Chapter II

Theory

2.1 Surfactant Theory

Historically , soap , sodium salts of fatty acids , has long been utilized for washing clothes , the face and the body, as well as for industrial and institutional use. After World War II , both laundry and toilet soaps were required for cleanliness and better health. They were produced in greater quantity and quality every year. At the same time , in the USA and Western Europe , a big innovation in the detergent industry began with new synthetic detergents base on alkyl benzene sulfonates and petrochemical products. New synthetic detergents were well accepted by customers because of the properties of easy handling , sufficient detergency even in hard water and scum free rinsing , which were the real defects of fatty acid soaps.

Synthetic surfactants can be synthesized by oleochemical (Fat & Oil) route and/or petrochemical route as shown below. [1]

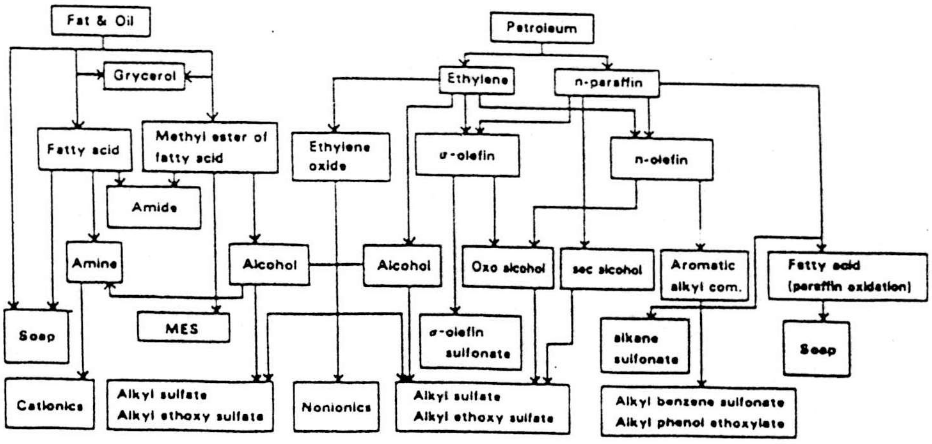
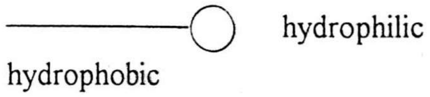


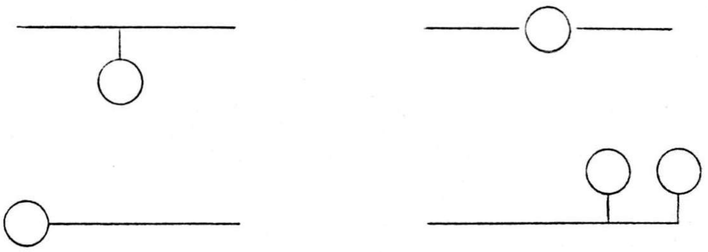
Figure 2.1 Synthetic route of typical surfactants.

2.1.1 Surfactant structure and classification

Surfactant are substances with molecular structures consisting of a hydrophilic and a hydrophobic part. The hydrophobic part is normally a hydro-carbon (linear or branched), e.q. , polyglycol ether groups. [3]



The sequence represents the arrangement of the hydrophilic as well as the hydrophobic part can vary , and is shown here only for as example



Due to this characteristic structure , these compounds have a special property , namely the interfacial activity , that sets them apart from organic compounds in general.

In solvents such as water , the surfactant molecules distribute in such a manner , that concentration at the interfaces is higher than in the inner regions of the solution. This behavior is attributable to their amphilic structure (hydrophilic part ; hydrophobic part)

All the phase borders , an orientating alignment of the surfactant molecules occurs. This results in a change of system properties. , e.q, a lowering of interfacial tension between water and the adjacent phase , a change of wetting properties as well as formation of electrical double layers at the interfaces. Inside the solution , on exceeding of a certain surfactant concentration , surfactant aggregates (micelles) form.

Surfactants are primarily applied in aqueous solution , so that classification by type of hydrophilic group is appropriate.

Classifying the surfactants by hydrophilic group , one differentiates [4]

Anionic Surfactant

Cationic Surfactant

Nonionic Surfactant

Amphoteric Surfactant ;

Anionic Surfactant

Substances are classified as anionic only if the charge on the hydrophobic part is negative . Surfactants in which the hydrophobic part carries no charge unless the pH is elevated to neutrality on above are also categorized as anionic (e.q., carboxylic acids).

Anionic surfactants are further subdivided into five major chemical classes and additional groups.

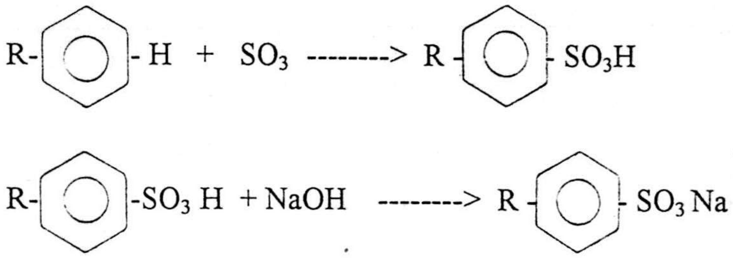
A. Acylamino acid (and salts)
    1. Acylglutamates
    2. Acyl peptides
    3. Sarcosinates
    4. Taurates
B. Carboxylic acids (and salts)
    1. Alkanoic acids (and alkanoates)
    2. Ester carboxylic acids
    3. Ether carboxylic acids
C. Phosphoric acids esters (and salts)
D. Sulfonic acids (and salts)
    1. Acyl isothionates
    2. Alkylaryl sulfonates
    3. Alkyl sulfonates
    4. Sulfosuccinates

E. Sulfuric acids ester

1. Alkyl ether sulfate
2. Alkyl sulfates

Main anionic surfactant which is used mostly in heavy duty (built) detergents is alkylaryl sulfonates (e.q. alkyl benzene sulfonate). Alkylaryl sulfates derived from long - chain alkyl groups foam well and are efficient wetting agents. The sulfonates with short - chain alkyl groups also lower the surface tension. They do not foam well but increase the solubility of other surfactants in the presence of inorganic salts. This property, hydrotropy, is particularly important in heavy duty built detergents. The alkylaryl sulfonates exhibit excellent stability even under adverse conditions.

Linear alkyl benzene sulfonate is produced by the sulfonation of LAB (Linear Alkyl Benzene) with SO_3 or oleum and neutralized with NaOH.



Cationic Surfactant

Substances are categorized as cationic if the charge on the hydrophobic part is positive. Substances in which the hydrophobic part carries no charge, unless the pH is lowered closed to neutrality or lower, also are included in this category of cationic surfactants (e.q., alkylamines)

Cationic surfactant are further subdivided into four major classes :

A. Alkylamine

B. Alkyl imidazolines

C. Ethoxylated amines

D. Quaternaries

1. Akylbenzyldimethylammonium salts
2. Alkyl betaines (and related compounds)
3. Heterocyclic ammonium salts
4. Tetra alkyl ammonium

Nonionic Surfactant

Substances are categorized as nonionic whenever the hydrophobic part carries no charge at the pH at which the amphiphile is normally used in cosmetic products.

Ethoxylation (or polyethoxylation) is a common characteristic of many nonionic surfactants. As a result , many nonionic could be classified as ethers or alcohols. For the sake of simplicity , these chemical functionality of the polyethoxyl groupings are rarely used in the following classification scheme. Nonionic amphiphiles can be chemically subdivided into five major classes and a number of subclasses :

A. Alcohols
B. Alkanolamides
    1. Alkanolamine - derived amides
    2. Ethoxylated amides
C. Amine oxides
D. Ester
    1. Ethoxylated carboxylic acids
    2. Ethoxylated glycerides
    3. Glycol esters (and derivatives)
    4. Monoglycerides
    5. Polyglyceryl esters
    6. Polyhydric alcohol esters and ethers
    7. Sorbitan / Sorbitol esters
    8. Triesters of phosphoric acid
E. Ethers
    1. Ethoxylated alcohols
    2. Ethoxylated lanolin
    3. Ethoxylated polysiloxanes

4. Propoxylated POE ethers
5. Alkylpolyglycosides

Amphoteric Surfactant

Substances are classified as amphoteric only if the charge on the hydrophobic part changes as a function of the pH. Surfactants that carry a positive charge in strongly acidic media, carry a negative charge in strongly basic media, and form Zwitterionic species at intermediate pHs are amphoteric

$[\ RNH_2\ CH_2CH_2COOH\ ]^+\ X^-$ Low pH ; Cationic Hydrophobe

$[\ RNH_2\ CH_2CH_2COO^-\ ]$ Intermediate pH ; Zwitterionic Hydrophobe

$[\ RNH\ CH_2\ CH_2\ COO\ ]^-\ B^+$ High pH ; Anionic Hydrophobe

In these structures X^- represents an unidentified anionic (e.q. Cl^-) and B^+ an unidentified cation (e.q., K^+).

In light of this definition, the number of truly amphoteric surfactants used in cosmetic is quite small. Amphoteric surfactants are subdivided into two major classes .

A. Acyl / dialkyl ethylenediamines and derivatives
B. N - Alkyl amino acids

2.2 Heavy Duty Liquid Detergent

Detergents for the cleaning of laundry textiles, are ideally composed of four major categories. [5]

- surfactant system
- builder system
- bleach system
- enzymatic system

A few additions will be added , such as optical brighteners , sud suppressor, soil suspending agents , perfume , for improved quality and external product appearance.

2.2.1 Surfactant systems

The surfactant systems adopted in a HDL detergent is highly development on the characteristics of the builder system used. However , particular attention has been given by the industry to achieve the most cost efficient surfactant system compatible with the builder technology adopted. The major contribution of surfactant to detergency is to remove greasy / oil type of soils which are largely to being perceived by housewife as one of the most difficult category of stains to remove.

Formula difference from Non - Built HDL and Built HDL

Non - Built HDL [6]	% W	Built - HDL [2]	% W
Alcohol ethoxylate 7EO	30.0	C_{12} LAS	12.2
C_{12} LAS (60 %)	16.7	Alkyl ether ethoxylate	2.8
Triethanomine	3.0	Triethanomine	1.0
Ethanol	5.5	Sodium tripolyphosphate	15.0
Potassium chloride	1.0	Sodium carbonate	5.0
Whitening agent	0.3 - 0.5	CMC	0.2
Water, dye , perfume	q.s.	Whitening agent	0.5
		Water, dye , perfume	q.s.

2.2.2 Builder Systems.

Good detergency requires the neutralization of hard water ions (mainly calcium and magnesium salts) present in the wash water. This sequestration function has traditionally been carried out by the STPP (Sodium Tripoly phosphate) in granular detergents . STPP is an ideal builder because ;

- its sequestration ability of both calcium and magnesium salts ,
- its low cost ,
- its availability in very large quantity at fairly low cost,
- its safety and easiness in use,
- its capacity of giving extra beneficial effects other than its strict sequestration ability (e.q. removal of particulate stains , provision of buffer capacity , contribution to the wash solution's ionic strength, significant contribution in whiteness maintenance ...).
- its significant contribution in making crisp spray drying beats.

Phosphate reduction / ban in granular detergents required for environmental reasons has been mostly realized by the adjunction of alternative inorganic builders (zeolites) and by the incorporation of organic builders at low levels (e.q. NTA, polyacrylates, carboxylic acid, DTPA , etc. ..).

There are two basic type of Heavy Duty Liquids which are referred to as

Non built (or Non structured)
Built (or structures)

The difference between the two technological approaches lies in the fact that " Non Built " products contain a totally soluble builder whereas " Built " formulations are those which contain a partially soluble builder.

The technology associated with " Built " system is really a study of the creation of a storage- stable , pourable suspension of inorganic builder (STPP or zeolite). It has been found that proper suspension of the phosphate / zeolite content can be achieved by using fine particles. Larger particles will segregate thus creating a gel-like non pourable liquid in the bottom part of the HDL bottle.

This approach needs the use of a high speed , high shear mixer which will negatively affect the production rate and the manufacturing cost.

2.2.3 Bleach System

Detergent with bleach systems are useful for special coloring - soil , ink, coffee, tea, juice , etc. The chemical bleaching agents, oxidizing bleach is hypochlorite bleach and peroxide bleach, destroy the chromophoric system or produce a modification of the dye compounds to small units which are water - soluble and therefore more easily removed from the fabrics being bleached.

Now detergent with bleach technology can be split into two approaches, peroxide bleaches and activated peroxide bleach. In relatively soil washing conditions , peroxide alone is an ineffective bleach , since it requires temperatures of at least 60 °C to achieve reasonable bleaching rates. As a result , bleach performance is obtained by combining peroxide bleaches with activated peroxide bleach (tetra acethylethylenediamine , TAED) in a system which reacts in solution to form peracetic acid. This system has improved low temperature (40 - 50 °C) bleach performance , but has increased the prevalence of dye - fading. [7]

2.2.4 Enzymatic System

In 1986, " enzyme " was synonymous with " protease enzyme " and most detergents contained that one enzyme. [8] Protease was supported the surfactant in detergent by catalyze the proteinaceous soil such as stains of milk, cocoa , blood , egg yolk , excrement , grass , etc.

Multiple enzyme systems are now of the technology to extend performance of classical cleaning agents. Lipase and cellulase are the two examples of enzymes.

Lipase is an example of an enzyme that has taken over and extended the role of conventional cleaning agents. In the history , oily soil will removed as the domain of surfactants , primarily nonionic surfactants. However , these surfactants are now supported by lipase , which catalyze the hydrolysis of oily , insoluble triglyceride soil as shown in Figure 2.2 . In this way , oily soil such as salad oil , cosmetics and sebum are converted into soluble , emulsified fatty acids that can be washed away by conventional detergents.

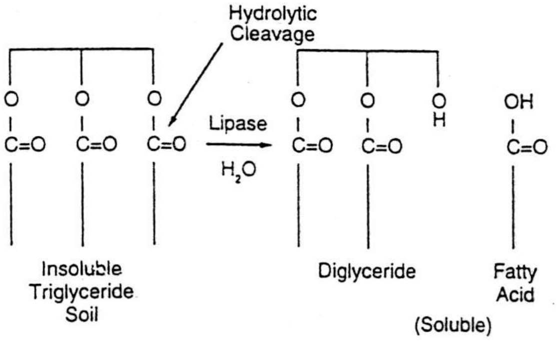


Figure 2.2 The lipase-catalyzed hydrolysis of triglyceride soil

Cellulase , which were first patented in 1970 , are a class of enzyme that catalyzes the hydrolysis of glycosidic linkages in cellulose as shown in Figure 2.3 Cellulase literally extends the life of cotton fabrics by facilitating the removal of the damaged microfibrils that cause cotton fabrics to look worn and faded.

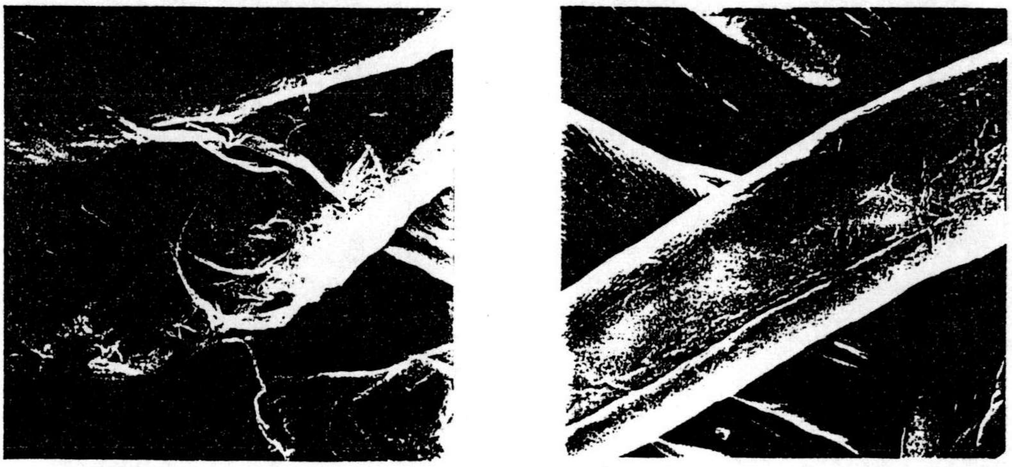


Figure 2.3(a) Cotton (cellulose) fibers damaged by repeated washing (no enzyme)
(b) Cotton fibers after repeated washing with a product containing enzyme

In heavy duty liquid formulation , detergent builder have a destabilize effect of enzyme. Consequently , there are some inventions to improve this problem by using enzyme stabilize system as published in US Pat. , No. 4,652,394 May 24, 1987 [9] and Thai Pat. , No. 1137 May 1, 1987, [2] etc.

2.3 Mixing of Liquid

Mixing is the most common operation in the chemical processing and allied industries . Both heat and mass transfer are greatly influenced by mixing. In fact , mixing is an integral part of all chemical processing. In spite of this , mixing has proved intractable to a rigid theoretical analysis. Thus, in comparison with the move theoretically developed chemical engineering operations , mixing is still regarded as something of an art. Liquids are mixed for a number of purposes , depending on the objectives of the processing step. These purpose include.

1. Suspending solid particles.
2. Blending miscible liquids.
3. Dispersing a gas through the liquid in the form of small bubble
4. Dispersion a second liquid ,immisible with the first,to form an emulsion or suspension of fine drops.
5. Promoting heat transfer between the liquid and a coil or jacket .

Often one agitator serves several purposes at the same time , as in the catalytic hydrogenation of a liquid. In a hydrogenation vessel the hydrogen gas is dispersed through the liquid in which solid particles of catalyst are coil and jacket.

2.3.1 Agitation Equipment

Liquids are most often agitated in some kind of tank or vessel, usually cylindrical in form and with a vertical axis. The top of the vessel may be open to the air, or it may be closed. The proportions of the tank vary widely, depending on the nature of the agitation problem. A standardized design such as that shown in Figure 2.4, however , is applicable in many situations. The tank bottom is rounded, not flat, to eliminate sharp corners or regions into which the fluid currents would not penetrate. The liquid depth is approximately equal to the diameter of the tank. An impeller is mounted on an overhung shaft, i.e., a shaft supported from above. The shaft is driven by a motor , sometimes directly connected to the shaft but more often connected to it through a speed- reducing gearbox. Accessories such as inlet and outlet lines, coils, jackets, and wells for thermometers or other temperature - measuring devices are usually included. [10]

The impeller creates a flow pattern in the system, causing the liquid to circulate through the vessel and return eventually to the impeller.

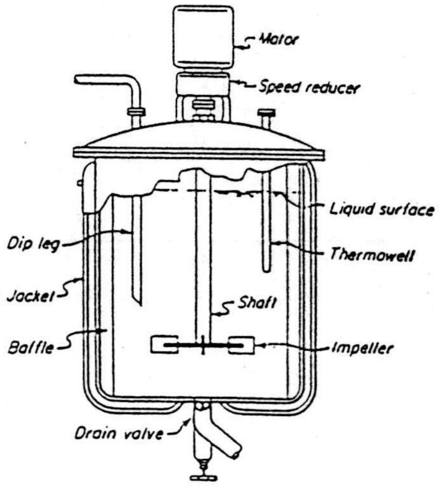


Figure 2.4 Typical agitation process vessel

Impellers

Impeller agitators are divided into two classes : those which generate currents parallel with the impeller shaft and those which generate currents in a tangential or radial direction. The first are called axial - flow impellers, the second radial - flow impellers.

The tree main types of impellers are propeller, paddles , and turbines. Each type includes many variations and subtypes . Other special impellers are also useful in certain situations, but the three main types solve perhaps 95 percent of all liquid - agitation problems.

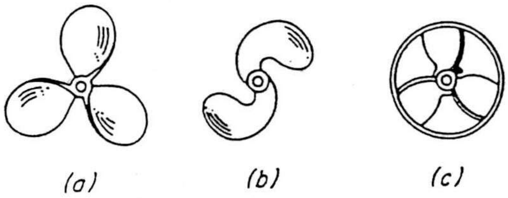


Figure 2.5 Mixing propellers :

(a) standard three blade ; (b) weedless; (c) guarded

Propellers

A propeller is an axial - flow , high - speed impeller for liquids of low viscosity. Small propellers turn at full motor speed, either 1,150 or 1,750 r/min. ; larger ones turn at 400 to 800 r/min. The flow currents leaving the impeller continue through the liquid in a giving direction until deflected by the floor or wall of the vessel. The highly turbulent swirling column of liquid leaving the impeller entrains stagnant liquid as it moves along, probably considerably more than an equivalent column from a stationary nozzle would. The propeller blades vigorously cut or shear the liquid. because of the persistence of the flow currents, propeller agitators are effective in very large vessels.

A revolving propeller traces out a helix in the fluid, and if there were no slip between liquid and propeller, one full revolution would move the liquid longitudinally a fied distance depending on the angle of inclination of the propeller blades. The ratio of this distance to the propeller diameter is known as the pitch of the propeller. A propeller with a pitch of 1.0 is said to have square pitch.

Various propeller designs are illustrated in Figure 2.5 Standard three-bladed marine propeller with square pitch are most common; four - bladed, toothed, and other design are employed for special purposes.Propellers rarely exceed 18 in. in diameter regardless of the size of the vessel. In a deep tank two or more propellers may be mounted on the same shaft, usually directing the liquid in the same direction. Sometimes two propellers work in opposite direction , or in " push - pull, " to create a zone of especially high turbulence between them.

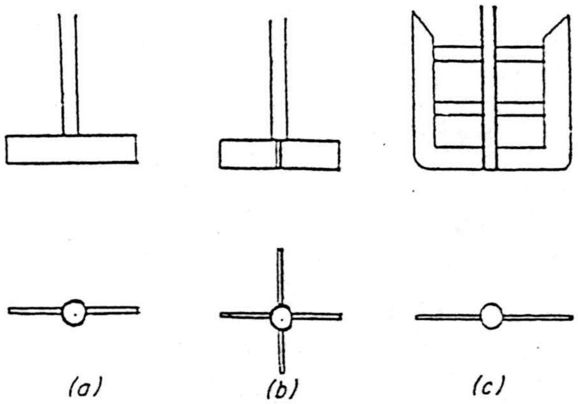


Figure 2.6 Paddle Impeller

(a) two-blade paddle (b) four-blade paddle
(c) anchor or gate paddle

Paddles

For the simpler problems an effective agitator consists of a flat paddle turning on a vertical shaft. Two - bladed paddle and four - bladed paddles are common. Sometime the bladed are pitched ; more often they are vertical. Paddles turn at slow to moderate speeds in the center of a vessel ; they push the liquid radially and tangentially with almost no vertical motion at the impeller unless the blades are pitched. The currents they generate travel outward to the vessel wall and then either upward or downward. In deep tanks several paddles are mounted one above the other on the same shaft. In some designs the blades conform to the shape of a dished or hemispherical vessel so that they scrape the surface or pass over it with close clearance. A deposit on a heat - transfer surface, as in conjunction with a higher - speed paddle or other agitator, usually turning in the opposite direction.

Industrial paddle agitator turn at speeds between 20 and 150 r/min. The total length of a paddle impeller is typically 50 to 80 percent of the inside diameter of the vessel. The width of the blade is one - sixth to one - tenth its length. At very slow speeds a paddle gives mild agitation in an unbaffled vessel ; at higher speeds baffles become necessary . Otherwise the liquid is swirled around the vessel at high speed but with little mixing.

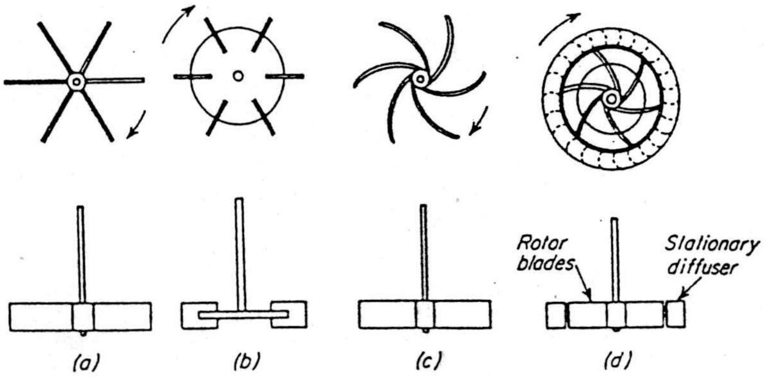


Figure 2. 7 Turbine impellers :

(a) open straight blade ; (b) bladed disk ; (c) vertical curved bladed; (d) shrouded curved blade with diffuser ring.

Turbines

Some of the many design of turbine are shown in Figure 2.7 . Most of them resemble multibladed paddle agitators with short blades., turning at high speeds on a shaft mounted centrally in the vessel. The blades may be straight or curved, pitched or vertical. The impeller may be open, semienclosed, or shrouded. The diameter of the impeller is smaller than with paddles, ranging from 30 to 50 percent of the diameter of the vessel.

Turbines are effective over a very wide range of viscosity. In low - viscosity liquids turbines generate strong currents which persist throughout the vessel, seeking out and destroying stagnant pockets. Near the impeller is a zone of rapid currents, high turbulence, and intense shear. The principal currents are radial and tangential. The tangential components induce vortexing and swirling , which must be stopped by baffles or by a diffuser ring if the impeller is to be most effective.

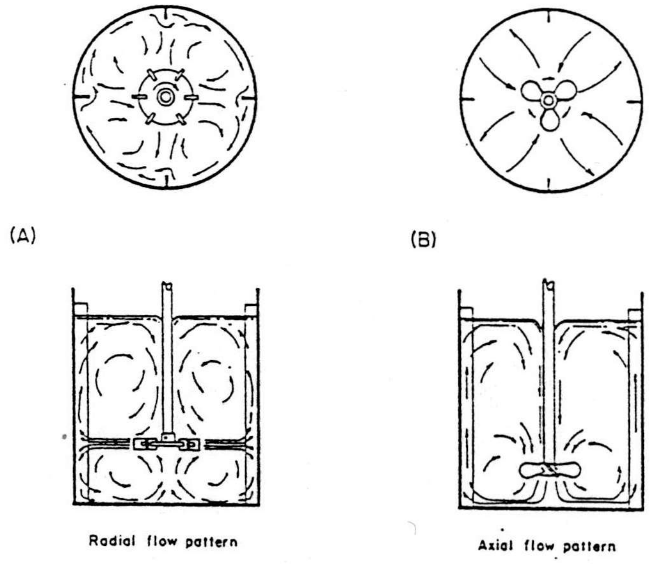


Figure 2.8 Radial and axial flow patterns.

2.3.2 Flow patterns

Agitators are used to produce flow and, subsequently, turbulence in a liquid mass. Each type of agitator cause high velocity liquid to flow through a vessel in a specific path , referred to as a flow pattern. Flat and curved blade turbines, mixing low or moderate viscosity liquids , produce radial flow patterns when used in a baffled vessel. Radial flow, shown in Figure 2.8(A) , is primarily perpendicular to the vessel wall.

The marine type propeller and pitched blade turbine produce axial flow patterns when centered in a baffled vessel containing low or moderate viscosity liquids. Axial flow, shown in Figure 2.8(B), is primarily flow parallel to the tank wall.

2.3.3 Standard Tank Configuration

The vessel configuration, shown in Figure 2.9 and known as the Standard Tank Configuration [11], provides adequate mixing for most processing requirements found in industry. However , it should be stressed that the Standard Tank Configuration an arbitrary which in some circumstances is not the best configuration to use. For special processing conditions such as mixing liquid with a high solids content, a high viscosity or a shear sensitive character this configuration may be impractical.

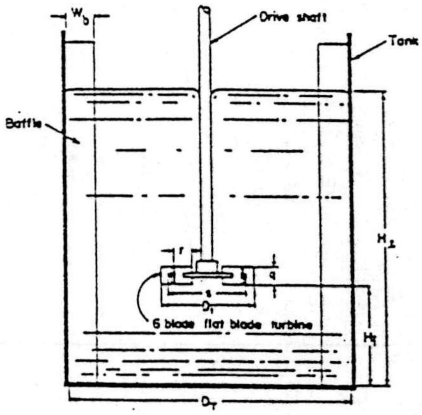


Figure 2.9 Standard Tank Configuration.

The Standard Tank Configuration has the following geometrical relationships ;

(1) The agitator is a 6 blade flat blade turbine impeller.
(2) Impeller diameter Di = 1/3 tank diameter Dt.
(3) Impeller height from the tank bottom Hi = 1.0 impeller diameter.
(4) Impeller blade width q = 1/5 impeller diameter.
(5) Impeller blade length r = ¼ impeller diameter.
(6) Length of impeller blade mounted on the central disk s = r/2 = 1/8 impeller diameter.
(7) Liquid height Hl = 1.0 tank diameter.
(8) Baffle number = 4, vertically mounted at the tank wall and extending from the tank bottom to above the liquid surface.
(9) Baffle width Wb = 1/10 tank diameter.

An analogous standard Tank Configuration may be used with other agitator types.

2.4 Mixing in Solid - Liquid Systems

The main objectives of mixing in solid - liquid system can be classified into two categories, uniform suspension of solid particles in liquid and reduction of diffusion resistance around solid particles. There are many significant factors in the design of an affective mixer for suspending a slurry homogeneously , vessel geometry , impeller instruction and operating speed .

The properties of solid - liquid systems also affect uniformity of solid suspension : [12]

1. particles density.
2. solids concentration
3. density of liquid phase
4. size, size range, and shape of solid particles,
5. viscosity of liquid phase and
6. hindered setting as a corollary to solid concentration and density of liquid phase.

2.4.1 The Degree of Mixing

The degree of mixing within a system is a function of two variables : the magnitude of eddy currents or turbulence formed and the force tending to dampen this formulation. The higher the ratio of applied to dampening forces, the higher is the degree of mixing. This relationship may be expressed in the well - known rate equation :[11]

$$\frac{\text{Driving Force}}{\text{Resistance}} = \text{Flow or Rate} \qquad (2\text{-}1)$$

Driving Force = the force producing eddy currents or turbulence.

Resistance = the force tending to dampen the formation of eddy currents or turbulence

Flow or rate = the degree of mixing

A high degree of mixing occurs when the entire liquid mass, confirmed in a vessel, is under turbulent flow conditions .

2.4.2 Mixing as a function of viscosity

Liquid viscosity affects the flow created by a rotating agitator. Viscosity is the property of a liquid to resist flow or a change in shape through internal forces and molecular attraction . The more viscosity a liquid, the greater is the quantity of energy required to produce a desired state of flow. Low viscosity liquids show little resistance to flow and therefore require relatively small amounts of energy per unit volume for a condition of mixing to occur . High viscosity liquids dampen the mechanical energy transmitted from a rotating agitator and require relatively large quantities of power per unit volume to reach a state of flow great enough for adequate mixing to occur.

The classification of mixing equipment is usually made on the basis of liquid viscosity Figure 2.10 shown the recommended viscosity ranges for a number of common agitator types.

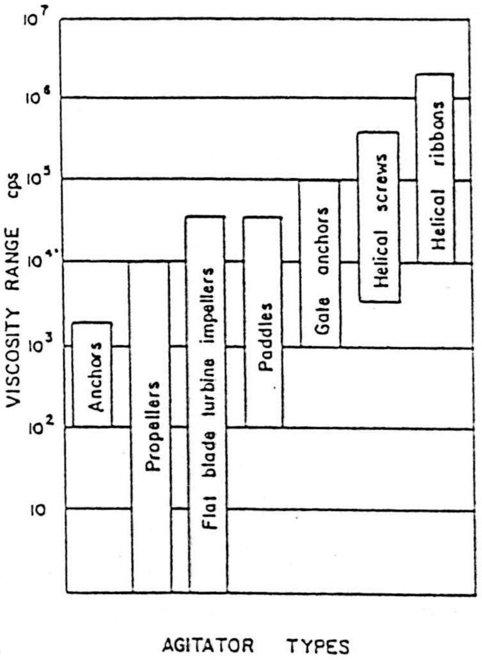


Figure 2.10 Viscosity range for agitator