# Chapter I

# INTRODUCTION

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The word surfactant derived from the contraction of the terms surface-active-agent and covers a group of molecules which are able to modify the interfacial properties of the liquids (aqueous or nonaqueous) in which they are present. The peculiar properties of these molecules reside in their amphiphilic character which stems from the fact that each surfactant molecule has both a hydrophilic part and a hydrophobic (lipophilic) part. As a result, they concentrate at the interfaces separating immiscible phases, thereby decreasing the interfacial tension.

Surfactants have the property of micelle formation that may be as fundamental as their property of being adsorbed at interfaces. It's the property of forming colloidal sized clusters in solution. Micelle formation, or micellization, is an important phenomenon not only because a number of important interfacial phenomena, such as detergency and solubilization that depend on the existence of micelles in solution, but also because it affects other interfacial phenomena, such as surface or interfacial tension reduction, that don't directly involve micelles ***(Hiemenz, P.C., et al, 1997)***. Changes in temperature, concentration of surfactant, additives in the liquid phase and structural groups in the surfactant all may cause change in the size, shape, and aggregation number of the micelle, with a structure varying from spherical through rod- or disk like to lamellar in shape ***(Winsor, P.A., 1968)***. It is well known that the physico-chemical properties of surfactants vary markedly above and

below a specific surfactant concentration that is called critical micelle concentration (CMC) (***Myers, D., 1988 and Krawezyk, M. A., et al, 1991).*** CMC values are important in virtually all of petroleum industry surfactant applications, where a surfactant must usually be present at a concentration higher than the CMC because the greatest effect of the surfactant, whether in interfacial tension lowering (***Shramm, L.L., 1994***) or in promoting foam stability (***Rieger, M.M., et al, 1997***), is achieved when a significant concentration of micelles is present.

## I.1. Classification of Surfactants

Depending on the nature of the hydrophilic moiety of the molecule, major surfactants can be divided into anionic, cationic, amphoteric, and nonionic classes. Regarding the hydrophobic moiety of the molecule, it is a hydrocarbon chain in most common surfactants; however, in some more specialized surfactants, this hydrophobic part can be a nonhydrocarbon chain such s a polydimethylsiloxane or a perfluorocarbon.

### I.1.1. Ionic Surfactants

#### I.1.1.1. Anionic Surfactants

By definition, the hydrophilic part of the molecule carries a negative charge.

##### I.1.1.1.1. Carboxylic Acids and Salts

This group of surfactants includes three classes; first, carboxylic acids which derived from oleochemistry,

carboxylates salts can be produced by alkaline hydrolysis of animal and vegetable glycerides or from neutralization of fatty acids obtained by acidification of carboxylates, fatty acid salts show good water affinity. Ester carboxylic acids are the second class, they are monoesters of di- and tricarboxylic acids. These esters are produced by condensation reactions involving different types of molecule; either an alcohol with a polycarboxylic acid, or a hydroxyacid with a carboxylic acid, they show good foaming properties. The third class is ether carboxylic acids, they are formed by the reaction of sodium chloracetate with ethoxylated alcohols. Due to the addition of ethoxylated groups, they are more soluble in water and keeping the best properties of nonionic surfactants, where they do not exhibit any cloud point and show good wetting and foam stability.

R-COONa  RO-(CH$_2$CH$_2$O)n-CH$_2$-COONa

### I.1.1.1.2. Sulfuric Acid Derivatives

This group of surfactants contains two main types; the first one is alkyl sulfates, they are organic esters of sulfuric acid where the sulfur atom is bridged to carbon atom of the hydrocarbon chain via an oxygen atom. They are produced by sulfation of the corresponding fatty alcohols, the process is achieved by using either sulfuric acid, chlorosulfonic acid, amidosulfonic acid, or a gaseous sulfur trioxide/air mixture. They are generally good foamers, show excellent oil/water emulsifying and detergency properties. Alkyl ether sulfates are the second type, they are resulting from the sulfation of an ethoxylated

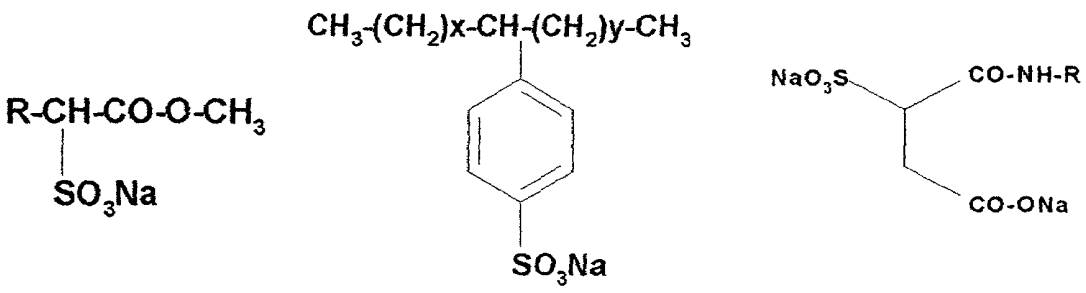
alcohol. Compared to alkyl sulfates, the alkyl ether sulfates show higher water solubility and, depending on the ethoxylation degree and they show foaming characteristics slightly lower than the corresponding alkyl sulfates.

$R\text{-}CH_2\text{-}O\text{-}SO_3Na$ $RO\text{-}(CH_2CH_2O)n\text{-}SO_3Na$

### I.1.1.1.3. Sulfonic Acids and Salts

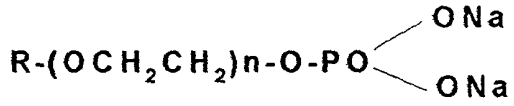
There is an important difference between the above alkyl sulfates and the alkyl sulfonates. In the latter, the sulfur atom is directly linked to the carbon atom. The C-S bond makes sulfonates not prone to hydrolysis and they can be stored in a concentrated sulfonic acid form. The sulfonating agents are the same as those used in the sulfating reaction (chlorosulfonic acid, oleum, or gaseous sulfur trioxide); at variance, the sulfonation takes place on a hydrogen atom directly linked to a carbon atom. Sulfonic acids and salts are divided to five groups; the first is alkyl sulfonates, which includes primary and secondary paraffin sulfonates and α-olefin sulfonates. paraffin sulfonates are generally formed by sulfoxidation of n-paraffins, they are very water soluble surfactants, good foamers, and good O/W emulsifiers. α-Olefin sulfonates derive from α-olefins that come from ethylene (Ziegler process) are preferred over those from petroleum cracking. The major sulfonation process uses sulfur trioxide as the reactant. The second type is alkyl aryl sulfonates, Linear chains are preferred over the branched ones due to their improved biodegradability, linear olefins or chlorinated straight chain paraffins with benzene in the presence of Friedel-Crafts-type

catalysts ($AlCl_3$ or HF) yields linear alkylbenzene (LAB). The sulfonation of LAB can be achieved using oleum, sulfuric acid, or gaseous sulfur trioxide. The sulfonate is obtained after neutralization of the sulfonic acid with an appropriate base. They exhibit good chemical and thermal stabilities, and used as emulsifiers, foaming, and dispersing agents. Sulfosuccinates are the third type, they generally result from the condensation of maleic anhydride with fatty alcohol, followed by sulfonation with sodium bisulfite ($NaHSO_3$). When using equimolar ratios, monoesters are obtained, whereas with excess alcohol, diesters are obtained. Disodium salts of monoesters deliver good detergency and foam properties. The forth type is sulfo fatty acid esters, the α-sulfo fatty acid esters that have the sulfonate group linked to the carbon adjacent to the ester, and the ψ-sulfo fatty acid esters which have an internal sulfonate group statistically distributed along the carboxylate chain. Finally, fatty acid isethionates and taurides, where isethionates are prepared by the reaction of a fatty acid chloride with sodium isethionate, and show good wetting, foaming, and emulsifying properties. But, taurides or taurates are acylamino alkane sulfonates, they are prepared by the reaction of a fatty acid chloride with N-methyl taurine, they show good foaming and emulsifying properties.



### I.1.1.1.4. Phosphoric Acid Esters and Salts

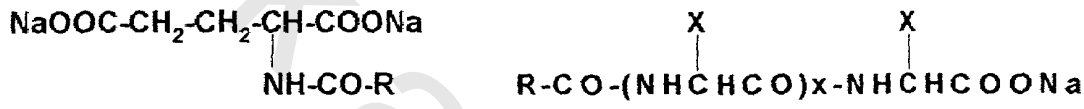
This class of surfactants includes alkyl phosphates and alkyl ether phosphates. These surfactants are produced by the reaction of fatty alcohols with two possible phosphating agents: orthophosphoric acid and phosphorus pentoxide. Resulting surfactants are mixtures containing mainly mono and dialkyl phosphoric acid esters; additionally, a small amount of unreacted phosphoric acid and unconverted alcohol. The sodium salts of alkyl phosphoric acid esters are readily water soluble and not affected by water hardness. When esterification is achieved with ethoxylated alcohols, it is possible to obtain a fine adjustment of the HLB and thereby vary the water solubility and wetting efficacy. Phosphate esters derived from straight alcohols remain stable at an extreme pH. Ethoxylated phosphate esters are only subjected to hydrolysis under acidic conditions. Phosphate esters show excellent heat stability. They impart antistatic and anticorrosion properties to the substrates on which they are adsorbed. Those with short alkyl chain exhibit hydrotropic properties.




### I.1.1.1.5. Acylamino Acids and Salts

This class of surfactants includes three groups; acyl glutamates which formed by the acylation of a natural amino acid, the acyl glutamates contain an amide function which can be hydrolyzed under extreme pH conditions. The second type is

acyl peptides, they are formed from hydrolyzed proteins. An acylation reaction occurs on the amine terminal functions and, possibly, on some side groups and thus leaves the carboxyl groups free, which must be neutralized. These surfactants are sensitive to hydrolysis, because of the presence of amide functions. Acyl sarcosides are the third type, they are the condensation products of fatty acids with N-methylglycine (sarcosine). The properties of sarcosinates are similar to those of isethionates.



### I.1.1.2. Cationic Surfactants

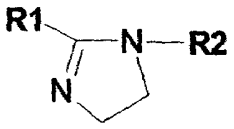
Cationic surfactants differ from anionic and nonionic ones by the fact that they carry a positive charge on the hydrophilic part.

#### I.1.1.2.1. Alkyl Amines

This class of surfactant includes primary, secondary, and tertiary alkyl amines, especially their salts. The salts of tertiary amines obtained by neutralization of the amines with inorganic or organic acids have enough solubility to be fully considered as effective cationic surfactants. Organic salts are generally more water soluble than inorganic ones but are prone to the conversion into amides. Salts of fatty amines can deliver a germicidal activity; their fungicidal efficacy is enhanced when the amine is neutralized with salicylic or o-chlorobenzoic acid.

### I.1.1.2.2. Alkylimidazolines

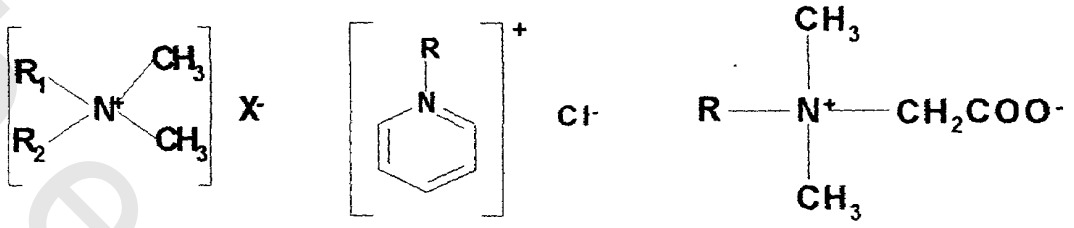
Imidazolines are formed by reacting a fatty acid with a substituted ethylene diamine, heating the resulting amido-ethylamine yields the imidazoline, which is a five membered substituted ring. The imidazoline ring break down and open upon hydrolysis. Therefore, it is presumed that in aqueous solutions, the active molecule is no longer the imidazoline ring but it is the corresponding amido- amine.




### I.1.1.2.3. Quaternary Ammonium Salts

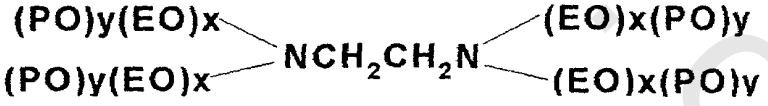
This class of surfactants contains a positively charged nitrogen atom linked to four alkyl or aryl substituents. At variance with other amines, the positive charge is permanent, regardless of pH. It includes three groups; the first is tetraalkyl (-aryl) ammonium salts. They are prepared by the reaction of the respective tertiary amines with a quateranizing agent (methyl chloride, benzyl chloride, dimethyl sulfate, and rarely, long chain alkyl halides), they can adsorb on various substrates and impart various useful conditioning effects (softening, antistatic, corrosion inhibition). The second group is heterocyclic ammonium salts. They are derived from heterocyclic aliphatic or aromatic compounds in which a nitrogen atom constitutive of the cycle is quaternized. Alkyl betaines are the third group, which are N-trialkyl derivatives of amino acids. The positive charge is always carried by a quaternized nitrogen, whereas the anionic site can be a

carboxylate (betaine), a sulfate (sulfobetaine or sultaine), or a phosphate (phosphobetaine or phostaine). Betaines are good foaming, wetting, and emulsifying surfactants.



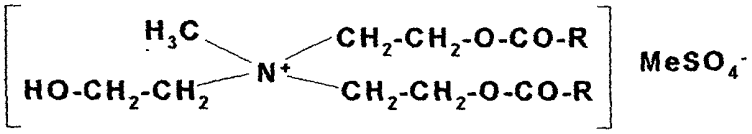
### I.1.1.2.4. Ethoxylated Alkyl Amines

Ethoxylated amines are formed by ethoxylation of primary or secondary fatty amines. With primary amines, the ethoxylation takes place initially on both hydrogens directly linked to the nitrogen and is pursued afterward on the terminal hydroxyl groups. The ethoxylation degree mainly governs the hydrophilic character of the fatty amine. Tetrafunctional products are obtained by successive reactions of ethylene diamine with ethylene oxide and propylene oxide; four block copolymer chains are obtained.



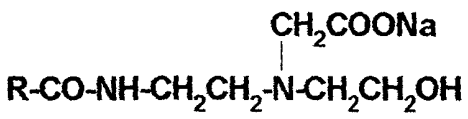
### I.1.1.2.5. Esterified Quaternaries

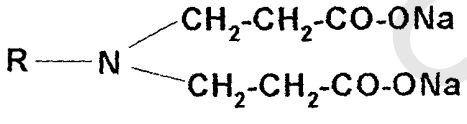
Esterified quaternaries (esterquats) are produced by the esterification of the hydroxyl groups of secondary or tertiary amino alcohols with selected fatty acids. The resulting esteramine is further quaternized by adequate quaternizing agents. They are also nonsensitizing agents in the dermatological sense and are readily biodegradable.



### I.1.1.3. Amphoteric Surfactants

These surfactants can carry a positive charge on a cationic site and a negative charge on an anionic site. The charge of the molecule must change with pH, showing a zwitterionic form at an intermediate pH. This class is divided to two types; acyl ethylenediamines and derivatives is the first type, they are made by the reaction of an alkylimidazoline with chloroacetic acid or with acrylic acid. These surfactants show amphoteric properties and zwitterionic form appears around neutral pH. The second type is N-alkyl amino acids or imino diacids; they can be produced by the reaction of chloroacetic acid or acrylic acid with an alkyl amine. Alkylation of the primary amine leads to the secondary or tertiary amine which is more easily protonated than the original primary amine. The sodium salts of alkylamino acids are readily soluble in acidic and alkaline solutions. These surfactants are used as foaming agents in fire-fighting foam production appliances.





### I.1.2. Nonionic Surfactants

By definition, the surfactant molecule does not carry any charge. These surfactants include the following types:

### I.1.2.1. Alcohols

Fatty alcohols are not generally considered to be true surfactants, despite their surface and interfacial activities, because these molecules exhibit very weak solubility in water. Alcohols are the precursors of other surfactants such as ethoxylated alcohols, which have been so far the most widely used nonionics. Fatty alcohols are synthesized by two major processes; Ziegler process which uses ethylene and trialkyl aluminum as major reactants and yields even numbered alcohols with some branching and secondary alcohols. The oxo-process is based on a hydroformylation reaction and uses an olefin, hydrogen, and carbon monoxide as raw materials and the transition metal hydrocarbonyl [HM(CO)n] as the catalyst; cobalt is the most commonly used metal. The resulting aldehydes are further converted to corresponding alcohols with hydrogenation catalysts.

### I.1.2.2. Ethers

This group of surfactants includes four types; alkoxylated alcohols which covering ethoxylated or propoxylated alcohols. Ethoxylated alcohols are produced from the reaction of fatty alcohols with ethylene oxide. Propoxylated alcohols are obtained with propylene oxide. Due to the low hydrophilicity of propylene glycol, this group does not increase water solubility of the molecule. Therefore, the same surfactant molecule generally combines ethylene oxide units to compensate for the hydrophobicity of polypropylene glycol chains. The second type is EO/PO block polymers, which is a polymeric surfactant, consists of the combination of the

assembly of polypropylene glycol chains and polyethylene glycol chains. A major property of EO/PO nonionics is their low foaming profile. The third type is alkylpolyglucosides, they are produced by the alkylation of short chain glucosides resulting from the acidic alcoholysis of polysaccarides such as starch. They are good emulsifiers, and provide good wetting and foam profile. Finally, Ethoxylated Oils and Fats is the fourth type, they are the ethoxylated derivatives of lanolin and castor oil. Ethoxylated products of lanolin and castor oil are good and excellent emulsifiers, respectively.

$$CH_3\text{-}(CH_2)x\text{-}O\text{-}(CH_2CH_2O)\text{-}H$$

### I.1.2.3. Alkanolamides

This class of surfactants divided to alkanolamides, which are N-acyl derivatives of monoethanolamine and diethanolamine, they are good foamers, and ethoxylated alkanolamides, which are produced by the reaction of an alkanolamide with ethylene oxide leads to an ethoxylated amide, they have benefits of thickening, and foam stabilization.

$$R\text{-}CO\text{-}NHCH_2CH_2OH$$

### I.1.2.4. Esters

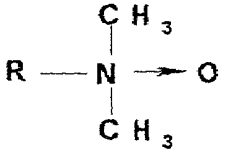
This class of surfactants contains many types; first, ethoxylated fatty acids which comprise monoesters and diesters that result from the reaction of fatty acids with either ethylene oxide or polyethylene glycol, they show foam quality poorer than other nonionics. They are chemically unstable, and readily hydrolyzed under acidic or alkaline conditions. The second type is glycol esters, glycerol esters, and ethoxylated

derivatives, they are derived from the condensation reaction of a polyhydroxyl compound with a fatty acid. Some of them can be directly extracted from natural sources. Ethoxylation can take place on free hydroxyl groups remaining after esterification. The third type is sorbitan and sorbitol esters and ethoxylated derivatives, sorbitan is generated from the dehydration of sorbitol molecule, which results in an internal ether bond. Properties of those surfactants are similar to those of glycol and glycerol counterparts. finallt the fourth type is alkyl carbohydrate esters, they are obtained by the transesterification of sucrose with fatty acid methyl ester or triglycerides, leaving methanol or glycerol as by products. They are good emulsifiers, and have good biodegradability.

$R\text{-}COO\text{-}(CH_2CH_2O)nH$ $R\text{-}COO\text{-}(CH_2CH_2O)n\text{-}OCO\text{-}R$

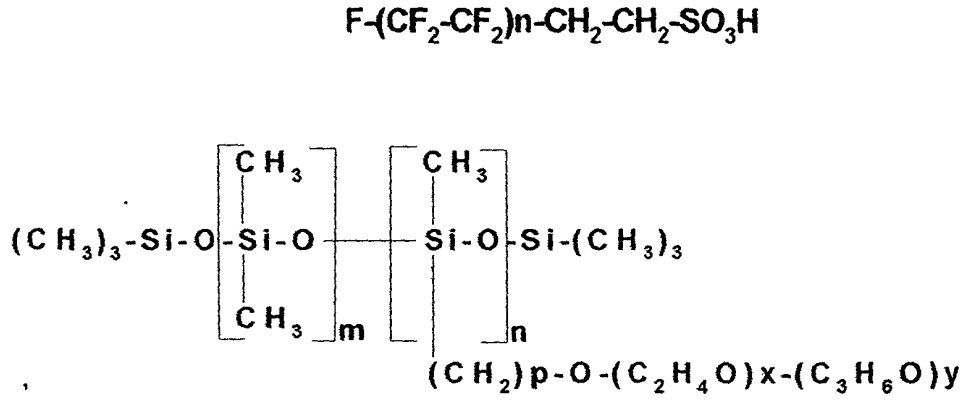
### I.1.2.5. Amine Oxides

Amine oxides are produced by the oxidation of tertiary amines using a 35% hydrogen peroxide solution as the oxidizing agent. The amine can carry various functional groups. They remain uncharged in neutral and alkaline conditions, but the amino group is generally protonated below pH 3. Amine oxides have foam boosting and stabilizing properties. They also have a dipolar moment of their hydrophilic head.



### I.1.3. Nonhydrocarbon Specialty Surfactants

This class of surfactants includes two groups; the first is alkoxylated polysiloxanes. They are structurally derived from polydimethylsiloxanes in which some methyl substituents are replaced by hydrophilic groups which can be of anionic, cationic, or nonionic nature. A striking feature of these surfactants is the fact that derivatives of dimethylsiloxanes remain liquid up to high molecular weights, their diluted solutions can decrease the surface tension to below 20 dyn/cm. The second group is fluorosurfactants, they from hydrocarbon surfactants by the hydrophobic moiety of the molecule, which is made of perfluoroalkyls chains. It is worth mentioning that fluorocarbon chains are in fact amphiphilic; this means that such molecular components repel both polar and nonpolar materials. It is ascribed to the fact that fluorine forms very strong covalent bonds with carbon. They show exceptional surface wetting capacity. Fluorosurfactants can wet surfaces of higher critical surface tension and prevent them from rewetting. The major drawback of them is that they are not environment friendly because they are resistant to biodegradation.



## I.2. Basic Principles in Foams

### I.2.1. Importance of Foams

Foams have long been of great practical interest because of their widespread occurrence in everyday life. *Table 1* contains some kinds of familiar foams. In addition to their wide occurrence, foams have important properties that may be desirable in a formulated product, such as fire-extinguishing foam, or undesirable, such as foam in an industrial distillation tower.

***Table 1: Some examples of foams in everyday experience***

| Group | product |
|---|---|
| Foods | Champagne, soda heads<br>Beer head<br>Whipped cream<br>Meringue |
| Detergency | Manual dishwashing suds<br>Machine dishwashing suds<br>Commercial bottle-cleaning process foam<br>Machine clothes-washing suds |
| Personal Care Products | Shaving cream<br>Hair shampoo suds<br>Contraceptive foams<br>Bubble bath foam |
| Process Industries | Foam blankets on electroplating baths<br>Sewage treatment effluent foams<br>Mineral or oil flotation froths<br>Foam fractionation<br>Pulping black liquor foam |
| Other | Fire extinguishing foams<br>Explosion suppressing foam blankets<br>Fumigant, insecticide, and herbicide blankets |

### I.2.2. Definition, Classification, and Structure of Foams

If a gas and a liquid are mixed together in a container, and then shaken, examination will reveal that the gas phase has become a collection of bubbles that are dispersed in the liquid: foam has been formed. Foams may not contain just gas and liquid, such as water, but solid particles, and even oil.

Colloidal species of any kind (bubbles, particles, or droplets), as they are usually defined, have at least one dimension between 1 and 1000 nm. Foams are a special kind of colloidal dispersion: one in which a gas is dispersed in a continuous liquid phase. The dispersed phase is sometimes referred to as the internal (disperse) phase, and the continuous phase as the external phase. In practical occurrences of foams, the bubble sizes usually exceed the size limit given, as may the thin liquid-film thicknesses.

There are two types of foams; wet foams or kugelschaum, which formed when bubbles are vigorously blown into viscous oil. Such foam, comprising spherical, well-separated bubbles. Wet foams in which the liquid lamellae have thicknesses on the same scale as the bubble sizes are sometimes referred to as gas emulsions. Here, the distinction of whether this is foam or not relates to stability. The second type is dry foams or polyederschaum, where in a persistent foam system; the spherical bubbles become transformed into foam cells, polyhedra separated by almost flat liquid-films. The polyhedra are almost, but not quite, regular dodecahedra.

A two-dimensional slice of a general foam system is depicted in *Fig. 1* the general foam structure is contained on the bottom

by the bulk liquid and on the upper side by a second bulk phase, in this case, gas. Within the magnified region, the various parts of the foam structure are clarified. The gas phase is separated from the thin liquid film, by a two-dimensional interface. In reality, a sharp dividing surface does not exist between gas and liquid properties. For generalized foam system there are some purposes should be defined, lamella which is defined as the region that encompasses the thin film, the two interfaces on either side of thin film, and part of the junction to other lamellae. The connection of three lamellae, at an angle of 120°, is referred to as the Plateau border. Because figure 1 represents only a two-dimensional slice, the Plateau border extends perpendicularly, out of the page. In three dimensions, four Plateau borders meet at a point at the tetrahedral angle, approximately 109°.

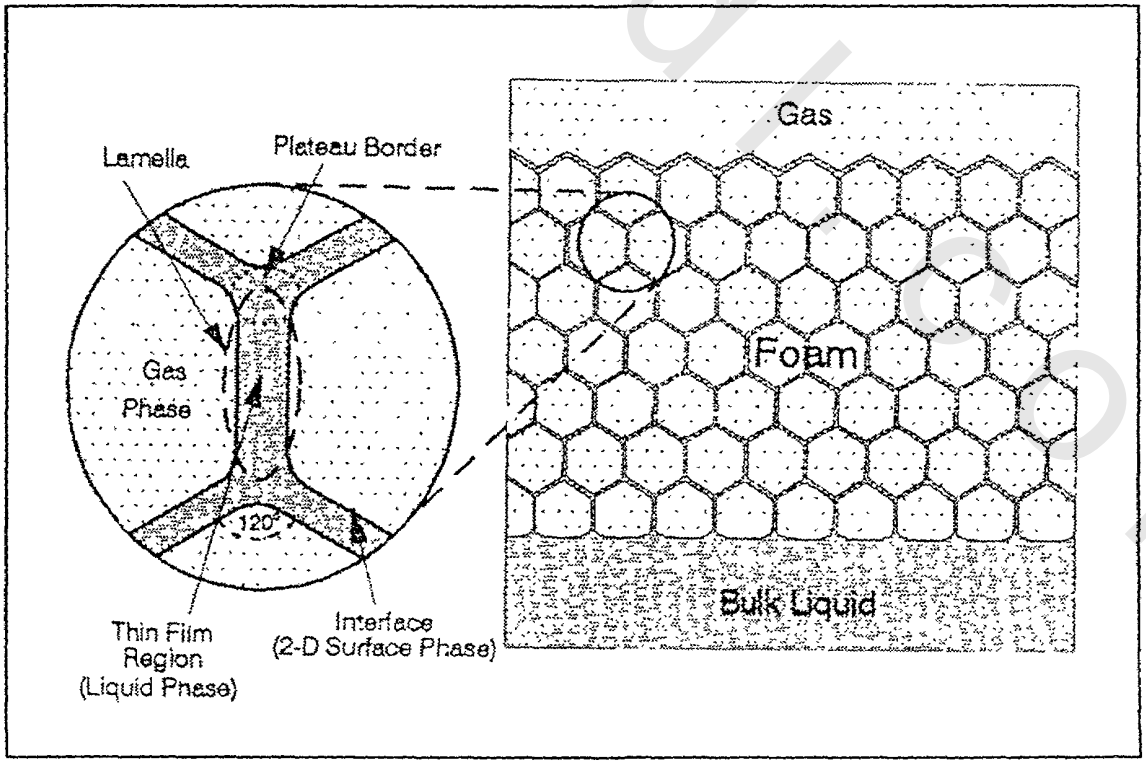



*Fig. 1: A generalized foam system*

### I.2.3. Making Thin Films and Foams

In pure liquids, gas bubbles will rise up and separate, more or less according to Stokes' law. When two or more bubbler come together, coalescence occurs very rapidly, without detectable flattening of the interface between them; that is, there is no thin film persistence. The adsorption of surfactant at the gas liquid interface promotes thin film stability between the bubbles and lends certain persistence to the foam structure. Here, when two bubbles of gas approach, the liquid film thins down to a persistent lamella instead of rupturing at the point of closest approach. It has been possible to make surfactant-stabilized, static bubbles and films with lifetimes on the order of months and years ***(Isenberg C., 1978)***.

### I.2.4. Arrangement of The Phases

The two-dimensional structure of such a foam illustrated in ***Fig. 1***, where the arrangements of films, which come together at equal angles, result from the surface tensions, or contracting forces, along the liquid-films. The bubbles in foam arrange themselves into polyhedra such that, along the border of a lamella, three lamellae always come together at angles of $120^{o}$; the border where they meet is a Plateau border. In three dimensions, four Plateau borders meet at a point at the tetrahedral angle, approximately $109^{o}$. Observations of dynamic foams show that any time more than three films come together; a rearrangement immediately takes place to restore junctions of only three films along lamella borders.

### I.2.5. Foam Stability

In the definition of foam stability, one considers stability against two different processes: film thinning and coalescence (film rupturing). In film thinning, two or more bubbles approach closely together. The liquid-films that separate them thin, but the bubbles do not actually touch each other, and there is no change in total surface area. In coalescence, two or more bubbles fuse together to form a single, larger bubble. In foam terminology, the thin liquid-films rupture and reduce the total surface area. Because foams are thermodynamically unstable, the term stable is used to mean relatively stable in a kinetic sense. It is important to distinguish the degree of change and the time scale. The stability of foam is determined by a number of factors involving both bulk solution and interfacial properties.

#### I.2.5.1. Surfactants and Surface Tension

Interfacial properties are very important in foam because the gas bubbles have a large surface area, and even a modest surface energy per unit area can become a considerable total surface energy. If a foam is prepared by dispersion of gas bubbles into water. For a constant gas-volume fraction, the total surface area produced increases as the bubble size that is produced decreases. Because a free-energy is associated with surface area, this increases as well with decreasing bubble size. Energy has to be added to the system to achieve the dispersion of small bubbles. If a sufficient energy cannot be provided through mechanical energy input, then another alternative is to use surfactant chemistry to lower the interfacial free-energy, or

interfacial tension. If a small quantity of a surfactant is added to the water, then the surface tension is significantly lowered. This decrease in turn would lower the amount of mechanical energy needed for foam formation.

The lamella in foam contains two gas-liquid interfaces separated by a layer of fluid thin-film, and each interface has a surface tension. For this reason, the term film tension is sometimes used. The surface tension of a fluid-film surface is similar to that of the bulk solution when the fluid-film is thick, but departs from the bulk solution value as the fluid-film thins.

Surfactants are compounds that have one part which has an affinity for the nonpolar media (the nonpolar hydrocarbon chain), and the other part has an affinity for polar media (the polar group). The most energetically favorable orientation for these molecules is at surfaces or interfaces as illustrated in ***Fig. 2***, so each part of the molecule can reside in the fluid for which it has the greatest affinity. Surfactants form oriented monolayers at interfaces and show surface activity. As there will be a balance between adsorption and desorption (due to thermal motions), the interfacial condition requires some time to establish. Because of this time requirement, surface activity should be considered a dynamic phenomenon. This condition can be seen by measuring surface tension versus time for a freshly formed surface. A consequence of surfactant adsorption at an interface is that it provides expanding force acting against the normal interfacial tension. Thus surfactants tend to lower interfacial tension. Gibbs has described the

lowering of surface free energy due to surfactant adsorption in terms of thermodynamics.

When surfactants concentrate in an adsorbed monolayer at a surface, the interfacial film may provide a stabilizing influence in thin-films and foams because they can both lower interfacial tension and increase the interfacial viscosity. Increased interfacial viscosity provides a mechanical resistance to film thinning and rupturing.

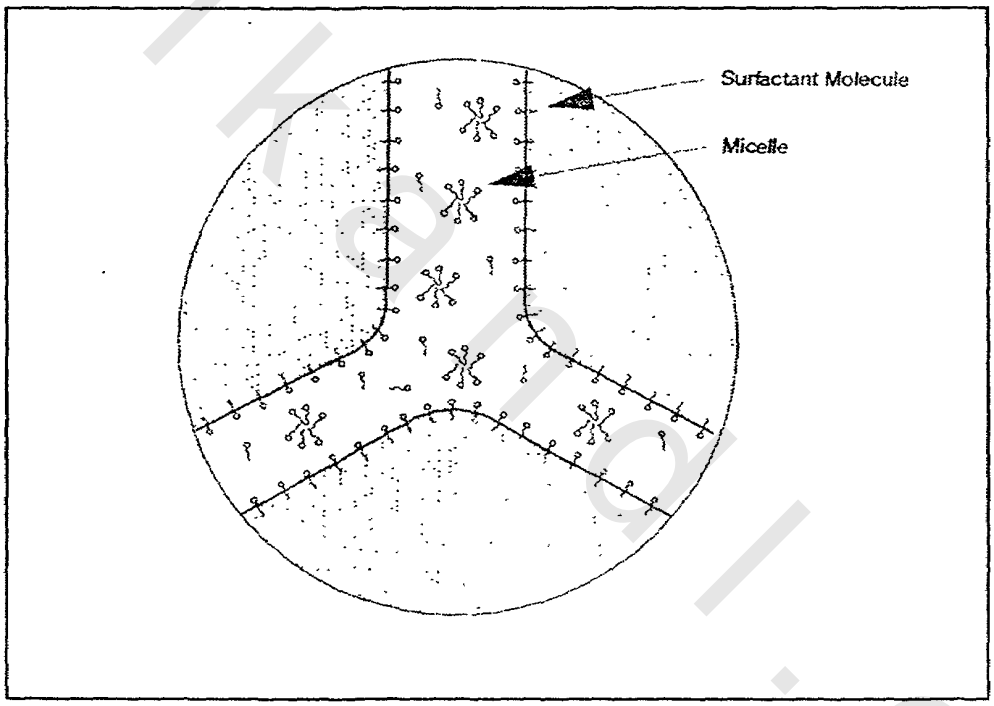



*Fig. 2: Surfactant associations in a foam lamella*

### I.2.5.2. Gravity and Laplace Capillary Suction

Immediately after foam generation, there will always be a tendency for liquid to drain due to the force of gravity. This liquid will drain by flowing downward through the existing liquid-films, the interior of the lamellae. Eventually the gas bubbles will no longer be even approximately spherical

(kugelschaum), and relatively planar lamellae will separate polyhedral-shaped bubbles (polyederschaum). At this point, the capillary forces will become competitive with the forces of gravity. At the Plateau borders the gas-liquid interface is quite curved, and this curve generates a low pressure region in the Plateau area (the Young-Laplace Equation). Because the interface is flat along the thin-film region, a higher pressure resides here. This pressure difference forces liquid to flow toward the Plateau borders and causes thinning of the films and motion in the foam. This thinning process will lead to film rupture and cause foam collapse.

**I.2.5.3. Surface Elasticity**

A foam film must be somewhat elastic in order to be able to withstand deformations without rupturing. The surface-chemical explanation for film elasticity comes from Marangoni and Gibbs ***(Clunie J. S.; et al, 1971)***. If a surfactant-stabilized film undergoes a sudden expansion, then immediately the expanded portion of the film must have a lower degree of surfactant adsorption than unexpanded portions because the surface area has increased as in ***Fig. 3***. This expansion causes an increased local surface tension that provides increased resistance to further expansions. Unchecked, further thinning would ultimately lead to film rupture. A local rise in surface tension produces immediate contraction of the surface. The surface is coupled by viscous forces to the underlying liquid layers. Thus, the contraction of the surface induces liquid flow, in the thin-film, from the low-tension region to the high-tension region. The transport of bulk liquid due to surface tension gradients is termed the

Marangoni effect and provides the resisting force to film thinning. This kind of resisting force exists only until the surfactant adsorption equilibrium is reestablished in the film, a process that may take place within seconds or over a period of hours. In thick films, this step can take place quite quickly; however, in thin films there may not be enough surfactant in the extended surface region to reestablish the equilibrium quickly, and diffusion from other parts of the film is required. The restoration processes are the movement of surfactant along the interface from a region of low surface tension to one of high surface tension and the movement of surfactant from the thin-film into the now-depleted surface region. Thus, the Gibbs-Marangoni effect provides a force to counteract film rupture, but is probably significant mainly for either rapid deformations or for stabilizing very thin films.

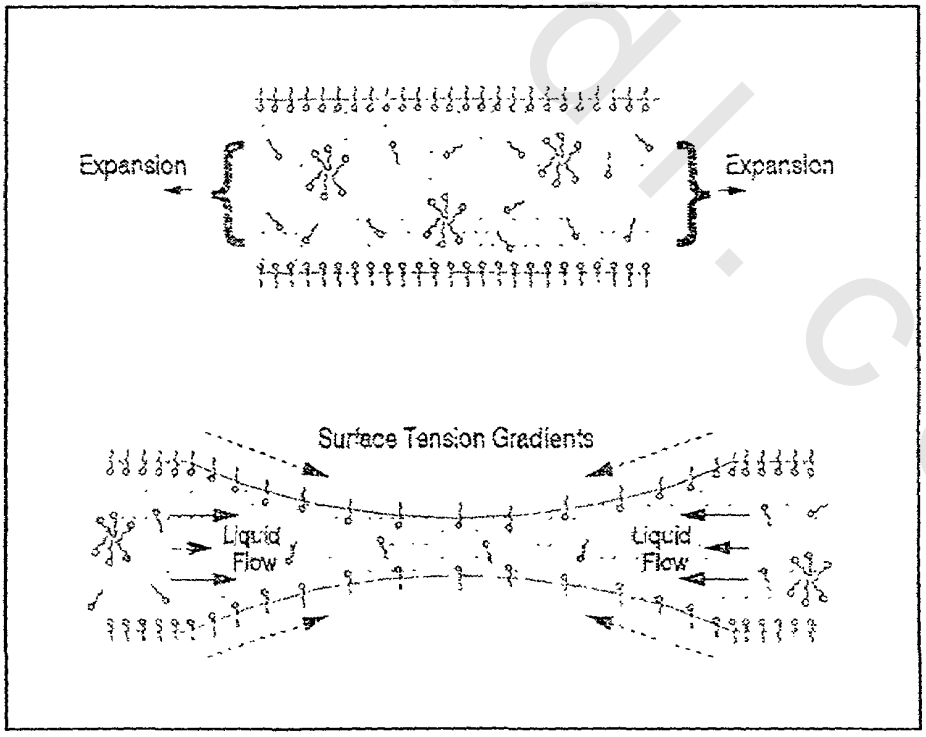



***Fig. 3: The origin of surface elasticity***

### I.2.5.4. Surface Rheology

Unlike in three dimensions, where liquids are often considered incompressible, a surfactant monolayer can be expanded or compressed over a wide area range. As bubbles in a foam approach each other, the thinning of the films between the bubbles, and their resistance to rupture, are thought to be of great importance to the ultimate stability of the foam. Thus, a high interfacial viscosity can promote foam stability by lowering the film drainage rate and retarding the rate of bubble coalescence ***(Joly M.; et al, 1964)***. Fast-draining films may reach their equilibrium film thickness in a matter of seconds or minutes because of low surface viscosity, but slow-draining films may require hours because of their high surface viscosity. Bulk viscosity and surface viscosity do not normally contribute a direct stabilizing force to a foam film, but rather act as resistance to the thinning and rupturing processes. The bulk viscosity will most influence the thinning of thick films, and the surface viscosity will be dominant during the thinning of thin films. The presence of mixed surfactant adsorption seems to be a factor in obtaining films with very viscous surfaces ***(Clunie J. S.; et al, 1971)***. For example, in some cases, the addition of a small amount of nonionic surfactant to a solution of anionic surfactant can enhance foam stability because of the formation of a viscous surface layer, which is possibly a liquid-crystalline surface phase in equilibrium with a bulk isotropic solution phase ***(Ross S., 1980)***. In general, some very stable foam can be formed from systems in which a liquid-crystal phase is present at lamella surfaces and in

equilibrium with an isotropic interior liquid. If only the liquid-crystal phase is present, stable foams are not produced. In this connection, foam phase diagrams may be used to delineate compositions that will produce stable foams ***(Ross S. and Morrison I. D., 1988)***.

### I.2.5.5. Surface Potential

#### I.2.5.5.1. Electric Double Layer and Repulsive Forces

Because the interfaces on each side of the thin-film are equivalent, any interfacial charge will be equally carried on each side of the film. If foam is stabilized by ionic surfactants, then their presence at the interfaces will induce a repulsive force that opposes the thinning process. The magnitude of the force will depend on the charge density and the film thickness. Having a charged interface influences the distribution of nearby ions in a polar medium. Ions of opposite charge (counterions) are attracted to the surface, while those of like charge (coions) are repelled. An electric double layer, which is diffuse because of mixing caused by thermal motion, is thus formed. The electrical double layer (EDL) consists of the charged surface and a neutralizing excess of counterions over coions, distributed near the surface. The EDL can be viewed as being composed of two layers: an inner layer that may include adsorbed ions and a diffuse layer where ions are distributed according to the influence of electrical forces and thermal motion. An indirect way to obtain information about the potential at foam lamella interfaces is by bubble electrophoresis, in which an electric field is applied to a sample causing charged bubbles to move toward an oppositely

charged electrode. The electrophoretic mobility is the measured electrophoretic velocity divided by the electric field gradient at the location where the velocity was measured. These results can be interpreted in terms of the electric potential at the plane of shear, also known as the zeta potential ***(Hunter R. J., 1981 and O'Brien R. W., 1978)***.

In the simplest example of foam stability, gas bubbles and the liquid-films between them would be stabilized entirely by the repulsive forces created when two charged interfaces approach each other and their electric double layers overlap. A third important force at very small separation distances where the atomic electron clouds overlap causes a strong repulsion, called Born repulsion. Therefore, in extremely thin films such as the Newton black films, Born repulsion becomes important as an additional repulsive force.

**I.2.5.5.2. Dispersion Forces**

Van der Waals postulated that neutral molecules exert forces of attraction on each other that are caused by electrical interactions between three types of dipolar configurations. The attraction results from the orientation of dipoles that may be, two permanent dipoles, dipole-induced dipole, or induced dipole-induced dipole (London dispersion forces). Except for quite polar materials, the London dispersion forces are the most significant of the three. For molecules, the force varies inversely with the sixth power of the intermolecular distance. For a liquid-film in foam, the dispersion forces can be approximated by adding up the attractions between all interdroplet pairs of molecules. The dispersion force in liquid-

film decays less rapidly as a function of separation distance than is the case for individual molecules ***(Hiemenz P. C., 1986)***.

**I.2.5.5.3. Total Interaction Energy: The DLVO Theory**

Derjaguin and Landau, and independently Verwey and Overbeek developed a quantitative theory for the stability of lyophobic colloids, known as the DLVO theory. The theory accounts for the energy changes that take place when two charged species approach each other and involves estimating the energies of attraction and repulsion, versus distance, and adding them together to yield the total interaction energy. ***Fig. 4*** shows an example of a total interaction energy curve for a thin liquid-film stabilized by the presence of ionic surfactant. Either the attractive van der waals forces or the repulsive electric double-layer forces can predominate at different film thicknesses. In the example, attraction forces dominate at large film thicknesses. As the thickness decreases, the attraction increases, but eventually the repulsive forces become significant, so that a minimum in the curve may occur. This is called the secondary minimum and may be thought of as a thickness in which a metastable state exists, that of the common black film. As the film thickness decreases further, repulsive forces increase but eventually the attractive forces dominate again, and a much stronger minimum may occur in the curve. This is referred to as the primary minimum; the film is now in a state of greater stability than before, that of the Newton black film. At smaller film thicknesses, repulsive forces dominate once more because of Born repulsion.

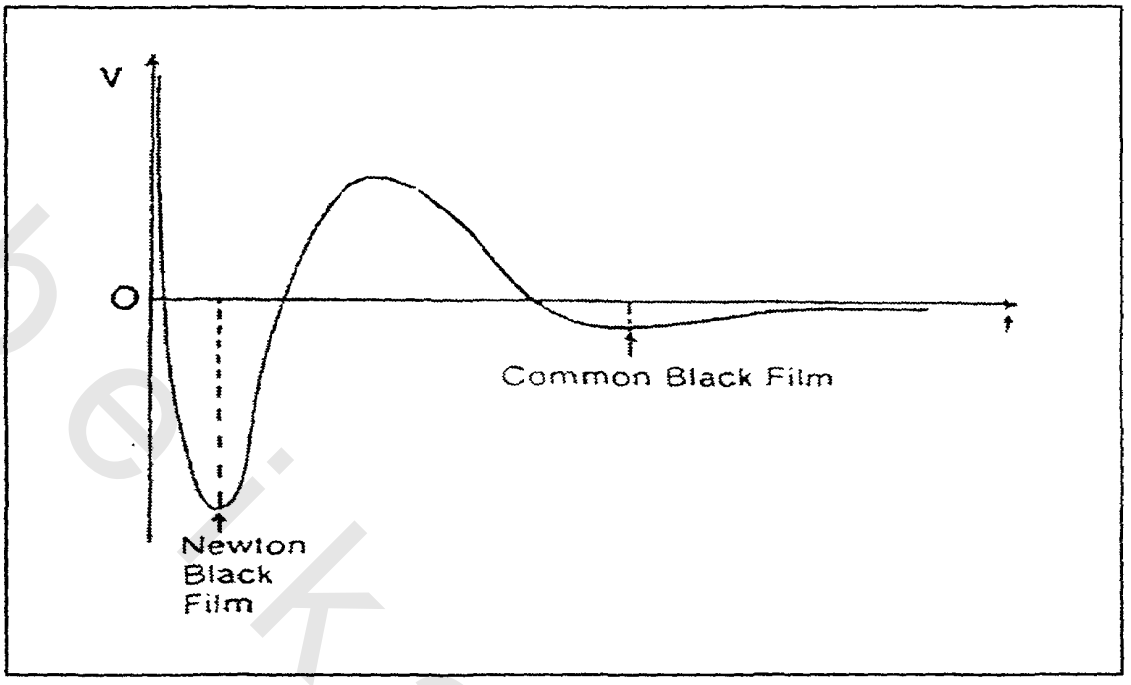



***Fig. 4: The total interaction potential energy, V, between the surfaces of a foam lamella as a function of the lamella thickness, t.***

### I.2.5.5.4-Disjoining Pressure

When the two interfaces that bind a foam lamella are electrically charged, the interacting diffuse double layers exert a hydrostatic pressure that acts to keep the interfaces apart. In thin lamellae, the electrostatic, dispersion, and steric forces all may be significant, and the disjoining pressure concept is frequently employed. The disjoining pressure represents the net pressure difference between the gas phase (bubbles) and the bulk liquid from which the lamellae extend ***(Derjaguin B. V.; et al, 1987)***, and is the total of electrical, dispersion, and steric forces that operate across the lamellae.

### I.2.5.6. Bubble sizes

Despite the fact that the bubbles in persistent foams are polyhedral and not spherical, it is nevertheless conventional to refer to the diameters of gas bubbles in foams as if they were spherical. Foam bubbles usually have diameters greater than 10 μm and may be larger than 1000 μm. Foam stability is not necessarily a function of drop size, although there may be an optimum size for an individual foam type. It is common but almost always inappropriate to characterize a foam in terms of a given bubble size because there is inevitably a size distribution. This size distribution is usually represented by a histogram of sizes, or, if there are sufficient data, a distribution function. Some foams that have a drop-size distribution that is heavily weighted toward the smaller sizes will represent the stable foam. In such cases, changes in the size distribution curve with time yield a measure of the stability of the foams. The bubble size distribution also has an important influence on viscosity. For bubbles that interact electrostatically or sterically, foam viscosity will be higher when bubbles are smaller. This condition results because the increased interfacial area and thinner films increase the resistance to flow. The viscosity will be higher when the bubble sizes are relatively homogenous, that is, when the bubble size distribution is narrow rather than wide.

### I.2.5.7. Second Liquid Phase

If an oil phase introduced into an aqueous foam. When an oil drop comes into contact with the gas liquid interface, it may form a bead on the surface or it may spread and form a film. If

the oil has a strong affinity for the new phase, it will seek to maximize its contact (interfacial area) and form a film. A liquid with much weaker affinity may form into a bead. Petroleum emulsions have been used to prevent formation of foams or to destroy foams already generated in various industrial processes ***(Bikerman J. J., 1953)***. Such a destabilizer may act by penetrating the interface and either remaining as a lens or spreading over the interface. Depending on the degree of entering and spreading of and insoluble agent, several consequences for foam stability can result. If the agent enters the gas-liquid interface, it may be able to bridge adjacent bubbles. This bridging will cause lamella ruptures because the lamellae will be less cohesive and will probably not have the conditions of low surface tension and the Marangoni effect. If the agent cannot bridge adjacent bubbles as long as it can enter the interface, it may also be able spread over the lamella surfaces, replacing the liquid medium as the phase in contact with the gas. In this case, because the new interface will normally not have the capability of stabilizing the lamellae, a reduction in foam stability will occur.

**I.2.5.8. Effect of Solids**

The presence of a dispersed particles can increase or decrease aqueous foam stability. One mechanism for the stability enhancement is the bulk viscosity enhancement that results from having a stable dispersion of particles present in the solution. A second stabilizing mechanism is operative if the particles are not completely water-wetted. In this case, particles would tend to collect at the interface in the foam

where they may add to the mechanical stability of the lamellae. On the other hand, quite hydrophilic particles may actually act to destabilize foam.

### I.2.6. Mechanism of Single-Foam Film Stability

The stability and structure of foams are determined primarily by the relative rate of coalescence of the dispersed gas bubbles ***(Mckendrick C. B., 1991)***. The process of coalescence in foams is controlled by the thinning and rupture of the foam films separating the air bubbles. Experimental observations suggest that the lifetime (stability) of foam films is determined primarily by the thinning time rather than by the rupture time. Hence, if the approaching bubbles have equal size, the process of coalescence can be split into three stages:

1- Formation of a thick lamella.
2- Thinning of the lamella to a film. By forming spots, the film may reduce its thickness by a single thickness transition when dark spots form in the thinning film at low surfactant concentration (below the CMC) or by multiple thickness transitions at concentrations several times higher than the CMC. Before the CMC, the thick foam film at a thickness corresponding to common black film (with about 10-100 nm thickness).
3- Ruptures, according to Vrij ***(Vrij A., 1966)***, due to an unbounded increase in the surface corrugations with time. However, very thin Newton black film ruptures because of nucleation (hole formation) according to Derjaguin and Gutop ***(Derjaguin and Gutop, 1962)*** and Derjaguin and Prokhorov ***(Derjaguin and Prokhorov, 1981)***.

Stages 1 and 3 for small size film occur very fast so that the lifetime of the intervening film is essentially given by stage 2. The driving force for the drainage of a thick film is the capillary pressure (suction at Plateau borders). The thinning rate and stability of the thin lamella are governed by the hydrodynamic and thermodynamic interactions between the two film surfaces. At the first stage of film thinning, at thickness >100 nm, the hydrodynamic interactions, which are greatly influenced by the deformation and mobility of the surfaces, dominate. When the film has thinned to <100 nm, thermodynamic interactions begin to dominate. The thermodynamic properties of thin liquid films are different from those of the bulk surfactant solutions. These films possess an excess chemical potential that is manifested as an excess pressure. Derjaguin and Kusakov ***(Derjaguin and Kusakov, 1936)*** coined the term disjoining pressure to characterize this excess pressure. Generally, the disjoining pressure consists of the electrostatic repulsion forces between the two overlapping surface double layers, the attractive van der Waals forces among all the molecules of the film, the steric forces due to steric hindrance in closely packed monolayers and, in the presence of micelles, the structural forces. The main stages in the formation and evolution of the thin liquid film between two equal size approaching foam bubbles can be summarized as:

a- When two equal bubbles approach each other, the result is hydrodynamic interaction, and a thick lamella is formed.

b- Deformation of the bubbles surfaces leads to a bell-shaped formation that is called a dimple.

c- The dimple gradually disappears, and a plane- parallel film of radius, R, is formed. The flat film drains under the combined actions of suction from Plateau borders and the disjoining pressure, Π. The mechanism of subsequent thinning of the film depends on the surfactant concentration.

d- At low surfactant concentrations (below CMC), when $d\Pi/dh > 0$, (where h is the liquid film thickness) the lamella favors the growth of corrugations at the film surfaces, and at a critical thickness, $h_{cr}$, either the film ruptures or a jump transition in thickness occurs, leading to a stable or metastable state is known as black spot formation because at these thicknesses the film appears grey or black.

e- The black spots increase in size and cover the whole film.

f- The formation of an equilibrium film whose lifetime can be virtually unlimited and is dependent upon the magnitude of the capillary pressure.

g- At high surfactant concentrations (several times higher than CMC), when the structural component of the disjoining pressure, $\Pi_{st}$, is positive, a long-range colloid, crystal-like structure is formed because of the internal layering of micelles inside the film ***(Nikolov A. D.; et al, 1988 and Nikolov A. D., and Wasan D. T., 1989)***.

h- The thinning film exhibits a number of metastable states, and its thickness changes in a stepwise fashion; the

stratification depends on the micellar concentration and film size.

i- The film attains an equilibrium state with no more stepwise changes, and the resulting film is generally stable and thick, and contains micelles.

All the stages are illustrated in ***Fig. 5***:

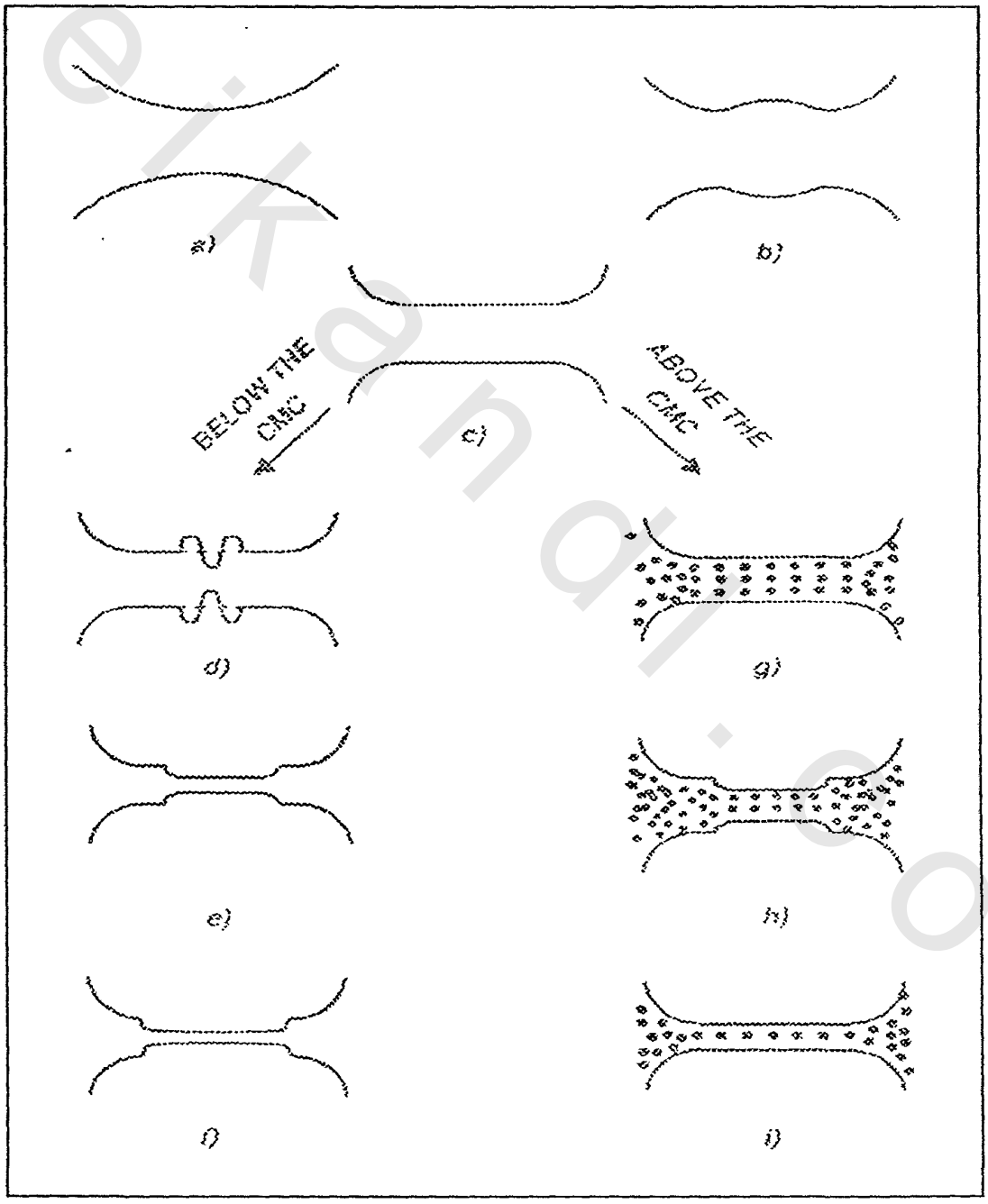



***Fig. 5: Main stages in the evolution of a thin liquid film***

### I.2.6. Aqueous Film Forming Foam (AFFF)

Aqueous film forming foams (AFFF) are used to put out polar (alcohols, ketones, and esters) and nonpolar (hydrocarbons) solvent fires. They are divided to two types; the first is protein-based foam compounds which are called film forming fluoroprotein (FFFP), they were the first foaming agents put to use. These compounds are synthesiszed from hydrolysis products of protein containing matter such as hoof meal, chicken feathers, and fish meal. The second one is the aqueous film forming foams (AFFF), these foams were greatly advanced the ability of fire fighting foams to suppress pool fires. AFFF compounds contain hydrocarbon and synthetically produced fluoroinated surfactants ***(Scheffey J. L., 1995 and Kissa E., 1994)***.

Generally, fire fighting foams are prepared from specific aqueous formulations, named foam concentrates diluted with water and applied with nozzle under the form of aqueous foams which contain 80% air.their very low apparent density (much lower than that of solvents) allow them to be deposited at the surface of burning liquids. The evaporationof the water resulting from the heat reduces the intensity of the fire and the foam generates a water film at the surface of the solvent which prevents the emission of flammable vapors. In addition, after extinction, the foam prevents the risk of fire burnback ***(Pabon M., and Corpart J. M., 2002)***.

### I.2.7. Formulations of Fire Fighting Foams

Afire fighting foams is obtained by the dilution of a foam concentrate in water. This water/foam concentrate mixture is

called a foaming solution or pre-mix ***(Gracia G., 1994).*** A synthetic foam concentrate made from surfactants also contain one or several fluorinated surfactants, which play a role in the formation of a foam as well as the formation of a water film at the surface of the solvent, also foam concentrate contains a foam stabilizer, and finally the concentrate contains a freezing point reducer. For those stored in refineries, civil airports, or drilling platforms ***Pabon M., and Corpart J. M., 2002)***.

## I.3. Literature Survey

### I.3.1. Chemical Structure Foamability and Foam Properties

***Bos M. A., et al, 2003*** studied interfacial rheological properties and their suitability for foam production and stability of two vegetable proteins compared to b-casein. Proteins used ranged from flexible to rigid/globular in the order of b-casein, gliadin and soy glycinin. Experiments were performed at pH 6.7. Network forming properties were characterised by the surface dilational modulus (determined with the ring trough) and the critical falling film length (Lstill) at which a stagnant protein film will break. Gliadin had the highest dilational modulus, followed by glycinin and b-casein, whereas glycinin formed the strongest film against fracture in the overflowing cylinder. The rate of decrease in the surface tension was studied at the air- water (Wilhelmy plate method) and the oil- water interface (bursting membrane) and the dynamic surface tension during compression and expansion in the caterpillar. Gliadin had the lowest equilibrium interfacial

tensions and b-casein the lowest dynamic surface tension during expansion. Hardly any foam could be formed at a concentration of 0.1 g/l by shaking. At a concentration of 1.4 g/l most foam was formed by b-casein, followed by gliadin and glycinin. It seems that in the first place the rate of adsorption is important for foam formation. For the vegetable proteins, adsorption was slow. This resulted in lower foamability, especially for glycinin.

***Martin A. H., et al, 2002*** studied a series of proteins with respect to their ability to form a network at the air/water interface and their suitability as foaming agents and foam stabilizers. Proteins were chosen with a range of structures from flexible to rigid/globular: $\beta$-casein, $\beta$-lactoglobulin, ovalbumin, and (soy) glycinin. Experiments were performed at neutral pH except for glycinin, which was studied at both pH 3 and pH 6.7. The adsorption process was followed with an automated drop tensiometer (ADT). Network forming properties were assessed in terms of surface dilational modulus (determined with the ADT), the critical falling film length ($L$still) and flow rate ($Q$still) below which a stagnant film exists (as measured with the overflowing cylinder technique), and the fracture stress and fracture strain measured in surface shear. It was found that glycinin (pH 3) can form an interfacial gel in a very short time, whereas $\beta$-casein has very poor network-forming properties. Hardly any foam could be produced at the chosen conditions with glycinin (pH 6.7) and with ovalbumin, whereas $\beta$-casein, $\beta$-lactoglobulin, and

glycinin (pH=3) were good foaming agents. It seems that adsorption and unfolding rate are most important for foam formation. Once the foam is formed, a rigid network might favor stabilizing the foam.

***Arnaudov L, et al, 2001*** performed foam tests and model experiments with sodium dodecylbenzenesulfonate solutions to clarify how the foam stability and the foaminess are affected by several oils of different chemical structure. The foam tests show that 2-butyloctanol (2BO, branched alkanol) and isohexyl-neopentanoate (IHNP, branched ester) exhibit a significant antifoam activity at concentrations as low as 0.005 wt %. n-Heptanol also acts as an antifoam, but at concentrations above 0.15 wt%due to its higher solubility in the surfactant solution. The model experiments prove that the antifoam activity of pre-emulsified oils is determined primarily by the barrier to drop entry, which controls the drop emergence on the solution surface. If the entry barrier is high (e.g., n-dodecanol and silicone oil), the oil drops remain arrested in the Plateau borders during the process of foam drainage, without being able to destroy the foam. Thus branched long-chain alkanols (like 2BO) and esters (IHNP) behave as active antifoams, because they combine the advantages of long-chain and medium-chain n-alkanolsslow solubility and low entry barrier, respectively. No direct correlation between the spreading behavior of the oils and their foam breaking activity is observed. The effect of these oils on the foamability of the solutions is far more complex. At

low concentrations (below and around their solubility limit) the oils reduce the dynamic surface tension of the solutions, facilitating in this way the formation of fresh surface and enhancing the foamability. At higher oil concentrations, however, the emulsified oil drops induce a coalescence of the foam bubbles during foaming and, as a result, the foamability of the solutions decreases. That is why the foamability is a nonmonotonic function of the oil concentration.

***Smith D. L., 1997*** showed that commercial surfactants, such as linear alkylbenzenesulfonate is not a single compound but a mixture of components. This mixture comprises different carbon-chain homologs, different phenyl isomers, and, in addition, the manufacturing co-product, dialkyltetralin sulfonate. Current manufacturing technology makes it possible to easily vary the average carbon chainlength. On the other hand, the phenyl isomer distribution and dialkyltetralin sulfonate content can be changed only within a certain range. Each of these variations in composition affects performance. This study reports on the effect of commercial alkylbenzenesulfonate composition on surface tension, solubility, viscosity, foam stability, and detergency. The study shows that average carbon chainlength affects all performance properties. Phenyl isomer distribution and dialkyltetralin sulfonate content affect only solubility and viscosity.

***Cohen L., et al, 1993*** investigated Foam height and foam stability of solutions of a linear alkylbenzene sulfonate (LAS)

were measured according to the Ross-Miles test to establish their relationship with ionic concentrations in the solution. The anionic concentration and water hardness were varied alternatively. The results obtained show different behavior for both parameters depending on the concentration of LAS and calcium. However, the results are in line with the proposed theoretical model based on the LAS-calcium precipitation boundary diagram. These tests were aimed at providing a scientific explanation to the complex foaming phenomena. Also, these tests emphasize how essential it is to know the position of the points tested within the LAS-calcium solubility diagram when evaluating the foam properties of an anionic surfactant.

***Moreno A., et al, 1988*** made a detailed study that conducted using pure isomers and homologs derived from commercial linear alkylbenzenes in order to evaluate their behaviors on several physicochemical parameters, namely: solubility, viscosity, detergency performance, foaming power, foam stability, and stability to water hardness. This study has been carried out using the sodium salt of the corresponding sulfonic acid. The effect of the isomers distribution was done using a pure phenyl decane product with different internal and external isomers content. It was found that the sodium salt of the more external isomers (2 phenyl mainly) is less soluble than the corresponding salt of the more internal isomers (4, 5 phenyl).

***Patist A., et al, 1998*** studied effect of tetraalkylammonium chlorides ($TC_{nAC}$ for n equals 1, 2, 3, and 4) on the micellar stability of sodium dodecyl sulfate (SDS) solutions was investigated and related to dynamic interfacial properties, such as foamability and foam stability as well as surface viscosity and surface tension. The slow relaxation time ($\tau$=2), which is directly related to the micellar stability, was determined using the pressure-jump technique. It was found that upon increasing the concentration of $TC_{nAC}$, the micellar stability increases, due to the ionic interactions between the oppositely charged $TC_{nAC}$ and the SDS headgroup. Beyond a critical concentration (depending on the alkyl chain length of $TC_{nAC}$), the micellar stability decreases again, which is attributed to the disruption of the molecular packing in the micelles as well as at the air/water interface. The location of a maximum in the micellar stability corresponds to maxima in foam stability and surface viscosity and to minima in foamability and surface tension. These maxima and minima shift to lower concentrations as the alkyl chain length of $TC_{nAC}$ is increased. This indicates that alkylammonium chlorides with longer chain length are more effective in decreasing the molecular packing of SDS in micelles as well as adsorbed monolayers.

***Colin A., et al, 1997*** discussed the possible origins of the reduced foamability of dilute solutions of chemically modified ethoxylated nonionic surfactants. First, the organization of the modified molecules at the interface is different from that of the standard ethoxylated compounds. After diffusion from the

bulk to the interface, the molecules undergo a rearrangement to take a folded conformation at the surface. This second process, observed in the dynamic surface tension measurements is much slower than the first one. Therefore, during the foam formation, the interfaces of freshly formed films are not sufficiently covered with the surfactant and, hence, are badly protected against film rupture. Moreover, the modified surfactants have a smaller surface viscoelasticity, thus enhancing the thinning and the breaking of foam films.

***Colin A. B., and Langevin D., 1997*** showed that the foamability of nonionic surfactants is reduced above the cloud point temperature. Above this temperature, the surfactant aqueous solution separates into two phases, a surfactant-rich phase and a surfactant-poor phase. The surfactant-rich phase plays the role of an antifoam. We show that the antifoam mechanism of action is the bridging of the foam films made with the dilute phase by tiny drops of the surfactant-rich phase which merge into the air-water surfaces of these foam films.

***Koczo. K., et al, 1987*** constructed a combined pneumatic and mechanical foam generator and tested by sodium-dodecyl-sulfate and sodium-dodecylbenzene-sulfonate solutions. The foams could be divided into three classes according to the proportion of air incorporated into the foam. For better understanding the foaminess the dynamic surface tensions of the solutions were measured under the same dilatational velocity as the beater products during foam forming.

***Friberg S. E., et al, 1992*** investigated stability of foams formed from water plus combinations of a hydrophobic, nonionic surfactant and an ionic, water-soluble one. When the total concentration of the two surfactants was kept constant, the foam stability was strongly increased for a certain ratio between them. Phase equilibria revealed this enhanced stability to be due to the presence of a lamellar liquid crystalline phase. In the region of two liquid phases (aqueous solution and solution rich in Igepal CO 210), the stability depended on the volume ratio between the two solutions in a more complex manner.

***Varadaraj R., et al, 1990*** determined effect of hydrocarbon chain branching on the foaming performance of a variety of sulfate, ethoxysulfate, and ethoxylate surfactants by the Ross-Miles test. Data from static and dynamic surface tension experiments were used to obtain a structure-property-performance correlation. Initial foam heights correlated with $\Pi$ (CMC), the effectiveness of surface tension reduction, while foam instability correlated with $R_{1/2}$, the rate of surface tension reduction at the air-water interface. Hydrocarbon chain branching resulted in increased $\Pi$ (CMC) and $R_{1/2}$. Consequently, surfactants wherein the hydrocarbon chain is branched exhibited high initial foam heights and low foam stability.

***Rusanov A. I., et al, 2004*** analyzed elasticity of open and closed thin foam films. The elasticity modulus of a closed film

is shown to be additive with respect to contributions from Gibbs elasticity and disjoining pressure. A detailed expression for the film elasticity modulus explains the pronounced maxima of foaminess and foam stability near the critical micelle concentration observed earlier in many experiments. A theory of transversal elasticity of thin foam films is formulated under conditions excluding the action of Gibbs elasticity. Near the critical micelle concentration, the theory predicts maxima of the transversal elasticity modulus and of the films thickness as functions of concentration at a given disjoining pressure. The prediction has been verified experimentally by measuring the film thickness in equilibrium foam as a function of height.

***Stubenrauch C., and Strey R., 2004*** constructed phase diagrams for thin foam films stabilized by a nonionic surfactant. The idea was born by synopsis of various disjoining pressure ($\Pi$) versus thickness (h) curves of foam films resembling p-$V_m$ isotherms of real gases. The new concept of interpreting the $\Pi$-h curves of foam films in terms of phase diagrams allows us to describe experimental observations much more precisely. Three logical consequences will be discussed here to illustrate the strength of this approach. First, the observations explained that common black films (CBF) rupture or form a Newton black film (NBF) within a certain pressure range rather than at a defined pressure. Both observations can be rationalized by invoking a nucleation process of holes or of the thinner NBF, respectively, in close analogy to the vapor to liquid condensation. Second, the

question whether the CBF to NBF transition is discrete or continuous is answered by analyzing under which conditions the supercritical state of a foam film can be reached. Third, the evidence of corresponding states is discussed.

***Kolaric´ B., et al, 2003*** stated that disjoining pressure isotherms of free-standing liquid films (foam films) consisting of different polyelectrolyte/ surfactant combinations are measured in a thin film pressure balance (TFPB). In dependence of the charge of polyelectrolyte and surfactant, a transition from an electrostatically stabilized common black film (CBF) to a sterically stabilized Newton black film (NBF) can be induced in some cases while for other polyelectrolyte/ surfactant combinations the film is a CBF up to several thousands of pascals. The thinner NBF is less stable, and the film breaks after a few minutes. An exchange of the polymers by monomers leads to the same kind of film as that for the respective polymer, while the addition of, for example, simple salt leads always to a transition from CBF to NBF. The typical stratification of polyelectrolyte/surfactant films is not observed in monomer/surfactant films.

***Sethumadhavan N. G., et al, 2003*** investigated the stability of the bulk-foam and single-foam lamellae using a mixture of two nonionic surfactants in ethanol-based aqueous solutions. The second virial coefficient, which is indicative of the intermicellar interactions in solutions containing both surfactants and ethanol, was measured. We found a good

correlation between the foam stability and the second virial coefficient. Surfactant formulations with a more positive virial coefficient lead to a more stable foam. The foam lamella stability was probed by using the capillary force balance. It was observed that the foam lamella thinned in a stepwise manner (stratified). It was found that, at an optimum surfactant formulation, foam stability was at its maximum when the foam lamella was stable and remained at a high equilibrium thickness with a low rate of thickness transition.

***Monin D., et al, 2000*** examined rupture of standing three-dimensional soap foams. A foam of controlled size and water content was produced in a vertical column and the evolution of its liquid fraction under gravitational drainage was followed by electrical conductivity measurements. Using simple models to describe simultaneously foam geometry and liquid drainage (syneresis), we measured coalescence events in a bulk foam. Various surfactants were used, indicating two mechanisms for foam destruction. In one case, the rupture of soap films is induced by the increase of capillary pressure resulting from liquid drainage: foam breaks at the top of the column and its level goes down with a constant velocity. In the other case, films are not influenced by drainage and their breakage is randomly distributed throughout the foam, which coalesces homogeneously in space. These two mechanisms are interpreted with microscopic arguments, based on monolayer elasticity and disjoining pressure isotherms.

***Magrabi S.A., et al, 1999*** characterized the bubble size distribution of aqueous foams, produced by a compressed-air foam generator. The time evolution of bubble size distribution in aqueous foams is experimentally measured using a CCD video camera. A computer model, which predicts the change in bubble size distribution with time, is used to simulate the coarsening and disproportionation of aqueous foams. As an extension of previous computer simulations, our model incorporates the variation in liquid fraction during the foam aging process, thereby enabling the simulation of both wet and dry foams. It is found that a Weibull-type distribution best approximates the narrow bubble-size distribution produced by a compressed-air foam generator. The modelled predictions show good agreement with the experimental measurements and a sensitivity analysis indicates a significant dependence of the model on drainage (hence on the thickness of the lamellae), the Henry constant, the gas diffusivity and the surface tension of the foam solution.

***Bhakta A., and Ruckenstein E., 1996*** showed that Drainage of the continuous phase liquid from a foam plays a pivotal role in determining its stability to collapse. A theoretical model for the drainage of the liquid during generation of a foam by bubbling and its subsequent collapse is presented. The model accounts for drainage in the films as well as in the plateau border channels. Drainage of the films is modeled using Reynold's equation for the flow between parallel flat circular disks under the influence of van der Waals, electrical double-

layer, and plateau border suction forces with film rupture occurring when the film thickness attains a certain critical value. Since this model accounts for collapse at the foam/gas interface during generation, it is able to predict the steady state height attained by pneumatic foams. The model is also able to predict the establishment of a drainage equilibrium when the opposing forces of gravity and plateau border suction gradient balance each other. The effect of various parameters such as superficial gas velocity, electrolyte concentration, and bubble size on the steady state height and collapse half-life (time required for the foam to collapse to half the steady state height) is examined. It is shown that, for a given system, there is an upper limit on the superficial gas velocity beyond which a steady state height will not be attained. With increasing salt concentration, the stability of a foam first increases, attains a maximum, and then decreases. The steady state height and the collapse half-life decrease with a decrease in bubble size due to an increase in the capillary pressure. It is shown that, for a given system, there is an upper limit to the salt concentration and a lower limit to the bubble size beyond which no drainage equilibrium is possible and complete collapse will occur. It is also shown that plots of dimensionless foam height versus dimensionless time practically coincide for most of the period of collapse, a feature which is consistent with some experimental results.

*Breward C., et al, 1997* discussed two basic building blocks that are needed to model foam drainage and hence foam

stability. The first concerns the flow of liquid from the lamellae to the Plateau borders and the second describes the drainage flows that occur within the borders. The mathematical modelling involves a balance between gravity, diffusion, viscous forces, and varying surface tension effects with or without the presence of mono-layers of surfactant. In some cases, mass transfer through the gas-liquid interface also causes foam stabilization, and must be included. Our model allows us to clarify which mechanisms are most likely to dominate in both the lamellae and Plateau borders and hence to determine their evolution. The model provides a theoretical framework for the prediction of foam drainage and collapse rates. The analysis shows that significant foam stability can arise from small surface tension variations.

***Khristov K., and Exerowa D., 1997*** studied foam stabilizing ability of anionic, cationic and nonionic surfactants with two methods, involving constant and variable capillary pressure in the foam liquid phase: the method of determining the foam lifetime at constant pressure and the Ross-Miles test. It is reported that the most important parameters for foam stability are the capillary pressure and the type of the foam films. It is proved that the foam lifetime $\tau_p$ determined at constant capillary pressure is a more precise and defined characteristics of foam stability.

***German J. B., 1989*** showed that Foams are thermodynamically unstable colloidal systems in which gas is maintained as a distinct dispersed phase in a liquid matrix.

Both drainage of the much denser liquid phase and bubble coalescence are otherwise spontaneous events that must be kinetically hindered for foam stability. Drainage between lamella and through the plateau borders is impeded by fluid viscosity and interaction with the film surfaces. The kinetic barrier to bubble coalescence and rupture is provided by the dynamic interfacial viscosity and elasticity of the surfactant or polymeric films surrounding the gas bubble. The major goal in understanding the stability of foams is to reconcile the molecular properties of components in the fluid and interfacial films with their macroscopic effects on foam stability. While considerable research has been conducted on the molecular basis of foaming properties of small surfactants, these are not readily translatable to higher density foams stabilized by large polymers such as proteins. The consensus of recent research suggests that the ability of polymers to form a coherent gel-like highly elastic film at the bubble interface is critical for foam stability. Consequently, the capacity of certain components to disrupt the integrity of existing films becomes important in the destabilization of these same foams. Methodologies to examine the molecular and interfacial properties of foam components in parallel with macroscopic measurements of foam stability and drainage are essential to further advances in this field.

***Lobo L., et al, 1993*** investigated the influence of the emulsified oil drops on the stability of an aqueous foaming system at the thin film level. In the first part of the paper we

evaluate the theories that use the classical entering and spreading coefficients to predict the effect of oil drops on foam stability. A differential interference microscope was used to observe the configuration of oil drops at the air-water surface, which is likened to air-water surface of foam lamellae. The microscopic observation show that the entering and spreading coefficients cannot consistently predict the configuration of the oil at the air-water surface and, consequently, cannot predict the effect of oil an foam stability. The reason for this inconsistency is that the classical theories do not account for the role of the pseudoemulsion film, which is formed between an air-water surface and the surface of an oil drop which is approaching it. It is the stability of this film that determines the configuration of the oil drop, as it was earlier suggested by Wasan and Nikolov (refs 10 and 11). In the second part of the paper, we use reflected light interference microscopy to observe the drainage and stability of the pseudoemulsion film. We observed, the first time, that the film thins in discrete steps, which is indicative of the presence of an ordered micellar structure within the film, and this structures was found to enhance the film stability. The film excess energy, which is determined from the film contacts angles, is used to quantitatively characterize the stability of the film. The contact angles of the curved, asymmetric pseudoemulsion film were measured by using interference microscopy in conjunction with the Laplace equations for the film meniscuses. The film meniscuses. The film excess energy calculations show that the equilibrium film thickness increases with increasing micellar

concentration as well as with decreasing oil drop size or film area. The effect of these two parameter s on the film stability is explained due to the formation of the ordered micellar structure (i.e., micellar layering) within the pseudoemulsion film.

***Kruglyakov P. M., et al, 1992*** described some theoretical and experimental studies of the properties of polyhedral foams, and some new methods for investigating foams in which a pressure gradient is created in the Plateau-Gibbs borders in the foams. The role of the foam film type in foam stability, and in particular, in the establishment of high foam stability, is demonstrated by performing model investigations of microscopic foam films and foams.

***Thomas P., et al, 1995*** predicted stability of gas-liquid foams is important in many situations, either when stability is required, as in fire-fighting foams, or when it is undesirable, such as in distillation or absorption columns. Foam stability depends on the structure of the foam and the properties of its component materials. This paper discusses the use of an optical version of computerized tomography to resolve aqueous three-dimensional foam Plateau borders. We use a video system to sample a large number of images from a 360 degree arc around an aqueous foam, and then construct a voxel representation of the Plateau border geometry.

***Chunzhou L., et al, 1993*** studied foam rheological properties experimentally in this paper. Foam behaves like a pseudoplastic fluid with a viscosity inversely proportional to shear rate. Its apparent viscosity is affected strongly by foam quality. From experimental results, the rheological parameters, K and n, are determined and two correlations are obtained. Additionally, the rheological properties of foam are related with the type and concentration of foaming agents, diameter of foam, temperature, etc.

***Koczo K., et al, 1987*** investigated the flow through a plateau border experimentally using special glass frame to withdraw a single plateau border from surfactant solution and to establish steady flow through it. Solutions containing sodium dodecyl sulfate and dodecanol, and also fire fighting foam-liquids were investigated. It was found that the dimensions of the plateau border and the flow rate at a given pressure drop were predominantly determined by the mobility of the surfaces. The change of the mobility with temperature was characteristic of the solution.

***Raymundo A., et al, 1998*** proposed a methodology to evaluate foaming capacity and stability. With this method the foam volume decay is followed and the overrun [(foam volume - solution volume)/solution volume] plotted against time. The integral of overrun decay for a fixed period was tried out as a single parameter to describe foam properties, i.e. foaming capacity and foam stability. It was concluded that using this

single parameter, the foaming stability index $(F.S.I.)_t$, the application of statistical experimental design methodology to optimise foaming becomes straightforward. As an example of an application of this method, the denaturation extent of the protein was optimised to improve the foaming properties of Lupin protein isolate.

***Nedyalkov M., et al, 1988*** studied experimentally gas permeability of Newtonian black foam films, formed on the top of a small bubble at the solution surface. The aqueous solutions contained sodium dodecylsulphate with concentrations in the range $1.5\times10^{-4}$ to $3\times10^{-3}$ mol/dm$^3$ and sodium chloride (constant concentration of 0.5 mol/dm$^3$). A dependence of the gas permeability coefficient on the surfactant concentration was obtained. The experimental results are discussed on the basis of a theory assuming the presence of clusters of molecule vacancies (holes) in the bilayer foam film, their number and size depending on the surfactant concentration. The experimental results are in agreement with this film structure and confirm the existence of flow through both the hole-free bilayer film and the holes. It was found that the holes of three molecule vacancies make the main contribution to gas permeability at low surfactant concentration. The diffusion coefficients through the hole-free film and through the three-vacancy holes are calculated.

***Maini B. B., et al, 1986*** presented results of experimental evaluation of foam stability under conditions of high pressure and elevated temperatures. Foams were generated by injecting

nitrogen gas through a gas sparger submerged under the test solution in pressure vessels equipped with glass windows. Results show that the drainage of liquid from foam generally follows first-order kinetics, while the decay of foam volume can be more complex.

***Malysa K., et al, 1991*** determined the influence of the vapors of *n*-amyl or *n*-decyl alcohol on the stability of single thin liquid films, single bubbles, and foam columns. It was found that the presence of surfactant vapors lowered the stability of foams and single foam films. The mechanism of the destabilizing action of the surfactant vapors on wet, dynamic foams under dynamic conditions is discussed. It is shown that the destabilizing action of the surfactant vapors is a further indication that surface elasticity forces are the main factor determining stability of wet, dynamic foams.

***Dhara D., and Shah D. O., 2001*** were investigated the effects of poly(ethylene glycol)s of different molecular weights on the micellar stability of sodium dodecyl sulfate in the concentration range from 50 to 600 mM. The presence of polymer was found to decrease micellar stability drastically. The decreased stability of micelles is explained by the increased population of small aggregates in the presence of polymer. This decreases the value of "resistance" for the micellar formation-dissolution process. The foaming property of SDS solutions in the presence of poly(ethylene glycol) was related to micellar stability.

***Shah D. O., et al, 1978*** showed that aqueous solutions of sodium dodecyl sulfate yield very unstable foam with a very high rate of drainage because they exhibit a relatively low surface shear viscosity. When a solubilizate, such as dodecanol is present in the system, the rate of drainage and thus foam stability prove to be a function of surface shear viscosity. In itself surface shear viscosity appears to be a function of the state of the film as well as the relative amount of the surfactants that is adsorbed at the surface. Systems of fatty acid — fatty alcohol (decanoic acid — decanol, octanoid acid — octanol) exhibit maximum foam stability at molar ratios of 1:3 and 9:1, respectively. At the same molar ratios in these systems, the rate of drainage is minimum and surface shear viscosity is maximum. Studies on mixed monolayers of stearic acid — stearyl alcohol showed minima in the average area per molecule at the 9:1 and 1:3 molar ratios. It is proposed that the molecular interaction which causes the reduction in the average area per molecule in the mixed monolayer also causes the maximum in surface shear viscosity, the minimum in the rate of drainage, and the maximum in foam stability.

***Khristov K., et al, 1979*** investigated the effect of the pressure in the Plateau-Gibbs borders of the foam upon its drainage and its stability. The principle of the method and the apparatus for applying pressure gradient in the Plateau-Gibbs borders of the foam are described. The kinetics of establishing of the capillary pressure in the Plateau-Gibbs borders of the foam in dependence of the height of the foam column, the applied

pressure difference and the type of the surfactant has been studied. The obtained results are qualitatively confirmed by an investigation of the foam water content change (calculated by measurements of its specific conductivity) at the same experimental conditions. The influence of the increased drainage rate and respectively the decreased foam water content on the foam stability when a pressure gradient is applied in its Plateau-Gibbs borders is discussed. It is shown that the time for the foam destruction when a pressure gradient is applied in the foam Plateau-Gibbs borders can be used for characterising the foam stability at definite conditions.

***Nekrasov A. G., et al, 2002*** developed new method of studying the foam stability based on the determination of the evolution time of foam cell at a given level of foam column. The method is based on optical measurements that allow one to determine the main structural parameters of a foam. Experimental results are reported for sodium dodecyl sulfate solutions.

***Pakharukov Y. V., et al, 2001*** proposed theoretical model that describes the dependence of foam stability on the surfactant concentration in a foam-forming solution. The model is based on the parameters reflecting a fractal structure and percolation properties of the foam. It is established that a time corresponding to the onset of the liquid out-flow from a foam column sharply increases in a certain narrow surfactant concentration interval.

## I.3.2. Aqueous Film Forming Foam (AFFF)

***Scheffey J. L., et al, 1995*** showed that proliferation of performance guidelines and specifications for firefighting foams has created divergent opinions on aviation fire protection standards. In this paper the technical basis for current U.S. and international aviation guidelines is presented. Issues associated with small- and large-scale fire tests are discussed. The correlation between fire test methods in the U.S. Military Specification for aqueous film-forming foam (AFFF) and current aviation fire protection guidelines is established. Trends and areas for further development are outlined.

***Woodman A. L., et al, 1978*** calculated spreading coefficients for aqueous film forming foams and hydrocarbon fuels from surface and interfacial tensions measurements made over a temperature range from 20 to 90°C.

***Jho C., 1987*** studied the spreading kinetics of aqueous solutions of a mixture of hydrocarbon and fluorocarbon surfactants on liquid hydrocarbon substrates. A commercial AFFF (aqueous film-forming foam) agent was used as the mixture of the surfactants. An empirical relation was established between the rate of spreading and experimental parameters involved in the spreading, such as the equilibrium and dynamic surface and interfacial tensions, the spreading coefficient, and the concentration of the spreading solution.

***Timms G., and Haggar P., 1990*** examined three types of foam concentration measurement techniques. Total fluorine content, optical absorption, and specific conductivity. Specific conductivity was found to be the most useful for field measurements and was therefore compared with the traditional refractive index approach. It was found that electrical conductance provides a more accurate method of estimating the concentration of AFFF solution than does the refractive index technique described in NFPA 11.

***Szönyi S., and Cambion A., 1990*** showed that addition of water-soluble polymers in multipurpose fire-fighting foam formulations allows an increase in the viscosity of lamellar solutions able to slow down water drainage and protect foams against the destructive action of hydrophilic or polar flammable liquids by forming a gelatinous pellicle. Usually, such foam concentrates must have a high polymer concentration, to be resistant against polar liquids fires; however, too high a viscosity of the foam concentrates generates suction problems. Thus, the structure of the polymer was modified by synthetic reactive fluorochemical agents with a view to greatly increasing the polar liquid repellency of multipurpose foam compounds while decreasing the polymer amount and consequently the concentrate viscosity.

***Pletnev M. Y., et al, 1988*** estimated hydrostatic stability of low-aeration foams prepared from solutions of different foaming agents for extinguishing fires, including film-forming, 'synthetic,' and new thixotropic. The last foam was

distinguished by high stability, insulating capacity, quenching efficiency, and good adhesion to surfaces, which ensures elevated operating indexes.

***Szönyi S., and Cambion A., 1992*** explained that aqueous Film Forming Foam agents (AFFF) that are foam compounds containing highly fluorinated synthetic surfactants are known to be very effective on fires of hydrocarbons, and totally ineffective on fires of polar liquids in the absence of thickening additives such as polysaccharides. The discovery of a new fluorinated surfactant which is alcophobic and oleophobic has enabled us to prepare a new multipurpose AFFF foam with Newtonian viscosity, whose extinguishing properties are perfectly adapted to both hydrocarbon fires and polar liquid fires, without the need of a thickening polysaccharide. This foam, when concentrated, is perfectly fluid and aspirable, even at very low temperature (-30°C). It can be used as a premixture at 3 to 6% concentrations and medium expansion; the composition of this foam compound can be modified so that it can be used at 1% concentration. The new AFFF/MP Newtonian foam compound can be formed starting from synthetic foaming bases or from a proteinic foaming base. Extinguishing foams produced from these new foam compounds provide satisfactory solutions in many cases of difficult or otherwise-impossible extinction.

***Scheffey J. L., and Leonard J. T., 1988*** showed that U.S. Navy air-capable ships require the staging of weapons near superstructures, which results in a fire and explosion hazard to

mission-critical flight operations areas. An aqueous film-forming foam (AFFF) fire suppression system was designed and tested which will rapidly control a flammable liquid-fuel spill fire in the weapons staging area. Factors which influenced the design of the system included limited available water and AFFF supply, severe wind conditions which dramatically change AFFF spray pattern coverage, and cooling requirements to prevent weapons explosions. The resulting fire suppression system utilizes AFFF discharged through non-air aspirating spray nozzles located near the weapons staging area deck.

***Gardiner B. S., et al, 1998*** examined the rheological properties of compressed-air foams and contains velocity profiles of foams flowing through straight horizontal tubes. It is shown that a master equation can be derived from the experimental data to account for a range of expansion ratios and pressures normally encountered during pumping of polyhedral-in-structure fire-fighting foams. The experimental data come from a Poiseuille-flow rheometer consisting of three stainless steel tubes 6.95, 9.9, 15.8 mm in diameter, with foam generated by mixing a pressurised solution of Class A foam with compressed air. Results are corrected for wall slip following the method of Oldroyd-Jastrzebski, which implies the dependence of slip coefficients on the curvature of the tube wall. The experimental results demonstrate the applicability of the volume equalisation method to the more expanded, polyhedral ($\epsilon > 5$) and transition, bubbly-to-polyhedral ($5 \geq \epsilon \geq$

4) foams. (The method of volume equalisation was introduced by Valkó and Economides to correlate the viscosity of low expansion foams ($\epsilon < 4$), characterised by spherical bubbles. The present results indicate that all data points align themselves along two master curves, depending on whether the foam consists of bubbles or polyhedral cells.

***Briggs A. A., 1979*** showed that Storage tanks contaminated by flammable residues require protection during repair or demolition. Nitrogen-filled high expansion fire-fighting foam has been proposed for this protection. In this series of tests a 500 tonne aviation fuel storage tank was filled with appropriate foam to observe foam behaviour with particular reference to oxygen contamination in aged foam. For comparison, gas inerting with nitrogen was included in the test series. In one test a hot cutting procedure was monitored for void formation and oxygen contamination of the foam. Oxygen contamination was low in foam up to three hours old. Voids and oxygen introduced by hot cutting were rapidly purged. The use of foam enabled the tank to be rendered inert using less nitrogen than with the gas alone and had the additional advantage that the inerting agent was visible.

***Pabon M., and Corpart J. M., 2002*** presented fluorinated surfactants and synthetic fire fighting foams. The fluorinated part of those surfactants can be obtained industrially either by electrofluorination or by telomerization. The fact that fluorine atoms are present in a surfactant molecule modifies its

behavior compared to classical surfactants. It gives to the molecule outstanding chemical and thermal stabilities. Fluorine also, produces in these surfactants very low surface tension in aqueous solution even when used at reduced concentrations. For those reasons, it is shown that fluorinated surfactants are particularly adapted to the formulation of film forming fire-fighting foams in which they are associated to classical hydrocarbon surfactants. Finally, a way of removing the mean components of a fire fighting foam from the wastewater resulting from fire fighting training or a real application is presented.

***Magrabi S. A., et al, 2002*** showed that drainage measurements are used for assessing the quality, water-retention ability and stability of aqueous foams used in fire-fighting applications. A new experimental technique is proposed in this paper, for measuring the drainage rate of liquid from compressed-air fire-fighting foams. The procedure outlined here provides advancement in precision over that prescribed by the standard for low expansion foams (NFPA 11, Standard for evaluating low expansion foams, NFPA, Quincy, MA, 1998). A comparative analysis of drainage characteristics in two commonly used class B fire-fighting foams was undertaken, from theoretical and experimental perspectives: (i) aqueous film forming foam and (ii) film forming fluoroprotein foam. It is demonstrated that even though both the foam solutions exhibited similar fundamental physical properties, the disparities in surface rheological properties cause the resulting

foams to have remarkably distinct drainage and coarsening characteristics. In addition, a drainage model is outlined, which allows the explicit prediction of the time evolution of liquid holdup profiles and drainage rates in fire-fighting foams. The existing drainage model is extended to stimulate fire-fighting foams made from protein based and synthetically produced surfactants.

***Manzello S. L., and Yang J. C., 2002*** presented an experimental study for droplets containing an alcohol-resistance aqueous film forming foam (AR-AFFF) impacting and boiling on a heated stainless steel surface. Experiments with solutions of 3% (volume fraction) AR-AFFF/distilled water were compared to ones with distilled water and 3% AR-AFFF/simulated seawater. The latter experiments were motivated by the practice of mixing AR-AFFF with seawater in many naval applications. The impact process was recorded using a high-speed digital camera at 1000 frames per second. For each fluid, the droplet impact Weber number was fixed, and the droplet evaporation lifetime was measured as a function of temperature. Collision dynamics were investigated for each fluid, with the temperature of the stainless steel surface varied from film evaporation to film boiling. It was observed that the addition of 3% AR-AFFF to water reduced the temperature for departure from nucleate boiling and the Leidenforst temperature dramatically compared to pure water. Droplets were observed to breakup violently for solutions of AR-AFFF/simulated seawater at film boiling. The results demonstrate that the collision dynamics depend on what type of water is mixed with AR-AFFF.