-1).

The process of emulsification is of great metabolic significance. In fact, *the fats have to be emulsified before they can be absorbed by the intestinal wall*. The process is accomplished by the bile juice secreted from liver.



**Fig. 14-1. A portion of the surface of an emulsified fat globule**

[Here, the emulsifier selected is a simple anion of a fatty acid *i.e.*, a soap. The projecting COOH groups are linked with water molecules by  $H_2$  bonds. Additional  $H_2$  bonding between the water molecules leads to the further stability of the resulting water 'cloud' around the fat droplet.]

(Adapted from Fairley JL and Kilgour GL, 1966)

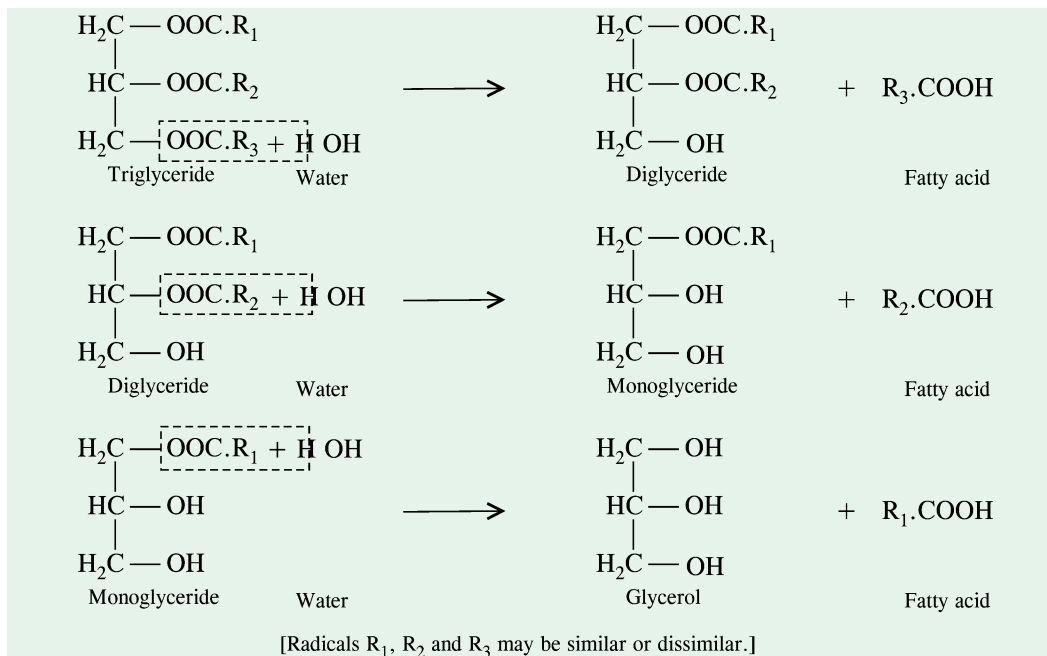
**9. Surface tension.** The force with which the surface molecules are held together is called the surface tension. When liquid fat is poured on water, it spreads uniformly over the surface of water in the form of a unimolecular layer and thus reduces the surface tension of water.

## CHEMICAL PROPERTIES

The chemical reactions of the fats reflect the reactivities of the ester linkage and the degree of unsaturation of the hydrocarbon chain.

### REACTIONS INVOLVING COOH GROUP

**1. Hydrolysis.** The fats are hydrolyzed by the enzymes *lipases* to yield fatty acids and glycerol. The lipases catalyze this reaction at a slightly alkaline pH (7.5 – 8.5) in a stepwise manner. The fats first split to produce *diglycerides*, part of these are then split to *monoglycerides*. Finally, part of the monoglycerides split to yield *fatty acid* and *glycerol*.



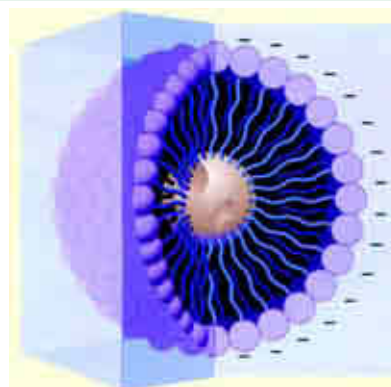
In the intestine, the absorption of mono-, di- and triglycerides is so rapid that very little free glycerol is formed.

**2. Saponification.** *The hydrolysis of fats by alkali is called saponification.* This reaction results in the formation of glycerol and salts of fatty acids which are called *soaps* (Fig. 14-2). The soaps are of

**Acid hydrolysis of a fat,** however, yields the free fatty acid and glycerol.

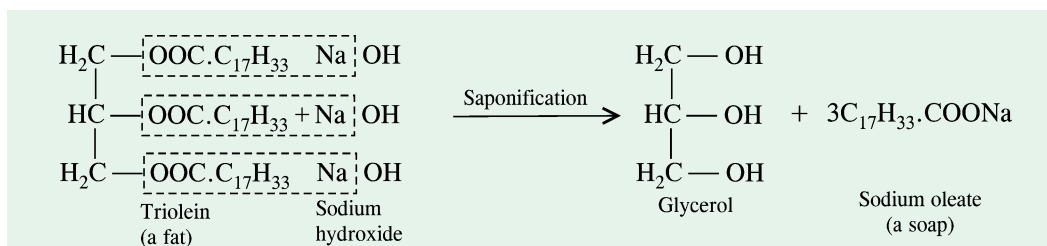
two types : hard and soft. *Hard soaps* such as the common bar

soaps are the sodium salts of the higher fatty acids. *Soft soaps* are the potassium salts of higher fatty acids and are marketed as semisolids or pastes. The fatty acid salts of calcium, magnesium, zinc and lead are, however, insoluble in water. Calcium soaps are used industrially as lubricating greases. Zinc soaps are employed in the manufacture of talcum powder and other cosmetics. Lead and magnesium soaps are used in paints industry to hasten the process of drying.



**Fig. 14-2. Soaps consist of fatty acids**

In this schematic drawing of a soap micelle, the nonpolar tails of the fatty acids are directed inward, where they interact with the greasy matter to be dissolved. The negatively-charged heads are located at the surface of the micelle, where they interact with the surrounding water. Membrane proteins, which also tend to be insoluble in water, can also be solubilized in this way by extraction of membranes with detergents.

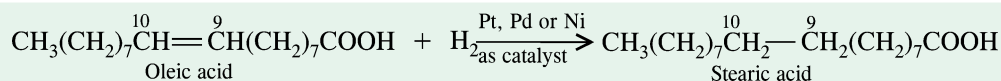


Soaps are important cleansing agents. Their cleansing property is due to their *emulsifying action* (*i.e.*, capacity to render more prolonged the mixing of oil and water). This is accomplished by means of negative charge the soap anion confers on oil droplets. The electrostatic repulsion then prevents the coalescence of soap and oil droplets into an oil phase.

**3. Hydrolytic rancidity.** When butter or other fats are stored, they often become rancid and hence unpalatable. Rancidity is caused by the growth of microorganisms which secrete enzymes like *lipases*. These split the fats into glycerol and free fatty acids. The fatty acids impart unpleasant odour and flavour to the fat. However, butter may be prevented from becoming rancid by refrigeration or by exclusion of water.

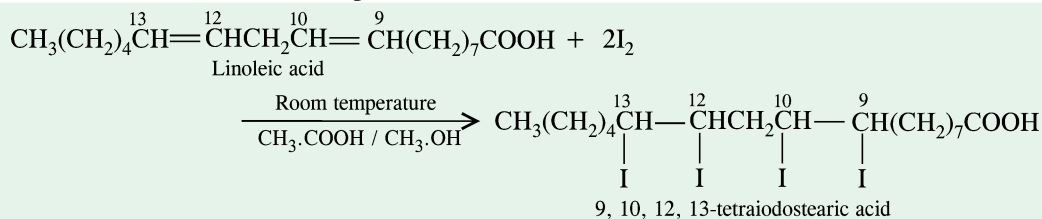
### REACTIONS INVOLVING DOUBLE BOND

**1. Hydrogenation.** Unsaturated fatty acids, either free or combined in lipids, react with gaseous hydrogen to yield the *saturated fatty acids*. The reaction is catalyzed by platinum, palladium or nickel. The addition of hydrogen takes place at the C—C double bond (*s*). Thus, 1 mole of oleic, linoleic or linolenic acid reacts with 1, 2 or 3 moles of hydrogen respectively to form stearic acid.



This reaction is of great commercial importance since it permits transformation of inexpensive and unsaturated liquid vegetable fats into solid fats. The latter are used in the manufacture of candles, vegetable shortenings and of oleomargarine.

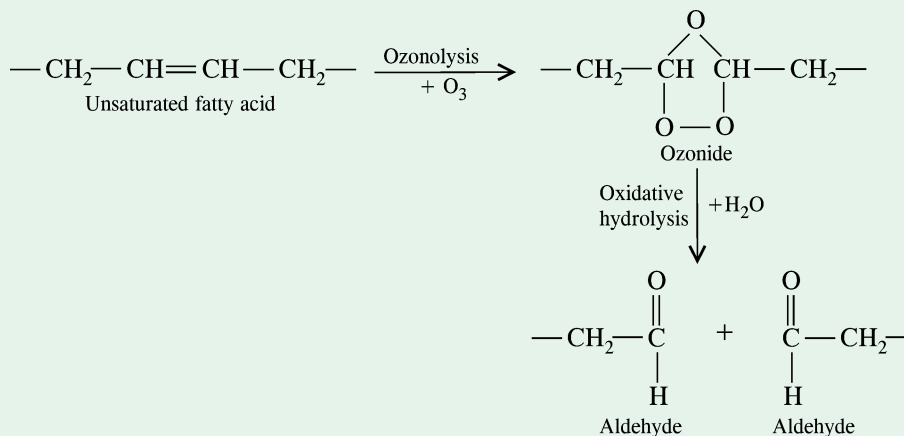
**2. Halogenation.** Unsaturated fatty acids and their esters can take up halogens like Br<sub>2</sub> and I<sub>2</sub> at their double bond (*s*) at room temperature in acetic acid or methanol solution.



This reaction is the basis of the 'iodine number determination'.

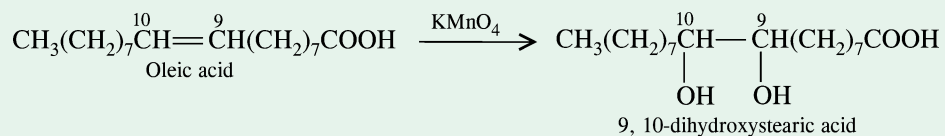
**3. Oxidation.** Unsaturated fatty acids are susceptible to oxidation at their double bonds. Oxidation may be carried with ozone or KMnO<sub>4</sub>.

(a) With ozone – An unstable *ozonide* is formed which later cleaves by water to give rise to 2 *aldehydic groups*.

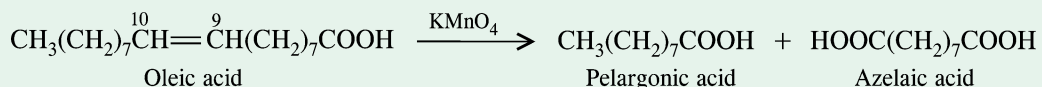


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(b) With  $\text{KMnO}_4$  – Under mild conditions, the *glycols* are formed at the sites of double bonds.



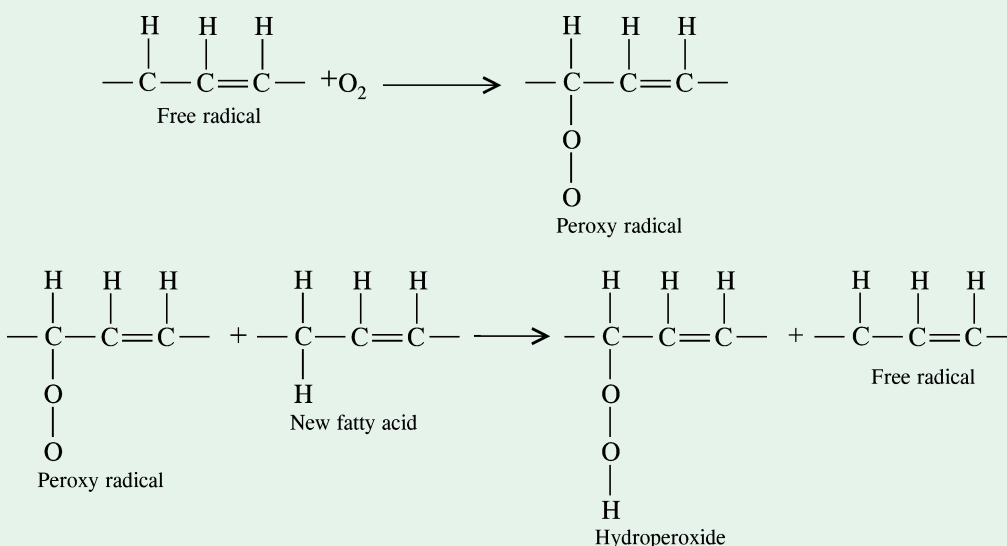
Under vigorous conditions, the same reagent cleaves the molecule at the double bond and oxidizes the terminal portions to the *carboxyl group*.



The oxidation reactions have been extensively used in establishing the position of double bond(s) in the fatty acid chain. This gives important clues regarding lipid structure.

**4. Oxidative rancidity.** Oils containing highly unsaturated fatty acids are spontaneously oxidized by atmospheric oxygen at ordinary temperatures. The oxidation takes place slowly and results in the formation of *short chain fatty acids* ( $C_4$  to  $C_{10}$ ) and *aldehydes* which give a rancid taste and odour to the fats. This type of rancidity or rancidification is called 'oxidative rancidity' and is due to a reaction called 'autoxidation'. Autoxidation proceeds by a free radical mechanism in which the  $\alpha$ -methylene group is primarily attacked. A hydrogen atom is removed from an  $\alpha$ -methylene group. This initiates a chain of reactions leading to oxidation (Holman, 1954).

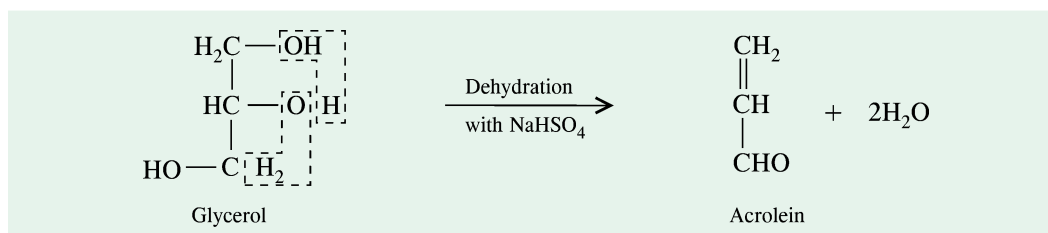
*Oxidative rancidity is observed more frequently in animal fats than in vegetable fats.* This is due to the presence, in the vegetable oils, of natural '**antioxidants**' such as tocopherols (= vitamin E), phenols, naphthols etc., which check autoxidation. Vitamin E is, therefore, some-times added to foods to prevent rancidity. Animal shortenings such as lard are nowadays protected against oxidative rancidity by the addition of synthetic antioxidants such as nordihydroguaiaretic acid (NDGA), tertiary butyl hydroxy anisole (BHA) etc. Linseed oil, a plant oil used as a base for paints, is highly rich in unsaturated fatty acids. It undergoes autoxidation when exposed to air, followed by polymerization to a hard, resinous coating as it 'dries' or oxidizes.



The action of antioxidants is opposed by a group of compounds present in the fats and oils. These accelerate the oxidation of the parent compound and are called *pro-oxidants*. Majority of these substances are formed during the processing and refining of fats. Among the noteworthy pro-oxidants are the copper, iron and nickel salts of organic acids like lactic, etc.

### REACTION INVOLVING OH GROUPS

**Dehydration (Acrolein test).** Fats, when heated in the presence of a dehydrating agent,  $\text{NaHSO}_4$  or  $\text{KHSO}_4$  produce an unsaturated aldehyde called acrolein from the glycerol moiety. Acrolein is easily recognized by its pungent odour and thus forms the basis of the test for the presence of glycerol in fat molecule.



### QUANTITATIVE TESTS

The reactions described above give valuable information about the chemical nature of fatty acids and the number of hydroxyl groups present in the fat molecule. Such chemical determinations involve various analytical tests. These are called *chemical constants* and include the following:

**1. Acid value.** It is the number of milligrams of KOH required to neutralize the free fatty acids present in 1 gm of fat. The acid number, thus, tells us of the quantity of free fatty acid present in a fat. Obviously, a fat which has been both processed and stored properly has a very low acid number.

**2. Saponification number.** It is the number of milligrams of KOH required to saponify 1 gm of fat. The saponification number, thus, provides information of the average chain length of the fatty acids in the fat. It varies inversely with the chain length of the fatty acids. *The shorter the average chain length of the fatty acids, the higher is the saponification number.*

**3. Iodine value (or Koettstorfer number).** It is the number of grams of iodine absorbed by 100 g of fat. The iodine number is, thus, a measure of the degree of unsaturation of the fatty acids in the fat. Oils like soybean, corn and cottonseed have higher iodine numbers (133, 127 and 109, respectively) than the solid fats such as beef fat or tallow (42) because the former possess more unsaturated fatty acids in the fat molecule. However, the iodine number gives no indication as to the number of double bonds present in the fatty acid molecule.

**4. Polenske number.** It is the number of millilitres of 0.1N KOH required to neutralize the insoluble fatty acids (*i.e.*, those which are not volatile with steam distillation) obtained from 5 gm of fat.

**5. Reichert-Meissl number.** It is the number of millilitres of 0.1N KOH required to neutralize the soluble, volatile fatty acids derived from 5 g of fat. The Reichert-Meissl number, thus, measures the quantity of short chain fatty acids (up to C 10 inclusive) in the fat molecule. The Reichert-Meissl numbers of coconut and palm oils range between 5 and 8. Butterfat is exceptional in having a high Reichert-Meissl number, ranging from 17 to 35. This high value makes possible the detection of any foreign fats which are, sometimes, adulterated in the manufacture of butter.

**6. Acetyl number.** It is the number of milligrams of KOH required to neutralize the acetic acid obtained by saponification of 1 gm of fat after it has been acetylated (The treatment of fat or fatty acid mixture with acetic anhydride results in acetylation of all alcoholic OH groups). The acetyl number is, thus, a measure of the number of OH groups in the fat. For example, the castor oil has a high acetyl number (146) because of high content of a hydroxy acid, ricinoleic acid, in it.



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Some examples of the value of these numbers in defining fats are given in Table 14–2.

**Table 14–2. Analytical values for some fats and oils**

<i>Fat/Oil</i>	<i>Saponification number (mg KOH/g)</i>	<i>Iodine value (g I<sub>2</sub>/100 g)</i>	<i>Reichert-Meissl number</i>	<i>Acetyl number</i>	<i>Acid value (mg KOH/g)</i>
<b>Animal fats</b>					
Halibut liver oil	170-180	120-135	–	–	1.0
Cod liver oil	180-190	140-180	–	–	0.5–5
Human fat	194-198	65-69	0.4	–	–
Lard	195-203	47-66	0.5–0.8	2.6	–
Beef fat	196-200	35-42	–	2.78.6	–
Butter	210-230	25-40	17-35	1.9-8.6	0.5-30
Cow's milk	216-235	26-45	–	–	–
<b>Plant fats</b>					
Castor oil	175-187	80-90	1.4	146-150	0.2-4
Corn oil	187-195	104-128	–	–	1.0-2
Linseed oil	188-195	170-195	1.0	4.0	1.0-4
Olive oil	190-195	80-90	0.6-1.5	10-11	0.2-3
Coconut oil	254-262	7-10	0.6-7.5	2.0	2.5-6

### FATS – FACTS AND FANTASIES

*Irrespective of the source, fat is the most concentrated form of dietary energy.* While sugars (carbohydrates) and proteins provide 4 Calories (kilocalories) of energy per gram, fat of any type provides 9 Calories. *There is no such thing as low-calorie fat.* Thus, by replacing fats of animal origin like 'ghee' and butter with vegetable oils like groundnut, sunflower, safflower, mustard, palm oil or any other, weight cannot be reduced. For weight reduction, the only rule is *to eat less and exercise more.* Despite the same Calorie content, the nutritional quality of different fats does differ. As already stated, the fats are composed of an alcohol component (usually glycerol) and a fatty acid component which may be saturated or unsaturated. Nutritionally, polyunsaturated fatty acids (PUFAs) are considered superior. While the human body can synthesize saturated fatty acids (SFAs) and monounsaturated fatty acids (MUFAs), it cannot synthesize the polyunsaturated fatty acids (PUFAs) and hence PUFAs are referred to as essential fatty acids (EFAs). Fats of animal origin (lard, cream, butter and 'ghee') are saturated whereas vegetable oils, except coconut, have varying degree of unsaturation. Fish oils too are unsaturated and have long-chain-length fatty acids. Table 14–3. lists fatty acid composition of some common fats and oils.



Table 14–3. Fatty acid composition of some common fats and oils (in g/100g)

Fat / Oil	Saturated	Mono-unsaturated	Polyunsaturated		Predominant fatty acids*
			Linoleic	$\alpha$ -linolenic	
Coconut <sup>a</sup>	90	7	2	< 0.5	SFAs
Palm kernel	82	15	2	< 0.5	SFAs
'Ghee' <sup>a,b</sup>	65	32	2	< 1.0	SFAs
'Vanaspati' <sup>b</sup>	24	19	3	< 0.5	SFAs
Red palm oil	50	40	9	< 0.5	SFAs + MUFAs
Palm oil	45	44	10	< 0.5	SFAs + MUFAs
Olive	13	76	10	< 0.5	MUFAs
Groundnut	24	50	25	< 0.5	MUFAs
Rape / Mustard <sup>c</sup>	8	70	12	10	MUFAs
Sesame	15	42	42	1.0	MUFAs + PUFAs
Rice bran	22	41	35	1.5	MUFAs + PUFAs
Cottonseed	22	25	52	1.0	PUFAs
Corn	12	32	55	1.0	PUFAs
Sunflower	13	27	60	< 0.5	PUFAs
Safflower	13	17	70	< 0.5	PUFAs
Soybean	15	27	53	5.0	PUFAs

\* SFAs = Saturated fatty acids      a : Mainly short medium-chain fatty acids (Coconut 77%; 'Ghee' 25%)  
MUFAs = Monounsaturated fatty acids      b : *Trans* fatty acids ('Ghee' 2%; 'Vanaspati' 53%)  
PUFAs = Polyunsaturated fatty acids      c : Long-chain monounsaturated fatty acids (50% Erucic acid ; 5% Eicosenoic acid)

Note that Rape / Mustard and Soybean are good sources of  $\alpha$ -linolenic acid.

It is long known that saturated fats raise blood cholesterol level whereas unsaturated fats lower blood cholesterol and also ensure a more favourable ratio of 'good' to 'bad' cholesterol. It is for this reason that the vegetable oils such as groundnut, mustard, rice bran, sunflower, safflower etc (except coconut oil, which is saturated) are regarded to be healthy, rather health-friendly fats. Therefore, these are prescribed for those suffering with high levels of blood cholesterol or those suffering from coronary artery disease.

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## PROBLEMS

1. Some fats used in cooking, such as olive oil, spoil rapidly upon exposure to air at room temperature, whereas others, such as solid shortening, remain unchanged. Why ?
2. Name the products of mild hydrolysis of the following lipids with dilute NaOH :
  - (a) 1-stearoyl-2,3-dipalmitoylglycerol
  - (b) 1-palmitoyl-2-oleoylphosphatidylcholine
3. A common procedure for cleaning the grease trap in a sink is to add a product that contains sodium hydroxide. Explain why this works.
4. Draw all the possible triacylglycerols that you could construct from glycerol, palmitic acid, and oleic acid. Rank them in order of increasing melting point.
5. Rank, in order of increasing solubility in water, a triacylglycerol, a diacylglycerol, and a monoacylglycerol, all containing only palmitic acid.
6. Why do eggs solidify after boiling while 'ghee' melts after heating ?
7. How can exercise make one thinner even though one does not lose any weight ?
8. Which type of diet is the more likely to lead to overconsumption and obesity, one rich in sugar or one rich in fat ?
9. Is it true that you will get rid of more fat if you exercise less strenuously ?
10. Which oils have greatest amount of the desirable monounsaturated fatty acid ?
11. Is margarine better for you than butter ?
12. Why can we blow a bubble with soap water but not with plain water ?
13. Why is it not possible to write on an oily paper ?
14. Why does butter turn rancid if left unrefrigerated for some time ?
15. Why do soap bubbles last longer than water bubbles ?
16. How is cooking oil refined ?
17. Why do phenyls and dettol turn water milky-white when mixed with it ?