Unit 6. Carboxylic Acids, Esters, Fats and Oils.

Carboxylic acids are also called Organic Acids. The functional group of carboxylic acids is known as Carboxylic group. The carboxyl group = -COOH = $-\overset{O}{\overset{\|}{C}}-OH$ or $-CO_2H$. It consists the two groups carbonyl group ($-\overset{O}{\overset{\|}{C}}-$) and hydroxyl group (-OH).

→ Monocarboxylic Acids – acids containing only one carboxyl group in their molecules. Eg. CH_3COOH, , etc

→ Acids containing two or more carboxyl group are called polycarboxylic acids.

Eg. Adipic Acid ($HOOC-(CH_2)_4-COOH$,  = phthalic acid (1,2-benzene dicarboxylic acid)

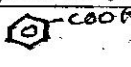
Classes of Carboxylic Acids

1. Saturated monocarboxylic Acids

Many saturated monocarboxylic acids occur in nature as constituents of fats, oils and waxes.

The general formula of monocarboxylic acids (saturated) $R-\overset{O}{\overset{\|}{C}}-OH$. R can be hydrogen, alkyl group.

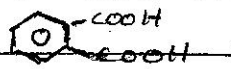
Formula	Common Name	IUPAC Name
$HCOOH$	formic acid (Ant)	methanoic acid
CH_3COOH	acetic acid (Vinegar)	ethanoic acid
CH_3CH_2COOH	propanoic acid	propanoic acid
C_3H_7COOH	butyric acid (butter)	butanoic acid

The simplest aromatic monocarboxylic acid is  benzoic acid

2. Polycarboxylic Acids

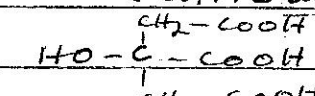
(a) The most common are those containing two carboxyl group (dicarboxylic acids).

1. HO–C(=O)–C(=O)–OH – ethanedioic acid (oxalic acid)
2. HO–C(=O)–CH_2–C(=O)–OH – propanedioic acid (malonic acid)
3. HOOC–$(CH_2)_2$–COOH – butanedioic acid (succinic acid)
4. HOOC–$(CH_2)_3$–COOH – pentanedioic acid (glutaric acid)
5. HOO–$(CH_2)_4$–COOH – hexanedioic acid (adipic acid)
6. HOO–$(CH_2)_5$–COOH – heptanedioic acid (pimelic acid)

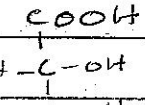
The simplest aromatic dicarboxylic acid is 1,2-benzene-dicarboxylic acid (phthalic acid) = 

(b) Tricarboxylic acid (hydroxytricarboxylic acid)

Eg: 2-hydroxy-1,2,3-propanetrioic acid (citric acid).



Occurs in citrus fruits (oranges, lemons, etc)

(c) 

(dihydroxydicarboxylic acid)

2,3-dihydroxybutanedioic acid (Tartaric acid)

occurs in grapes

Hydroxy carboxylic acid ↓ contain OH group in their molecules. Act as alcohols and as acids.

HO–CH_2–COOH = hydroxyacetic acid (glycolic acid)

CH_3–CH(OH)–COOH = α-hydroxypropionic acid (lactic acid)

HO–$(CH_2)_2$–COOH = β-hydroxypropionic acid

HO–$(CH_2)_3$–COOH = γ-hydroxybutyric acid

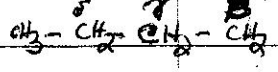
Nomenclature of Carboxylic Acids

Many carboxylic acids are named in the common system (Known by their common names) than by their systematic names (IUPAC). Their common are derived from the sources from which they are obtained.

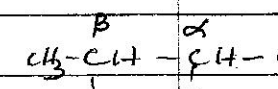
A. Straight chain Monocarboxylic Acids

$HCOOH$	Formic acid	"Ant"
CH_3COOH	Acetic acid	"Vinegar"
CH_3-CH_2-COOH	Propionic acid	"Milk"
$CH_3-(CH_2)_2-COOH$	Butyric acid	"Butter"
$CH_3(CH_2)_3-COOH$	Valeric acid	"Valerian plant"
$CH_3-(CH_2)_4-COOH$	Caproic acid	"Goat"
$CH_3-(CH_2)_{14}-COOH$	Palmitic acid	
$CH_3-(CH_2)_{16}-COOH$	Stearic acid	

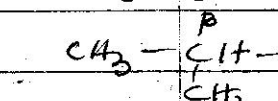
B. Branched chain and Substituted Carboxylic Acids



: α-methylhexanoic acid



: α,β-dimethylbutyric acid



: 2-chloro-β-methylvaleric acid

C. Dicarboxylic Acids

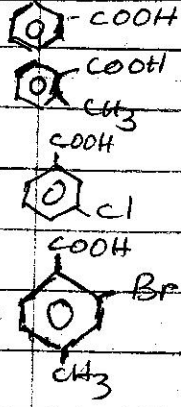
$HOOC-COOH$	Oxalic acid
$HOOC-CH_2-COOH$	Malonic acid
$HOOC-(CH_2)_2-COOH$	Succinic acid

$HOOC-(CH_2)_3-COOH$ Glutaric acid

$HOOC-(CH_2)_4-COOH$ Adipic acid

$HOOC-(CH_2)_5-COOH$ Pimelic acid

D. Aromatic carboxylic acids



Benzoic acid

O-methylbenzoic acid

M-chloro benzoic acid

O-bromo-p-methyl benzoic acid

II. IUPAC Names of Carboxylic Acids

A. Straight Chain Monocarboxylic Acids

$HCOOH$ methanoic Acid

CH_3COOH ethanoic acid

CH_3CH_2COOH propanoic acid

$CH_3-(CH_2)_2-COOH$ butanoic acid

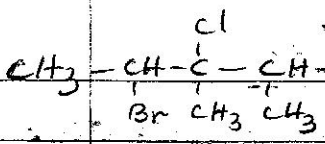
$CH_3-(CH_2)_3-COOH$ pentanoic acid

B. Branched Chain and Substituted Monocarboxylic Acids

$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-COOH$: 3-methylbutanoic acid

$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-COOH$: 2,3-dimethylbutanoic acid

$CH_3-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{Br}{|}}{CH}-COOH$: 2-bromo-3-chlorobutanoic acid



: 4-bromo-3-chloro-2,3-dimethylpentanoic acid

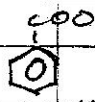
C. Dicarboxylic Acids are named as Alkanedioic Acids

HOOC-COOH — Ethanedioic acid

HOOC-CH_2-COOH — Propanedioic acid

HOOC-$(CH_2)_2$-COOH — Butanedioic acid

D. Aromatic Carboxylic Acids



Benzene Carboxylic acid



2-bromobenzene carboxylic acid



3-bromo-4-chloro-2-methyl benzene carboxylic acid

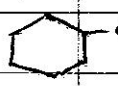
E. Cyclo Alkane Carboxylic Acids



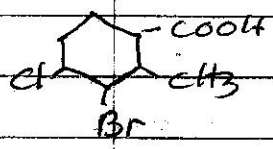
cyclopropane carboxylic acid



cyclopentane carboxylic acid



cyclohexane carboxylic acid



3-bromo-4-chloro-2-methylcyclohexane carboxylic acid

Preparation of Carboxylic Acids

1. Oxidation Primary Alcohols and Aldehydes.

(oxidizing agents: acidified $KMnO_4$ or $K_2Cr_2O_7$ or dilute nitric acid)

$$RCH_2OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} R\text{-}CHO \xrightarrow{[O]} RCOOH$$

(Alcohol) (Aldehyde) Carboxylic acid

Eg. a) $CH_3CH_2OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} CH_3CHO \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} CH_3\text{-}COOH$

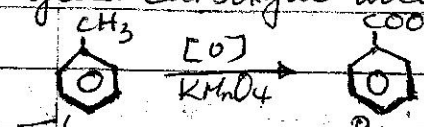
Ethanol — Ethanal — Ethanoic Acid

b) $C_6H_5\text{-}CH_2\text{-}OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} C_6H_5CHO \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} C_6H_5COOH$

Benzoic Acid

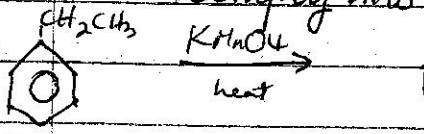
2. Oxidation of Alkyl Benzenes

Alkyl benzenes on oxidation with potassium permanganate yield carboxylic acid.



Toluene — Benzoic Acid

(whatever the length of the attached alkyl groups, it is converted simply into $-COOH$.)



3. Preparation of Acetic Acid (Ethanoic Acid)

Acetic acid is one of the important carboxylic acids. It is used as food preservative. It is prepared in the laboratory by the oxidation of ethanol with $KMnO_4$. It can also by prepared by passing ethanol vapors through copper oxide tube.

Ethanol is manufactured by the fermentation of ethanol by a process Known as Quick Vinegar Fermentation Process.

$$CH_3-CH_2-OH \xrightarrow{[O]} CH_3-COOH$$

FATTY ACIDS

Fatty acids are carboxylic acids with long hydrocarbon chains. Fatty acids are found in all cells. Animal fatty acids more saturated than vegetable fatty acids. Most fatty contain an even number of c-atoms. Fatty acids that contain carbon to carbon single bonds in their hydrocarbon chain are called saturated fatty acid. Fatty acids that contain some (one or more) c to c double bonds are referred to as unsaturated fatty acids.

Examples of naturally occurring fatty acids.

$CH_3-(CH_2)_{10}COOH$	Lauric acid
$CH_3-(CH_2)_{12}COOH$	Myristic acid
$CH_3-(CH_2)_{14}COOH$	Palmitic acid
$CH_3-(CH_2)_{16}COOH$	Stearic acid
$CH_3(CH_2)_{18}COOH$	Arachidic acid

Properties of Carboxylic Acids

1. State : the lower aliphatic acids containing upto 9 c-atoms are liquids while the higher members are colorless waxy solids. Benzoic acid and most of its derivatives are also colorless solids.

2. Odor

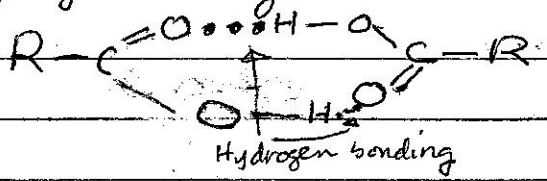
The odors of the lower aliphatic acids progress from sharp irritating odor of methanoid acid and ethanoic acid to the distinctly unpleasant odor of the butanoic, pentanoic and hexanoic acids. The higher acids have little odor. B/C they have very low volatility.

3 Boiling Point

Boiling points of carboxylic are higher than those of the corresponding alcohols, aldehydes and Ketones.

Cpd	Mmass	Name	Boiling Point(K)
CH_3COOH	60	Ethanoic acid	391
$CH_3CH_2CH_2-OH$	60	Propanol	370
$CH_3-CH_2-CH_2-CH_3$	58	Butane	309
CH_3CH_2CHO	58	Propanal	322
CH_3COCH_3	58	Propanone	329

The higher boiling points of carboxylic acids are caused by the hydrogen bonding b/n their molecules.



4 Solubility in Water

As carboxylic acid molecules can associate with water molecules, carboxylic acids are soluble in water. Water solubility of carboxylic acids decreases with increase in molecular mass.

But the solubility of carboxylic acids in organic solvents is not affected as molecular mass increases.

∴ Benzoic acid is sparingly soluble in water.

Chemical Properties of Carboxylic Acids

Chem. rxns. of carboxylic acids are due to the carboxyl group (-COOH).

1. Acidic character of carboxylic Acids

→ Turn blue litmus to red

$$R-\overset{\overset{O}{\|}}{C}-OH(aq) \rightleftharpoons R-\overset{\overset{O}{\|}}{C}-O^-(aq) + H^+(aq)$$

[or $R-\overset{\overset{O}{\|}}{C}-OH(aq) + H_2O(l) \rightleftharpoons R-\overset{\overset{O}{\|}}{C}-O^-(aq) + H_3O^+$)

carboxylate ion

Carboxylic acids are weak acids; about 1% ionized in water.

$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$

1. Reaction with Metals

React with active metals such as Na, K, Mg, Ca, etc forming salt and H_2 gas.

$$2R-\overset{\overset{O}{\|}}{C}-OH(aq) + 2Na(s) \rightarrow H_2(g) + 2RCOO^-Na^+(aq)$$

Eg. $2CH_3COOH(aq) + 2Na(s) \rightarrow H_2(g) + 2CH_3COO^-Na^+(aq)$

sodium acetate

2. Reaction with Bases

React with bases forming salt and water.

$$R-\overset{\overset{O}{\|}}{C}-OH(aq) + NaOH(aq) \rightarrow RCOO^-Na^+(aq) + H_2O(aq)$$

Eg. $CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$

Displace CO_2 from carbonates (bicarbonates)

$2CH_3COOH(aq) + Na_2CO_3(aq) \rightarrow 2CH_3COO^-Na^+ + CO_2(g) + H_2O(l)$

$\rightarrow$ $RCOOH(aq) + NaHCO_3(aq) \rightarrow RCOO^-Na^+(aq) + CO_2(g) + H_2O(l)$

→ React with NH_3 to form an Ammonium salt

$RCOOH(aq) + NH_3(aq) \Rightarrow RCOO^-NH_4^+(aq)$

$CH_3COOH(aq) + NH_3(aq) \Rightarrow CH_3COO^-NH_4^+(aq)$

Ammonium acetate

3. Formation of Esters

Carboxylic Acids react with Alcohols forming Esters and water

$$RCOOH(aq) + R'-OH \rightleftharpoons RCOOR' + H_2O$$

The forward rxn is called esterification and the reverse rxn is called hydrolysis.

Eg. $CH_3-COOH(aq)$ (Acetic Acid) $+ CH_3-OH(aq)$ (Methanol) $\overset{H^+}{\rightleftharpoons}$ $CH_3-COO-CH_3$ (Dimethyl ester) $+ H_2O$

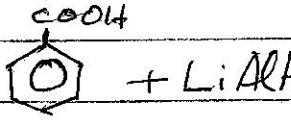
 $+ CH_3CH_2-OH \overset{H^+}{\rightleftharpoons}$? $+ H_2O$

4 Reduction

Carboxylic acids are reduced to primary alcohols when treated with lithium aluminium hydride

$RCO_2H + LiAlH_4 \xrightarrow[H_2O]{ether} RCH_2OH$

$CH_3CH_2COOH + LiAlH_4 \xrightarrow[H_2O]{ether} CH_3-CH_2-CH_2-OH$ - 1-propanol



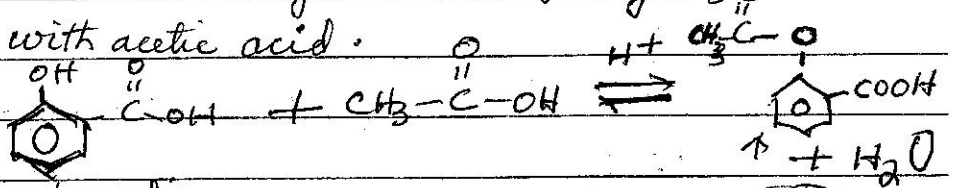
USES of Carboxylic Acids

→ Acetic acid is used as a solvent, and as a starting material in the preparation of acetates, acetic anhydrides

→ Acetic acid also used to prepare Vinyl acetate polymer which is used in paints and adhesives.

→ Vinegar contains about 8-10% acetic acid which is used in many food items.

→ Aspirin the common pain killer, is prepared by the rxn of salicylic acid (2-hydroxybenzoic acid) with acetic acid.



Salicylic acid

Acetyl Salicylic Acid (Aspirin) (ASA)

→ Long chain carboxylic acids are used for making soaps shampoos and detergents.

→ Carboxylic acids are used in the manufacture of greases, crayons, plastics.

→ They are also used commercially as raw materials for the production of synthetic odors and flavors.

ESTERS

Esters occur widely in nature. They are formed by the rxn b/n carboxylic acids and alcohols.

$$RCOOH + HOR' \overset{H^+}{\rightleftharpoons} RCOOR' + H_2O$$

The general formula: $R-\underset{\text{Acid Portion}}{\overset{O}{\overset{\|}{C}}}-\underset{\text{Alcohol Portion}}{O-R}$

Most esters have highly pleasing odors.
Eg. Butyl acetate smells like banana oil (amyl acetate)
Esters are used as solvents, flavoring extracts and perfumes.
- As esters are derivatives of C. acids and alcohols, their names are formed from acid portion and alcohol portion. The first part is the name of the alkyl groups from the alcohol used in the esterification rxn. The second part comes from the acid. The ending of the acid is changed from -oic acid to - oate.

Eg. $CH_3-(CH_2)_2\overset{O}{\overset{\|}{C}}-OH + CH_3-CH_2-OH \rightleftharpoons$

$CH_3-(CH_2)_2-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3 + H_2O$

ethylbutanoate

Formula	Common name	IUPAC Name
$CH_3COOC_2H_5$	Ethyl acetate	Ethyl ethanoate
$HCOOCH_3$	Methyl formate	Methyl methanoate
CH_3COOCH_3	Methyl acetate	Methyl ethanoate
$HCOOCH_2-CH_2-CH_3$	Propyl formate	Propyl methanoate
$C_6H_5COOCH_3$	Methyl benzoate	Methyl benzoate
$HCOOCH_2CH_3$		
$CH_3CH_2COOCH_3$		
$CH_3COOCH_2CH_2CH_3$		
$CH_3COO-C_6H_5$		
CH_3CH_2COO		

Physical Properties of Esters

→ They have pleasant odor

→ B.point of esters increase with increasing molecular mass

→ Branched chain esters have lower b.pt than their straight chain isomers

→ Esters have lower b.points than carboxylic acids and alcohols comparable molecular mass

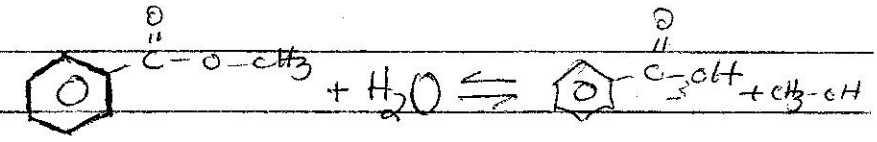
→ Esters of low molecular masses are fairly soluble in water which decreases with increase molecular mass

→ All esters soluble in organic solvents

Chemical Properties of Esters

1 **Hydrolysis**

$$R-\overset{O}{\overset{\|}{C}}-OR' + H_2O \overset{H_3O^+}{\rightleftharpoons} R-\overset{O}{\overset{\|}{C}}-OH + R'-OH$$

Eg. 

→ Base-catalyzed hydrolysis of esters is called **Saponification**.

$$R-\overset{O}{\overset{\|}{C}}-OR' + NaOH \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-O^-Na^+ + R'OH$$

Eg.

$$CH_3-(CH_2)_{16}-\overset{O}{\overset{\|}{C}}-OH + NaOH \rightleftharpoons$$

Methyl octadecanoate $CH_3-(CH_2)_{16}-COO^-Na^+ + CH_3-OH$

Sodium octadecanoate (SOAP)

Saponification = soap forming rxn.

2 **Reduction**

Ester are reduced to primary alcohols.

$$R-\overset{O}{\overset{\|}{C}}-OR' \xrightarrow[H^+]{LiAlH_4} R-CH_2OH + R'OH$$

Example

$$CH_3-(CH_2)_3-\overset{O}{\overset{\|}{C}}-OCH_3 \xrightarrow[H^+]{LiAlH_4}$$

(Methyl pentanoate) $CH_3-(CH_2)_3-CH_2-OH + CH_3-OH$

(1-pentanol) (methanol)

Preparation of Esters

1 Esters are prepared by reacting carboxylic acids and alcohols in the presence of inorganic acid as catalyst.

$$R-\overset{O}{\overset{\|}{C}}-OH + R'-OH \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} R-\overset{O}{\overset{\|}{C}}-OR' + H_2O$$

Example

$$CH_3-\overset{O}{\overset{\|}{C}}-OH + CH_3-CH_2-OH \overset{H_2SO_4}{\rightleftharpoons} CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3 + H_2O$$

ethyl ethanoate

Uses of Esters

Most esters of small acids and alcohols are non-toxic, non-corrosive liquids.

Esters are used

1 as solvents for oils, fats, nail polishes, varnishes, paints, gums and resins.

2 in the preparation of polyesters

3 in the preparation of fragrances in perfumes (good fruity smells), artificial flavors

4 in the preparation of plastizers (octyl phthalate)

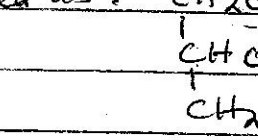
5 in the preparation of medicines.

Some common fruits and the esters responsible for their flavors

Fruit	Ester Present
Apple	Ethyl isovalerate
Pineapple	Methyl butanoate + Ethyl butanoate
Banana	isopentyl acetate
Orange	octyl acetate

Fats and Oils

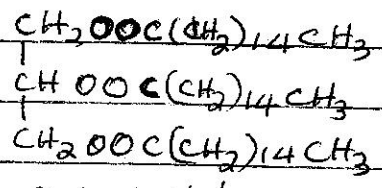
Fats and oils belong to a class of biomolecules called lipids. They are triesters of glycerol. They are called collectively triglycerides. The distinction b/n fats and oils depends on their physical states. If the triglyceride is solid or semi-solid at ordinary temperature; it is fat. If it is fluid it is oil. Fats and oils are widely found in nature, especially in living things. Generally they are represented as:



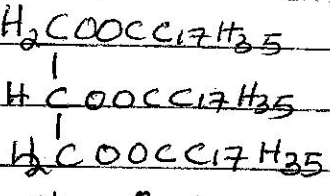
(triester)

R, R' and R'' are parts of higher fatty acids forming ester with glycerol.

Example



Glyceraltripalmitate.



Stearin (Glyceraltrioctadecanoate)
(Glyceraltristreate)

Physical Properties of Fats and Oils

→ They are greasy to touch and have lubricating properties

→ They are not readily volatile and can be burned without leaving and residue.

→ Fats like butter and tallow are solids at room temperature.

→ Oils are liquids at room temperature and are mainly obtained from plants

Eg. cornoil, peanut oil, cottonseed oil, olive oil, soyabean oil, etc.

→ All oils and fats are colorless, odorless, neutral in pure state.

→ They are soluble in organic solvents.

Hardening of Oils

Oils can be converted to fats by catalytic hydrogenation (addition of hydrogen atoms). The process of converting oils to hard fats is known as hardening of oils. This reaction is used in the preparation of margarine.

Soaps and Detergents

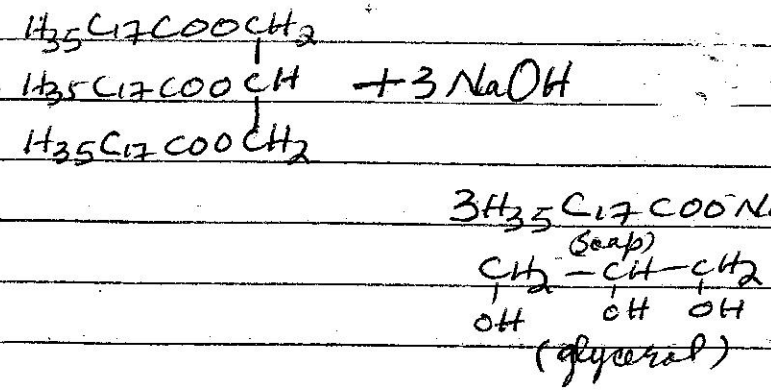
Soaps are sodium and potassium salts of higher fatty acids (long HC chain fatty acids).

They are prepared by the alkaline hydrolysis of oils or fats (Saponification).

Na - salts of higher fatty acids form hard soaps.

K - salts of higher fatty acids form soft soaps (baby soaps)

Detergents are synthetic substances which are used as substitutes to soaps.

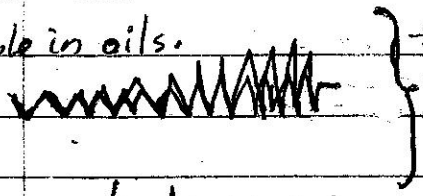


The term detergent is applied to a variety of cleaning materials used to remove dirt (soil + oil) from clothes, dishes and a host of other things.

Surfactant (surface active agent)

Surfactants are cpds that lower the surface tension b/n two liquids, b/n a gas and a liquid, or b/n a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants.

Detergents are surfactants. One end of a surfactant molecule is water soluble and the other (long H.C. chain) is readily soluble in oils.



hydrophobic hydrophillic
(Fat or oil soluble) (Water soluble)

(Saponification is a special case of hydrolysis)
The hydrophobic part of detergents and soaps penetrate dirt and break it into smaller pieces that can float on the surface of the cleaning solution there by making cleaning practicable.
Soaps do not clean in hard water.
Detergents can clean in both hard and soft water.
Soaps do not clean in hard water b/c the $Ca^{2+}_{(aq)}$, Mg^{2+} and other ions present in hard water react with soap forming an insoluble solid (scum) which has no cleaning ability.

$$2\,C_{17}H_{35}COONa^+(aq) + Ca^{2+}(aq) \rightarrow (C_{17}H_{35}COO^-)_2Ca(s) + 2Na^+(aq)$$

(In the other hand detergents clean in hard as well as soft water. B/C they do not form form a hard substance that doesn't clean -

Long chain alcohols when treated with H_2SO_4, produce sulfates with surface active properties.

eg. $C_{12}H_{25}OH + H_2SO_4 \rightarrow C_{12}H_{25}-O-SO_3H + H_2O$.

$C_{12}H_{25}-O-SO_3H + NaOH \rightarrow C_{12}H_{25}-O-SO_3Na + H_2O$

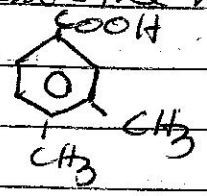
Sodium lauryl sulfate

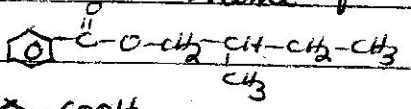
Soaps are basic

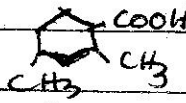
Detergents are neutral

EXERCISE

1 Give the name (IUPAC) 2. IUPAC name of





3. 

4 Which of the following is 2,4-dimethyl heptanoic acid

A) $CH_3-\underset{CH_3}{CH}-\underset{CH_3}{CH}-CH_2-COOH$

B) $CH_3-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-CH_2-COOH$

C) $CH_3-CH_2-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-COOH$

D) $CH_3-CH_2-\underset{CH_3}{CH}-\underset{CH_3}{CH}-CH_2-CH_2-COOH$

5 Which of the following is an ethyl butanoate?

A) $CH_3CH_2CH_2COOCH_2CH_3$ C) $CH_3-CH(CH_3)COOCH_2CH_2-CH_3$

B) $CH_3COOHCH_2CH_2CH_2CH_3$ D) $CH_3-CH_2-COOCH_2-CH_2-CH_3$

6 What are the products of:

$CH_3CH_2COOCH_3 + H_2O \overset{H^+}{\rightleftharpoons}$

7 What is the difference b/n soaps and detergents?

8 What are the products of the base hydrolysis of an ester

9 Write the structural formula of

a) 3-chlorobutanoic acid

b) γ-hydroxybutyric acid

c) Stearic acid

d) 2-hydroxy-1,2,3-propanetrioic acid

10 What is a fatty acid? Give two examples

11 Define

a) Soaponification

b) Hydrogenation

c) Lipid

d) Hardening of oils

12 Write the general structural formula of a fat (oil) molecule.

Rancidity

Fats and oils are reactive substances. When they are exposed to air at high temperatures they spoil (undergo hydrolysis and oxidation). When a fat and oil develop unpleasant smell and flavor, we say they have become rancid. Thus rancidity is due to spoilage (deterioration)