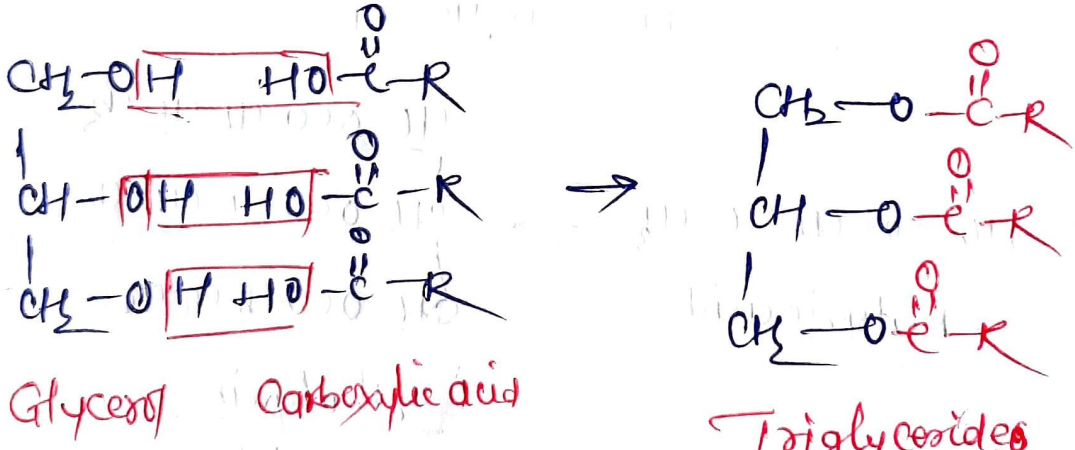
UNIT-III

FATS & OILS

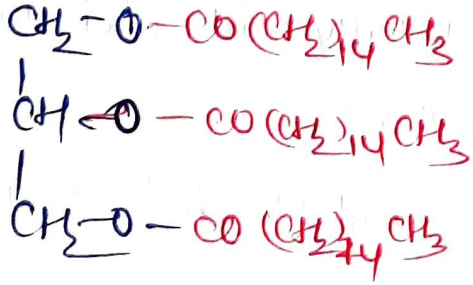
* Fats & oils belong to the naturally occuring group of compounds called Lipids
* Lipids are constituents of plants & animals that are insoluble in water & soluble in organic solvent (ether, benzene)
* Fats & oils are those lipids which are saponifiable, while other such as steroids

Chemistry :→ Triesters of Glycerol with long chain carboxylic acid (12-20-C). These are known Triglyceride



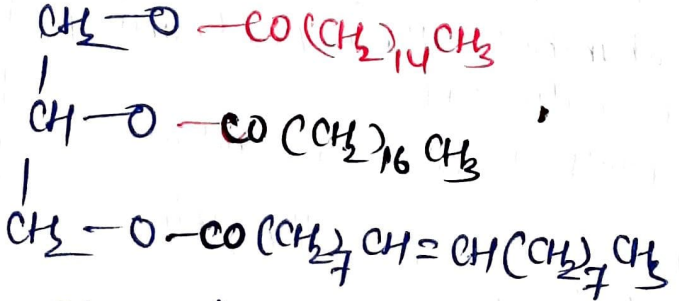
Glycerol Carboxylic acid Triglycerides

* Three group of (-OH) glycerol esterified with same acid, this triester known as simple glyceride. & when esterified with two or more different acid it called - Mixed glyceride



Glycerile Tripalmitate

(Simple glycerol)

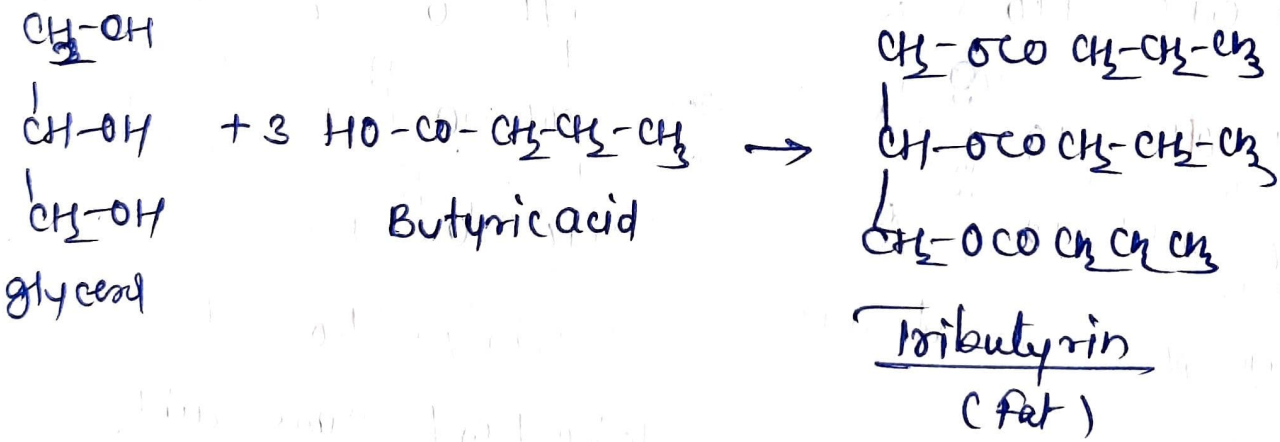


Glyceryl palmito stearo oleate

(Mixed glycerol)

ex. of common fatty acid —

			MP °C
① Myristic acid	$CH_3(CH_2)_{12}COOH$	14-C	58
② Palmitic acid	$CH_3-(CH_2)_{14}COOH$	16-C	63°C
③ Stearic acid	$CH_3(CH_2)_{16}COOH$	18-C	70
④ Oleic acid	$CH_3(CH_2)_7\overset{10}{CH}=\overset{9}{CH}(CH_2)_7\overset{1}{COOH}$ (18-C)		4 °C
⑤ Linoleic acid	$CH_3(CH_2)_4\overset{13}{CH}=\overset{12}{CH}-CH_2-\overset{10}{CH}=\overset{9}{CH}-(CH_2)_7\overset{1}{COOH}$		-5°C



Tributyrin
(Fat)

Fats	Oil
① Solid/Semi solid at room temp	① liquid at room temp
② Fats contains large amount of saturated fatty acid (stearic a, palmitic acid)	② oils contains large amount of unsaturated fatty acid (oleic acid)
③ Melt at high temperature	③ Melt at low temp.
④ Fats are generally animal derived	④ oils are vegitable derived fat
⑤ Fats are more stable	⑤ Fats are less stable

Lard (Fat of hog) - Solid fats

Hydrolysis → 45% oleic acid + 5% linoleic acid + 32% palmitic ā
18% Stearic acid

Olive oil (Vegitable oil) → 84% oleicā + 4% Linoleic ā
+ 9% palmitic acid + 3% stearic acid

Nomenclature of fats

↳ Ester of glycerol (Trihydric alcohol)

$CH_2-OCOC_3H_7$
$CH-O-COC_3H_7$
$CH_2-O-CO-C_3H_7$

Glycerol tributyrate
(Tributyrin)

$CH_2-OCOC_{17}H_{35}$
$CH-O-COC_{17}H_{35}$
$CH_2-OCOC_{17}H_{35}$

Glycerol tristearate
(Tristearin)

In case of mixed fat/Triglyceride, the name of the acidic groups are given as, 1, 2, 3, or α, β, α'

$CH_2O-CO-C_{17}H_{35}$
$CH-O-CO-C_{15}H_{31}$ – β-palmito-α,α'-distearin
$CH_2-OCOC_{17}H_{35}$ Glycerol-2-palmito-1,3-distearate

Occurance

1) Plants – in roots, seeds, fruits ex- cotton seed, ground nut, caster bean, coconut, olives etc

2) Animal: Animal fats around intestine & kidney
- Lard (Fat of hogs)
- Tallow (Fat of kettle, sheep & horses)

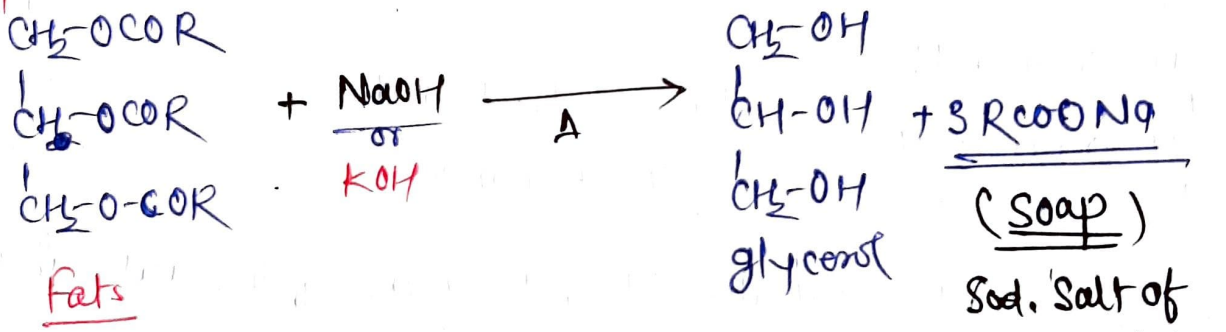
PHYSICAL PROPERTIES

↳ Fats are solid & oils are liquid in nature having greasy feel
↳ Pure fats/oils are colourless, odourless, & tasteless
↳ insolube in water & soluble in organic solvents like ether, $CHCl_3$, benzene
↳ They ~~readily~~ readily form emulsions when agited with water in the pnce of soap, gelatin or other emulsifiers

CHEMICAL REACTION / PROPERTIES

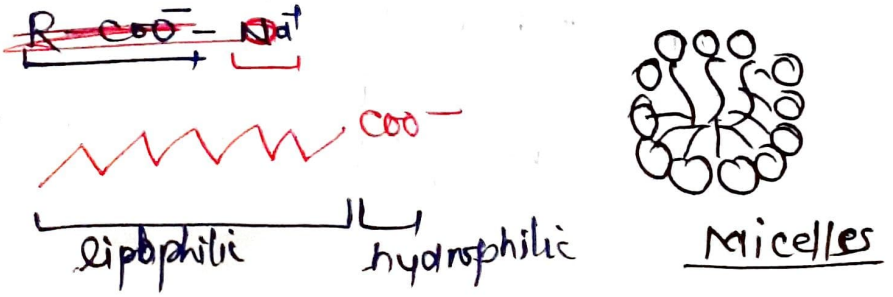
1. **Hydrolysis** – They are readily hydrolysis in the presence of alkali (NaOH), acid and superheated steam (water) under pressure.

(A) By alkali

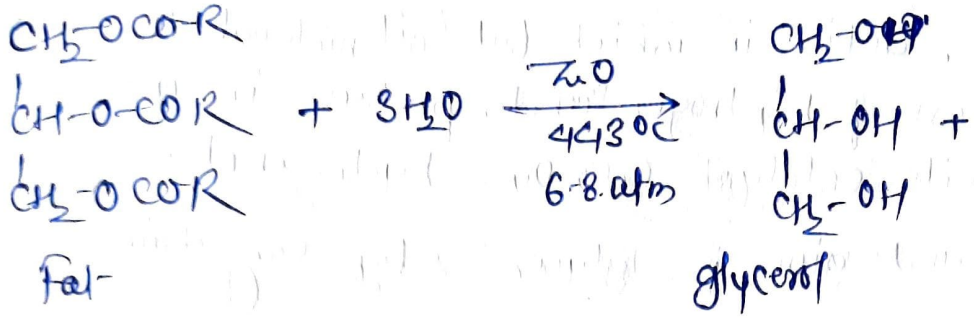


Soap Formation
"Saponification"

* Common soaps are mixture of Sod. Salt of ≥ 12 C atm fatty acid.
* Soap : hydrophilic (head) – lipophilic (tail)
  : Soap they dissolve both water & lipid.



(B) By water



(C) By Enzyme - hydrolysis can be done by adding enzyme lipase to an emulsion of fat in water

(D) By acid - Mineral acid causes hydrolysis of fats, ~~which are obtained by~~ for this mixture of sulphonic acid which are obtained by sulfonation of mixture of oleic acid & benzene.

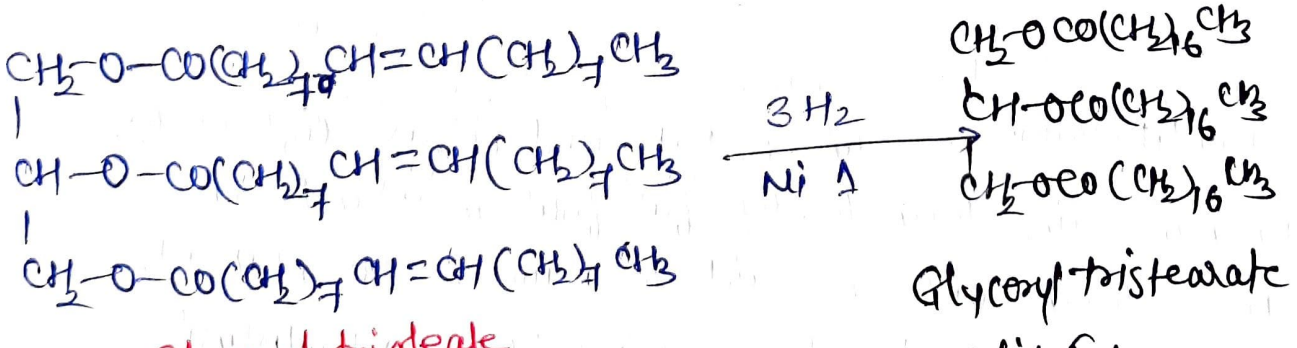
2. Hydrogenation :- Liq oil $\xrightarrow[Ni\ Pressure]{H_2\ gas}$ Semisolid fat

↓

unsaturated fatty acid (Oleic & Linoleic)

——— Saturation (Saturated glyceride)

Hydrogenation process is called "Hardening"



Glyceryl trioleate

Liq veg. oil

MP : −17°C

(Triolein)

Glyceryl tristearate

Solid fat

MP : 54°C

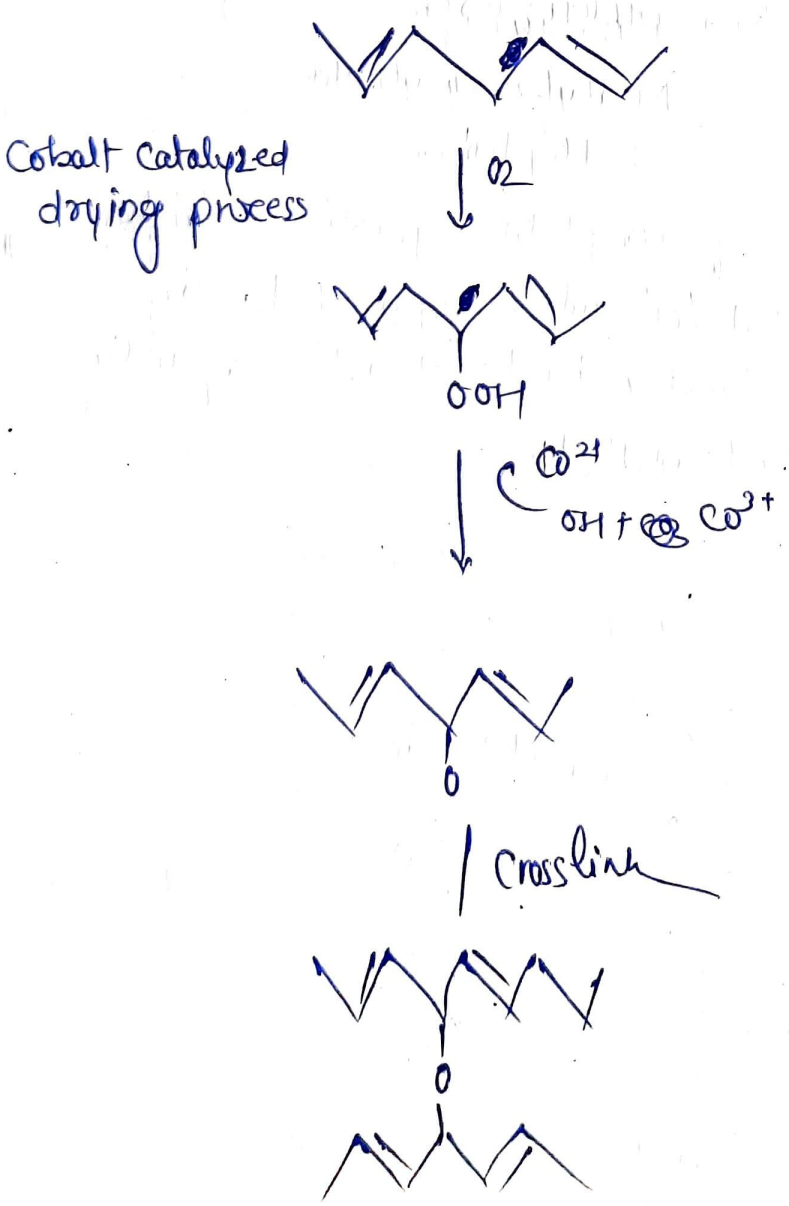
(Tristearin)

Partial Hydrogenation of veg. oil is used for the manufacturing of Vegetable Ghee (Dalda)

Hydrolytic Reaction

$CH_2-O-COR$
$CH-OCOR$ + $3H_2O$ $\xrightarrow[\text{moisture}]{\text{lipase}, \Delta}$ Glycerol + 3 R-COOH
CH_2-OCOR Fatty acid

(5) **Drying of oils** - When highly unsaturated oils are exposed to air, they undergoes oxidation & polymerization to form a thin waterproof film, is called a **Drying oil** & reaction is called as **Drying.**



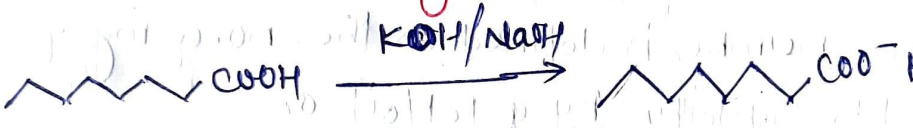
ANALYSIS OF FATS AND OILS

Analytical Constant – Acid Value, Saponification Value, Ester Value, Iodine value, Acetyl value, Reichert Meissl (RM) value

① Acid Value / Acid No. :- Also known as Neutralization No.

- It is defined as the no. of mg of KOH required to complete neutralize free fatty acid present in 1 g of fats/oil

"How much KOH in mg required to neutralize 1 g of Fat (FFA)



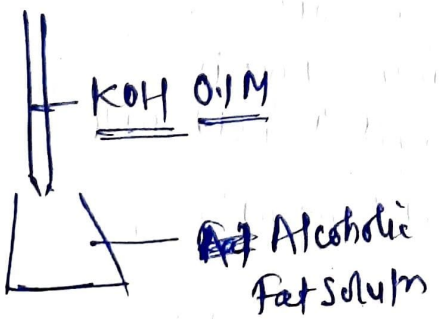
⇒ It is a measure of free fatty acid (FFA) present in fat or oil

⇒ Normally, refined oil should be free from any FFA. Oils on decomposition - due to chemical or bacterial contamination - Yield free fatty acid

Principle:- By direct titration method, oil/fats in alcoholic media are directly titrated against standard potassium hydroxide KOH or Sod. hydroxide (NaOH) Solution

Procedure (i) 1.0 g Fat/oil sample + 50ml of mixture equal vol. of (95%) ethanol & ether (previously neutralized with 0.1 M KOH to phenolphthalein solution)

(ii) Titrated with 0.1 M KOH until colour changes (phenolphthalein used as indicator.



$$\text{Acid Value} = 5.61 \frac{n}{w}$$

n = burette reading (vol. of KOH in ml)

w = Sample weight of fat (g)

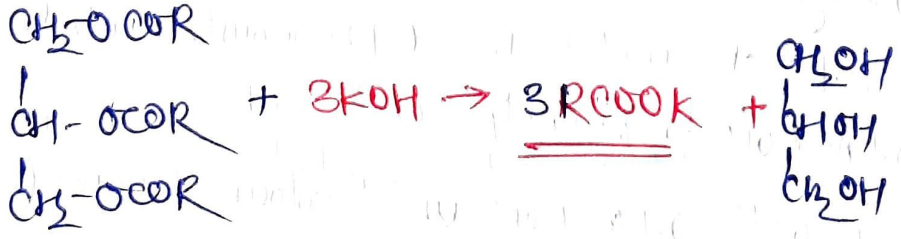
The Acid Value is a measure of amount of FFA which have been liberated by hydrolysis from the glycerides due to action of moisture, temp. & lypolytic enzyme lipase

Significance - (1) High Acid Value indicated that the given sample of fat/oil is of low quality and stored in under improper condition.

B. Saponification Value - Koettstorfer Number

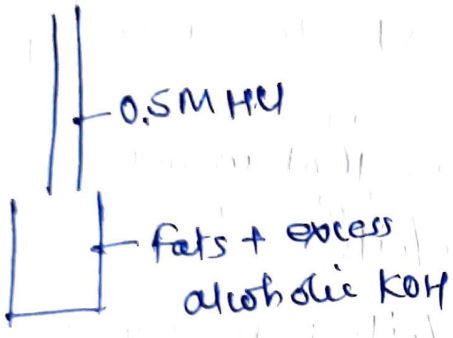
- Saponification number is defined as the no. of mg of KOH required to saponify 1g of fat/oil or
- no. of mg of KOH required to neutralised the fatty acid formed from completed hydrolysis of 1g of fat/oil
- Sap. No. is a measure of avg. mol. wt of fatty acid present

Principle: - Saponification is the process by which the fatty acid in the Triglyceride or fat are hydrolysed by an alkali to give glycerol & potassium salt of fatty acid



- Procedure (1) a known quantity of fat is refluxed with an excess amount of alcoholic KOH
  (2) After Saponification the remaining KOH is estimated by ~~titt~~ titrating it against a std acid (0.5M HCl)
  (3) The obtained value is used to determination of Saponification no.

B.



Mass of fat required = 3 × Mol wt KOH
= 3 × 56 = 168 g of KOH
= 168000 mg of KOH

Sap. No = $\frac{168000}{W}$

OR

$$\text{Saponification Value} = \frac{28.05\,(b-a)}{MW \text{ (M. wt of fat)}}$$

a = back reading (Vol. of burate)
b = Vol. of KOH mixed with fat (blank titration)
W = wt of fat

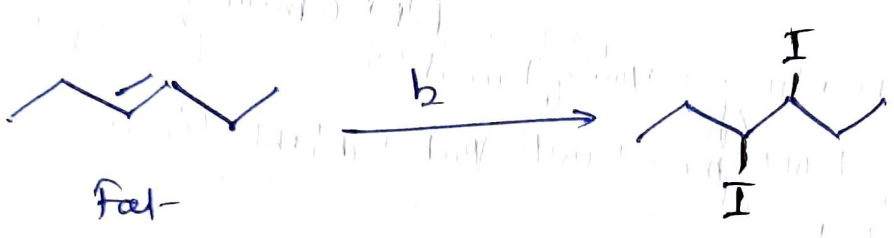
Significance =

1. Sap. value indicates the length of carbon chain of the acid present in that particular fats/oil
2. Sap. value of fat $\propto \frac{1}{\text{M wt of fat}}$
3. higher Sap. value, - greater % of short chain acids not in fat
4. Sap. value Give idea about mol. wt of fats
5.

Examples	Sap. value	Iodine Value
Coconut fat	250-260	8-10
Butter fat	210-230	26-28
Lard	193-200	46-70
Olive oil	187-196	79-90
Sunflower oil	188-194	140-156

C. Iodine No. / Iodine Value

- Define as the no. of gms of iodine that would added to C=C present in 100 g of Fats/oils
- The degree of unsaturation of Fat/oils is measured by its Iodine No.



Fat-

Principle - Back Titration

① Sample of Fat (W) is taken in CCl4 is treated with a known excess of Iodine monochloride solution in glacial acetic acid (Wijs solution)

② Then excess of Iodine monochloride is treated with KI

③ The liberated iodine estimated by titration with 0.1M Sod. thio sulfate solution using starch solution as indicator (back titration)

0.1M $Na_2S_2O_3$
158 gm/l

Fat + excess Iodine monochloride solution

$$\text{Iodine Value} = \frac{1.269\,(b-a)}{W}$$

a = burate reading ml
b = excess vol. of Iodine mono chloride
w = sample wt

Significance

① The Iodine Value is a measure of the amount of unsaturat° (no. of (=)) in fats

② Iodine value ∝ unsaturation (no. of =)

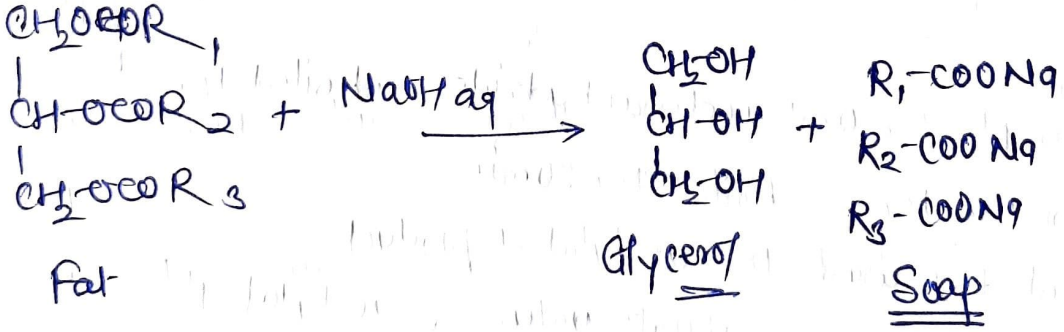
③ Unsaturated lipids are more ~~soluble~~ susceptible to rancidity.

A. ESTER NUMBER (ESTER VALUE)

- Is the no. of mg of KOH required to saponify the ester present in 1g of ~~fat~~ substance.

Ester Value = Saponificat° Value − Acid Value

* Sap. No. − no. mg KOH = hydrolysis of 1g fat
* Acid Value − no of KOH = neutralize FFA in 1g fat



Fat → Glycerol + Soap

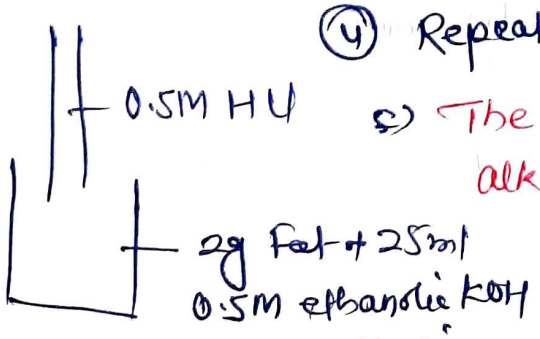
Procedure

① 2g Sample Fat + 25ml, 0.5M ethanolic KOH

② boiled under reflux condenser on a water bath for 1h

③ Add 20 ml of water & titrate the excess of alkali with 0.5M HCl using a further 2ml of phenolphthalein indicator (back)

④ Repeat the procedure with out sample



⑤ The difference b/w the titrats represents the alkali req. to saponify the ester.

Significance :-

The Ester value shows the amount of alkali consumed in saponification of esters and is possible identify & differentiate the fats with this value

E. Acetyl Number (Acetyl Value)

- is the no of mg of KOH required to acetic acid liberated by the hydrolysis of 1g of the acetylated substance

$$\text{Acetyl Value} = \frac{1335(b-a)}{(1335-a)}$$

a = Saponification value

b = Sap. value of the acetylated substance

Procedure -

1. 10g Sample + 20ml acetic anhydride — boiled for 2h
2. + 600ml water — boiled for 30min
3. Seperated & wash the acetylated product
4. determine the saponification value of acetylated substance (b-ml)
5. Determine the saponification value of substance (a)

Significance :

1. It is the measure of hydroxy acid in lipid
2. Increased no. of acetyl value indicates more amount of free fatty acid.

⑥ Reichert-Meissl number (RM value)

- It is defined as the ml of 0.1N KOH required to completely neutralize the soluble volatile fatty acids, distilled from 5g of fat

→ RM value is the useful in testing the purity of butter since it contains a good amt of volatile fatty acid (butyric acid, caproic acid, & caprylic acid)

- RM value range of Butter (25-30), while it is the <1 for most other edible oils. Thus the adulteration of butter can be easily tested by this sensetive RM value

Principle:-

① Fat is saponified using glycerol-alkali solution & acidify with H_2SO_4 to liberated fatty acid.

② The liberated liberated fatty acid are steam distilled & the steam volatile fatty acid are collected (as condensate). The cooled condensate of volatile fatty acid is filtered for seperation of water soluble & water insoluble fatty acid

③ The water soluble fatty acid is titled with alkali to give RM value

④ Water soluble insoluble fatty acid is titrated to give polenske value

Significance:-

① It is a measure of water soluble steam volatile fatty acid chiefly butyric & caproic acid not in oil or fat

② No any other fat contains butyric & glycerides, and therefore the RM value of the butter fat is higher than other fat

③ These determination have been used mostly principally for analysis of butter & Margarines.