ORGANIC CHEMISTRY-II

UNIT 3 NOTES

FATS AND OILS

- FATTY ACIDS - REACTIONS
- HYDROLYSIS, HYDROGENATION, SAPONIFICATION
- ANALYTICAL CONSTANT
  - ACID VALUE
  - SAPONIFICATION VALUE
  - ESTER VALUE
  - IODINE VALUE
  - RM VALUE

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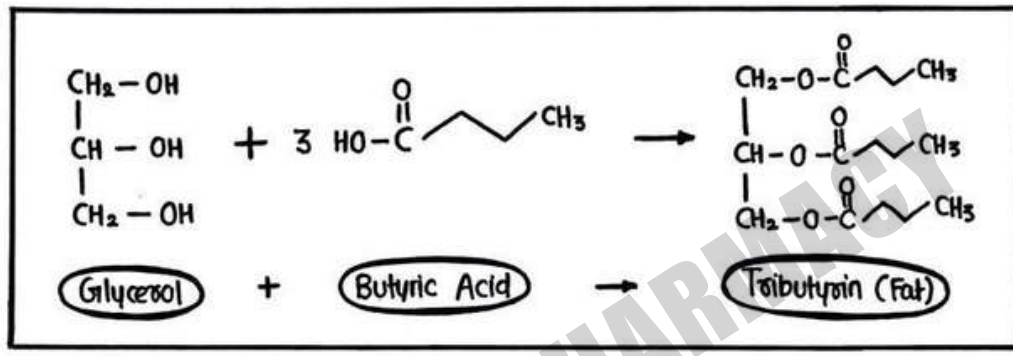
FATS & OILS

- Fats & Oils are the type of Simple Lipids.
- They are the triesters of Fatty Acids & Glycerol.
- They are also known as Triglycerides.
- They are generally insoluble in water but soluble in Organic Solvents.



FATTY ACIDS

- Fatty Acids are long chain hydrocarbons that contains carboxylic acid group at the end
- Fatty Acids are of two types

① Saturated Fatty Acids (Lauric Acid , Palmitic Acid)

② Unsaturated Fatty Acids . (Oleic Acid)

GLYCEROL

- Glycerols are nothing but the type of Alcohol.
- Its IUPAC name is Propane-1,2,3-triol.
- They combines with Fatty Acids to give Fats & oils.

Types Of Fat / Oils

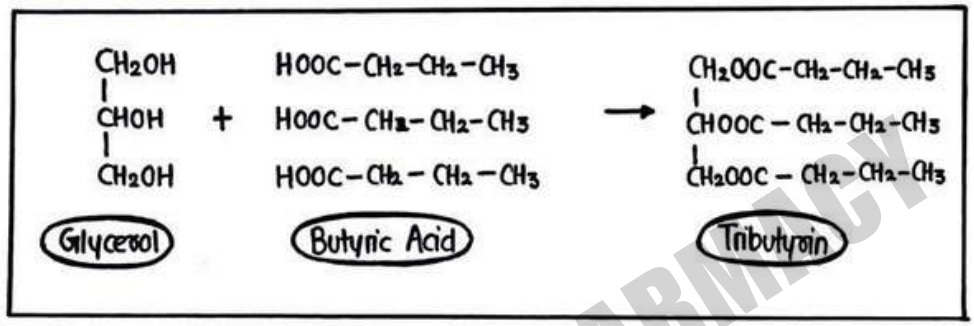
They are of generally two types

① Simple Fats/ Oils

② Mixed Fats/ Oils

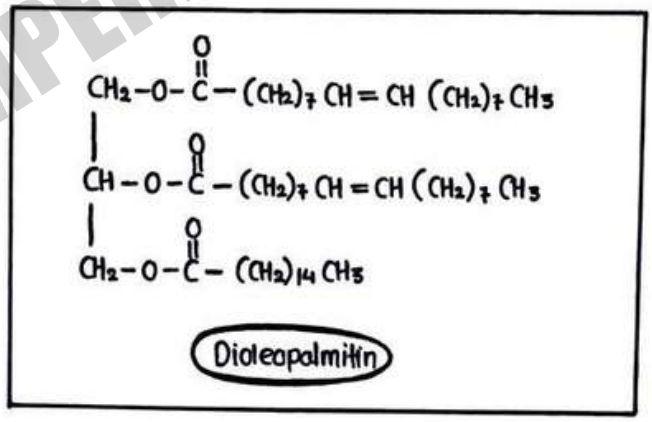
Simple Fat / Oils

When Glycerol combines with 3 same Fatty Acids then resultant Triglyceride is known as Simple Fat/oil.



Mixed Fat / Oil

When Glycerol combines with 3 different Fatty Acids then resultant triglyceride is known as Mixed Fat / Oil.



Difference Between Fat & Oils

Fats	Oils
• Fats are generally solids or semi-solids at room temp. • Fats contains large amount of saturated Fatty Acids • They have high Melting Point > 20°C • They are more stable • Source : Mainly Animals • No Double Bond • Example : Butter, Cream	• Oils are liquids at room temperature. • They contain large amount of unsaturated Fatty Acids. • They have low Melting Point < 20°C • They are less stable. • Source : Mainly Plants. • Have Double Bond • Example : Coconut Oil, Olive Oil.

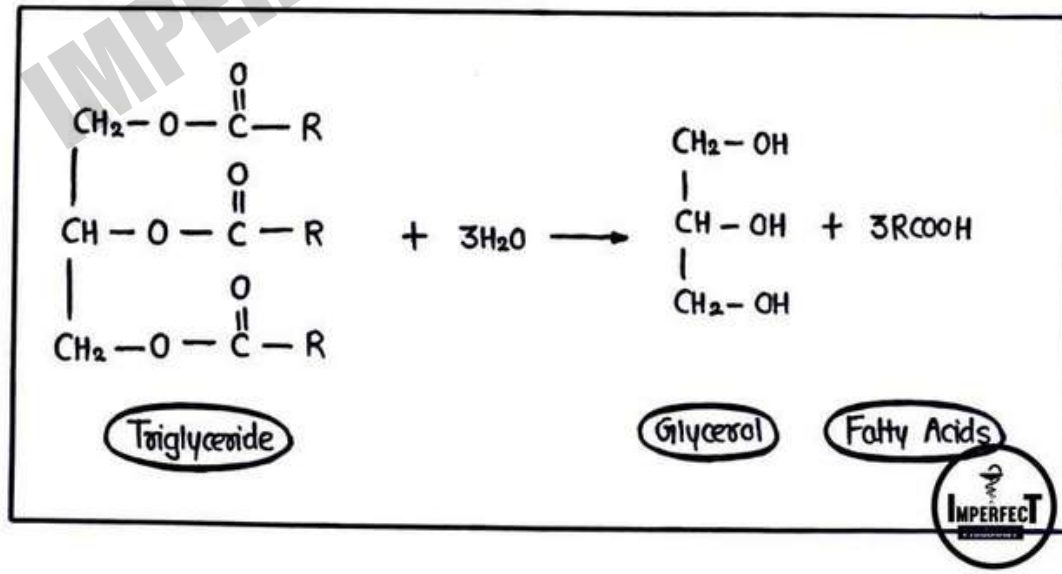
Reactions Of Fat & Oils

Fats & Oils gives following chemical reactions :

① Hydrolysis
② Saponification
③ Hydrogenation
④ Hydrogenolysis
⑤ Rancidification
⑥ Drying

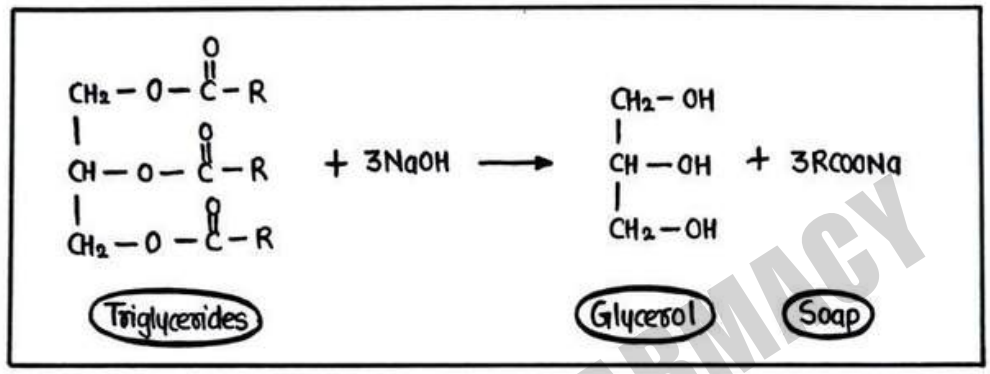
① Hydrolysis

- Hydrolysis of Fats & Oils involves breakdown of triglycerides into Glycerol & Fatty acids through the addition of water.
- In human body, they are hydrolysed by enzyme called Lipase, found in digestive tract of body.
- The Glycerol & Fatty Acids produced are further metabolized for energy through various biological process.



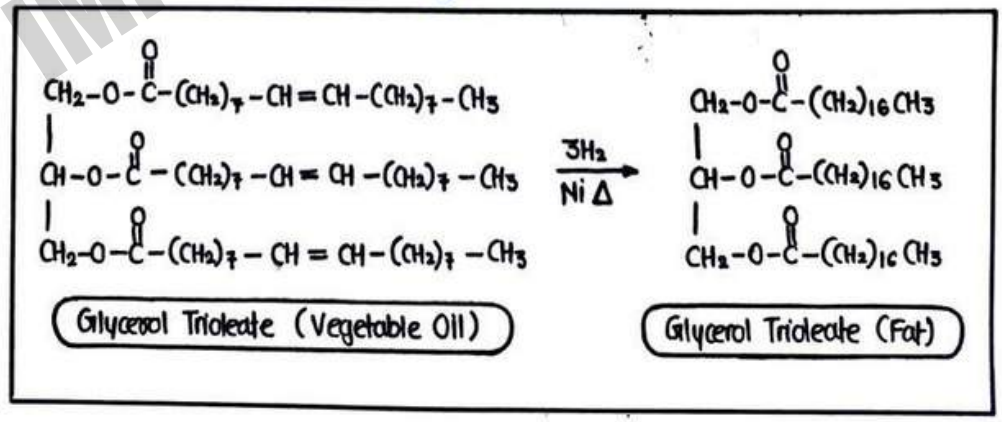
② SAPONIFICATION

- Saponification is also a type of Hydrolysis.
- It is the process of converting Fats & oils into Soap & Glycerol through Hydrolysis
- When Fats & oils are hydrolysed in the presence of strong base like NaOH or KOH, they produce glycerol & soap (salt of Fatty Acids)
- The process is also known as 'Soap Formation'



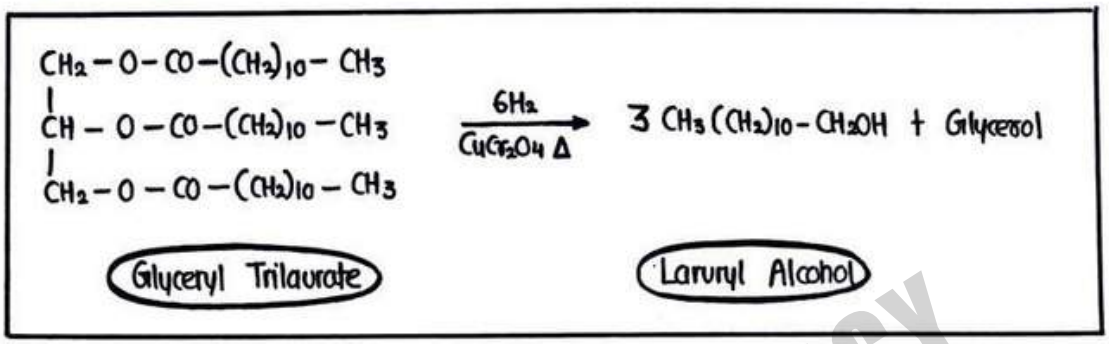
③ HYDROGENATION

- Hydrogenation is the process of converting Unsaturated triglycerides to saturated one by adding hydrogen in the presence of metal catalyst (Ni).
- The process is used for converting Oils into Fats.



④ HYDROGENOLYSIS

- Hydrogenolysis also known as Hydrogenation involving Cleavage.
- Hydrogenolysis involves breakdown of Fats & oils into Glycerol & long chain primary alcohols in the presence of copper chromite catalyst using hydrogen at high temperature.



⑤ RANCIDIFICATION

When Fats & Oils are exposed to heat, light, air or moisture, they develope unpleasant odour & sour taste, the phenomenon is known as Rancidity. Rancid Oils are not consumable.
Rancidity is mainly caused by two types of reactions :

Oxidation : It occurs due to the oxidation of Carbon-Carbon double bonds in fats & oils to produce volatile Carboxylic Acids.

Hydrolysis : It involves hydrolysis of fats & oils to produce Fatty Acids & Glycerols that are responsible for unpleasant taste.

⑥ DRYING

- When highly unsaturated Oils exposed to air, they undergo Oxidation & Polymerization to form a thin waterproof film, Such oils are known as Drying Oils and the reaction is refered as Drying.
- Linseed Oil. which is rich in linolenic acid is a common drying oil used in Oil- based paints.

ANALYTICAL CONSTANTS

The various analytical constants for Fats & Oils are given below :

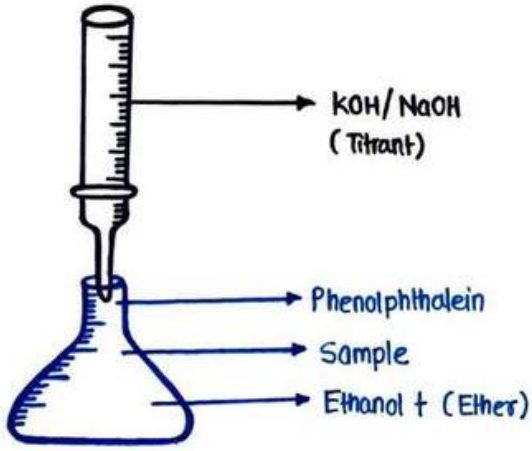
① Acid Value
② Saponification Value
③ Ester Value
④ Iodine Value
⑤ Acetyl Value
⑥ RM Value

① ACID VALUE

- Acid Value is defined as no of mg of KOH required to completely neutralize free fatty acids present in 1 gram of Fat & Oil.
- Normally, Free fatty acids are also present in Fats / Oils, when they kept stored for longer period of time.
- Acid Value is simply measure of FFF (Free Fatty Acids) present in Fat or Oils.
- It is also known as Acid Number.
- Normally, refined oils should be free from any free fatty acids.

Principle

- The Acid Value is determined by titrating the Fat / Oil against KOH / NaOH solution using Phenolphthalein as an indicator.
- 10 gram of sample is dissolved in 50 ml mixture of equal volumes of Ethanol & Ether in the conical Flask.
- Titrate the above solution with 0.1 M KOH solution using phenolphthalein indicator.



Calculation

Acid value can be calculated using following equation

$$\text{Acid Value} = \frac{V_{NaOH} \times N \times 56.1}{W}$$

Here, V_{NaOH} = Volume of NaOH (Titrant) used
N = Normality of NaOH sol.
W = Weight of sample (g)

Significance

- Acid value measures the amount of Free Fatty Acids which have been liberated by hydrolysis due to air, moisture etc.
- Higher acid value indicates that given sample of Fats / Oil are of low quality & stored under improper condition.
- Edible & Pharmaceutical oils should be free from acidity.

② Saponification Value

- The term saponification stands for 'Soap Making'.
- Saponification is defined as number of miligrams of KOH required to convert 1 gram of Fat / Oil into Soap.
- It is also known as Saponification Number.

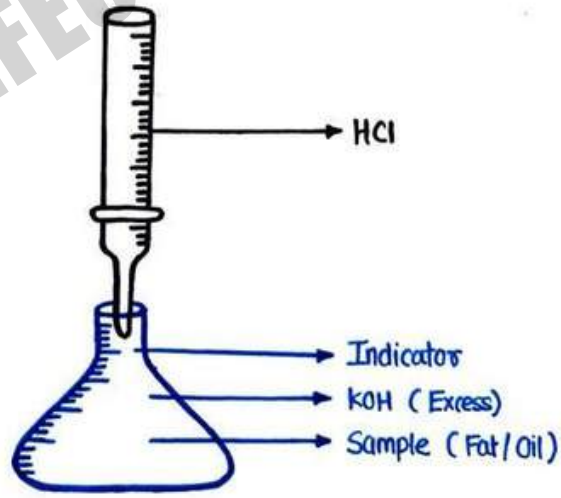
Principle

For the determination of saponification value, we performed two titrations:

① Sample Titration
② Blank Titration

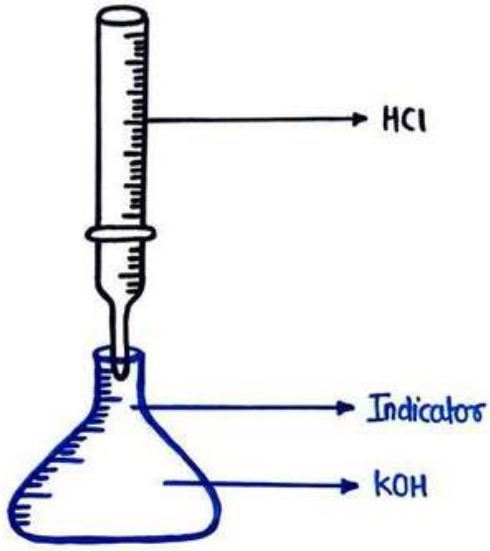
Sample Titration

- First we add an excess amount of Alcoholic KOH to a known quality of oil for soap formation in the conical flask.
- After Saponification, the remaining KOH is determined by titrating it against a standard acid (HCl).



BLANK TITRATION

In blank Titration, we perform the same titration as previous one but without sample.



Determination

Saponification value can be determined using following formula :

$$\text{SAPONIFICATION VALUE} = \frac{28.5 \times (B_{HCl} - A_{HCL})}{W}$$

Here B_{HCl} = Volume of HCl consumed in blank Titration
A_{HCl} = Volume of HCl consumed in Actual (Sample) Titration.
W = Weight of sample taken.

SIGNIFICANCE

- It indicates length of carbon chain of Fatty acids, Higher the S.V., shorter the acid chain present in oil or fat.
- It also gives idea about Average Molecular Weight, Higher the S.V., lower its Molecular weight.

③ ESTER VALUE

- It is defined as number of miligrams of KOH required to saponify the esters in 1 gram of fat or oil.
- In simple words, difference between saponification value and acid value gives the ester value.

Principle

- Ester value is determined in two steps.
- First we perform the titration to determine Acid Value.
- Then we perform the titration to determine Saponification Value.

Determination

Ester value can be determined using following equation :

ESTER VALUE = Saponification Value − Acid Value

SIGNIFICANCE

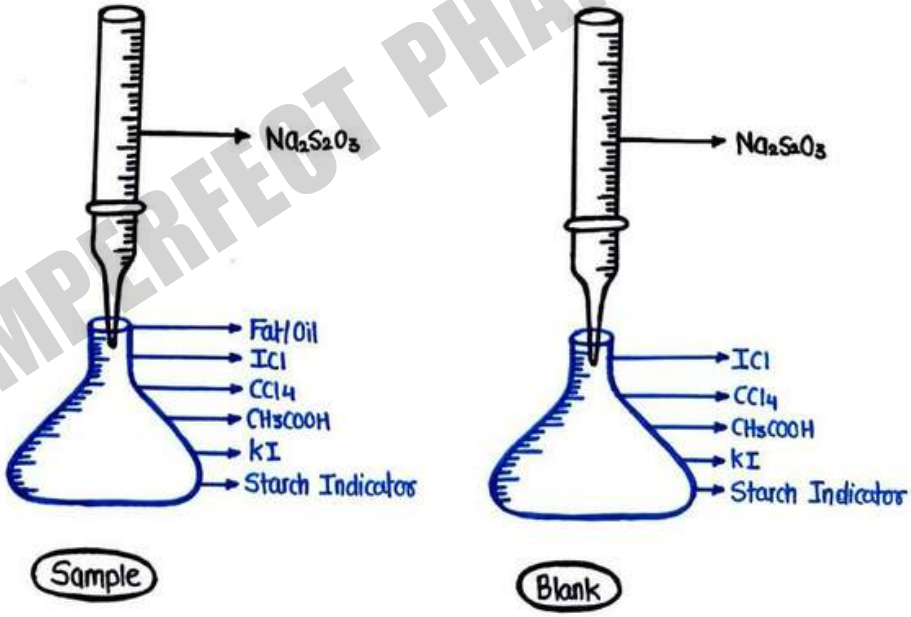
- Ester value is a measure of the amount of esters present in a fat or oil.
- In the analysis of fats & oils, ester value is significant particularly in industries like food & cosmetics, where sensory characteristics of products are crucial.
- High Ester value may indicate a higher concentration of Flavour or Fragrance.

④ Iodine Value

- Iodine value is simply defined as number of grams of iodine absorbed by 100 gram of fat or oil.
- Each oil has its specific Iodine Number.
- It measures the degree of unsaturation of oil / fat.

Principle

- Iodine number is defined by Wijs Method.
- The Oil / Fat sample taken in CCl_4 (Carbon Tetrachloride) & then treated with excess amount of iodine - monochloride solution in Glacial acetic acid.
- Now the remaining iodine monochloride is treated with potassium Iodide
- The liberated iodine is then titrated with sodium Thiosulphate solution.
- The same process is again repeated for blank Titration without sample.
- Starch solution is used as indicator.



Determination

Iodine value can be determined by using given formula:

$$\text{Iodine Value} = \frac{(B-S) \times N \times 12.69}{W}$$

Here, B = Volume of thiosulphate for Blank Titration
S = Volume of thiosulphate for Sample Titration
N = Normality of thiosulphate solution
W = Weight of sample (g)

SIGNIFICANCE

- Iodine value measures the degree of unsaturation of oils.
- Greater the iodine value, more will be unsaturation & higher the susceptibility to oxidative rancidity.
- Low iodine number is desirable in oils.

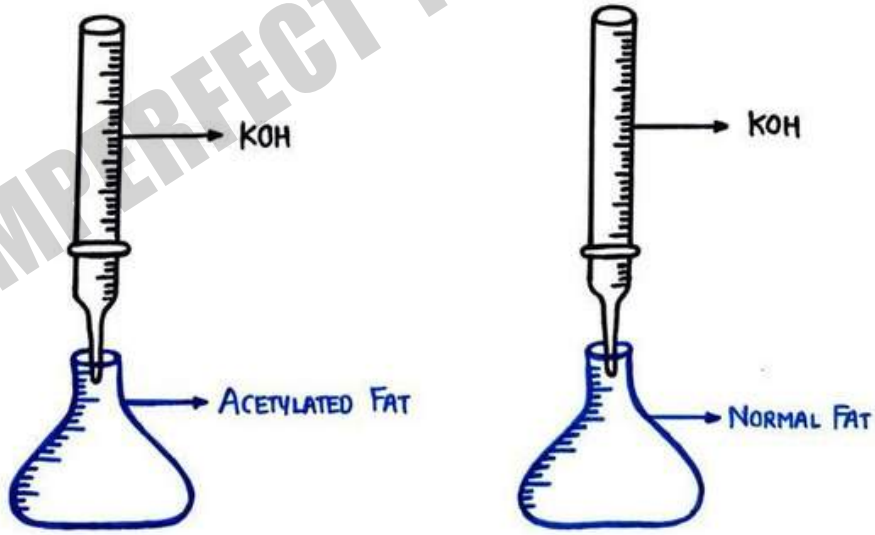
⑤ Acetyl Value

- The Acetyl value is defined as miligrams of KOH required to neutralize the acetic acid produced when 1 gram of Fat / Oil is acetylated with Acetic Anhydride.
- It basically indicates the number of free hydroxyl group present in the substance.

Fat / Oil + Acetic Anhydride $\xrightarrow{\text{Acetylation}}$ Acetic Acid

Principle

- First we acetylating the oil with a measured quantity of acetic anhydride in water & boil the solution.
- After that we titrate the above sample with standard KOH solution.
- Another titration is perform for a normal fat / oil with adding the Acetic Anhydride solution.



Determination

The Acetyl Value can be calculated by given formula:

$$\text{ACETYL VALUE} = \frac{1335\,(b-a)}{1335-a}$$

Here, b = saponification value of acetylated substances
a = saponification value of Fat sample

SIGNIFICANCE

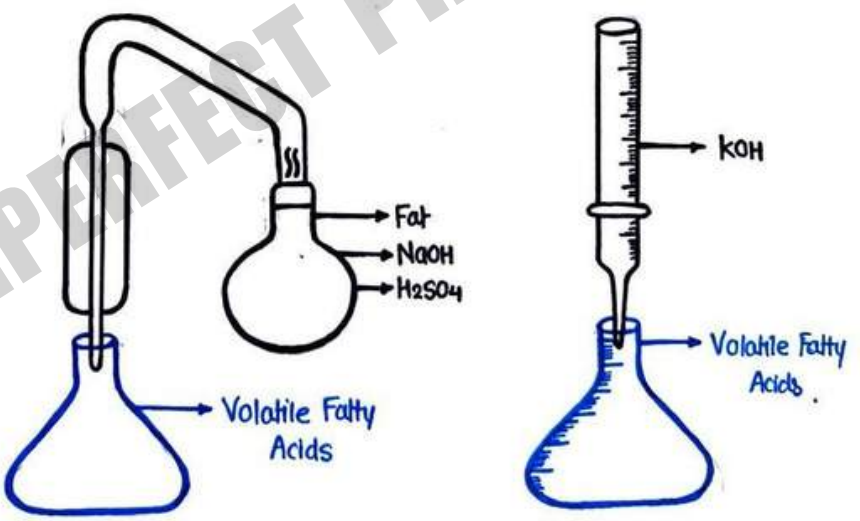
- Acetyl Value is the measure of number of OH groups present in Fat/oil.
- Increased number of Acetyl value indicates more amount of Free Fatty Acids.

RIECHERT - MEISSL (RM) VALUE

- The Reichert - Meissl value is the number of mililitres of 0·1 N KOH required to neutralize the soluble, volatile fatty acids derived from 5 g of Fat or oil.
- The RM value indicates the amount of soluble volatile Fatty Acids present in a given sample of Fat / Oil.

Principle

- The Fat is first saponified by heating with Glycerol Sodium hydroxide solution & then split by treatment with dilute sulphuric acid
- The liberated volatile acids are immediately steam distilled & then condensate.
- The soluble volatile acid is then filtered out & estimated by titration with standard Sodium Hydroxide (KOH) solution.



Determination

RM Value can be calculated by using given formula :

$$\text{RM VALUE} = \frac{\text{Volume of 0.1 N KOH req. to neutralize volatile F.A.}}{\text{Weight of Fat sample (in grams)}}$$

SIGNIFICANCE

- RM Value is useful in testing the purity of butter since it contains a good concentration of volatile Fatty Acids.
- Butter has RM value of range 25-30 while it is less for most other edible oils.
- Thus, any adulteration of butter can be easily tested by RM Value.

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