

# Surfactants and their Investigation for Petroleum Industrial Applications

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**Abstract:** *In recent decades due to the rapid development of household chemicals and cosmetic industry, the researches on surfactants have become increasingly important. Therefore, surfactants are used more and more areas. Surfactants for petroleum industrial application have been introduced in this study. Demanding analytical and impact assessment methods are needed for the development of modern surfactants. A commonly used combined method is not known thus the best option is a unique combination of the properly selected methods.*

**Keywords:** *petroleum industrial application, surfactants, method, method development*

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## 1. INTRODUCTION

Nowadays a wide variety of surfactants has been found on the market, from 1 \$/kg to more than 20 \$/kg. The possibilities for the production technologies varies widely, it can be simple hydrolysis or multi-stage, high-pressure synthesis. For this reason the cost of the raw materials influence significantly the cost of the surfactants. The materials of surfactants are usually grouped according to their origin (natural or synthetic materials derived from petroleum processing). Mainly the lipophilic groups cause the diversity of surfactants [1; 2].

In the past 35 years, the market share of non-ionic surfactants has increased to 40% of the total surfactant production. The non-ionic surfactants do not form ions in aqueous solution. Consequently they are compatible with different types of materials therefore they can be applied for complex compounds.

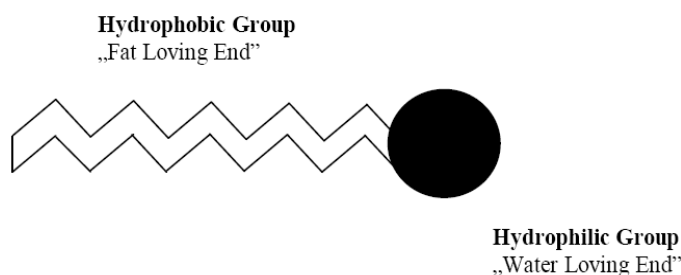
The non-ionic surfactants are less sensitive for electrolytes; particularly in the presence of divalent cations thus they keep their effect even in high salinity, hard water. They are good surface active agents, wetting agents and emulsifiers. Some of them have good foaming properties and non-toxic nature, so they can be used in pharmaceuticals, cosmetics and food. Nowadays the non-ionic surfactants occur in a wide variety of household and industrial products [3].

## 2. PROPERTIES OF AMPHIPHILIC COMPOUNDS

In several solutions the amphiphilic molecules and the unsettled polymers form arranged units which have different properties. In analytical chemistry it is important that the chemical balance has not been affected by these units therefore it allows to use their specific properties to improve analytical methods or develop new, unknown methods.

Amphiphilic molecules

The amphiphilic surfactants consist of a hydrophilic and a hydrophobic part as the figure shows below.



**Fig1.** *The Structure of a Surfactant [4]*

Depending on their chemical structure there are anionic, cationic, zwitterionic and non-ionic surfactants. The hydrophobic part can have different lengths (typically 8-20 carbons) and some chains can be unsaturated. Aggregation behaviour depends on the surfactant structure, concentration, solvent properties and the method of production.

Their properties and chemical function can be changed by the modification of the structure which occurs on the hydrocarbon chain or hydrophilic head.

#### *Modification of polar head*

Acid-base, redox and chelating polar groups can be added to the molecule. The addition of the appropriate reactive counter ion to the ionic amphiphilic compounds may be suitable in the case of certain chemical reactions.

#### *Modification of hydrophobic tail*

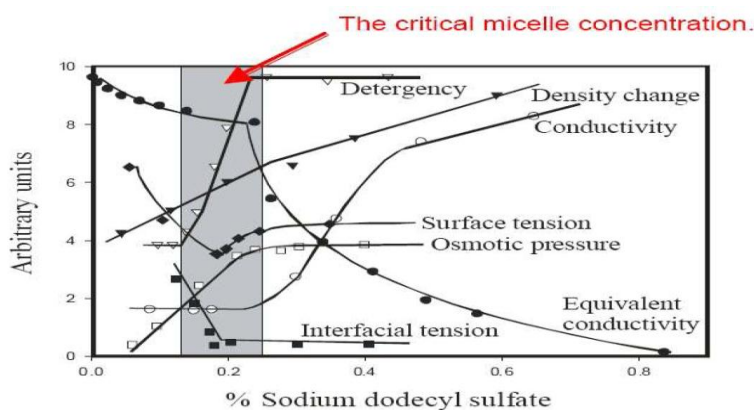
The most widely used options are the followings:

- the full or partial replacement of hydrogen atoms of hydrocarbon chain by fluorine
- dual hydrocarbon chain linkage to the hydrophilic moiety
- fluorinated hydrocarbon mixed double chain
- formation of gemini structure, where two amphiphilic units are connected via the hydrocarbon tail
- formation of bolaform structure, where the two last hydrophilic groups are connected to the same hydrocarbon chain.

The modification of hydrophobic tail can change significantly the properties of the amphiphilic molecule, for example the fluorinated surfactants are not linked to the oil phase in an oil/water system therefore they are poor emulsifiers in this medium. However, they can greatly reduce the interfacial tension and their chemical and thermal stability is excellent [5;6]

### 3. CRITICAL MICELLE CONCENTRATION (CMC)

Amphiphilic compounds form micelles in aqueous solutions when they reach a certain concentration. This concentration is relatively well-defined, it is possible to determine if a property or the change of a property has been investigated in a function of increasing concentration. Each characteristic starts to change nearly in the same range.



**Fig2.** The determination of CMC[7]

The CMC is a critical parameter for the amphiphilic substances. The surface tension, the turbidity, the conductivity, the density, the osmotic coefficient, the diffusion, the viscosity and solubility are properties used in the determination of CMC value.

The most common method used for defining CMC is the measurement of the surface tension, but also known routine measurements based on colour, absorption spectra or amount of solubilizate.

Factors affecting the CMC:

- Hydrophobic group: In non-ionic amphiphilic compounds increasing the number of carbon atoms in the hydrocarbon chain decreases the CMC.

- Hydrophilic group: The effect of CMC is different in ionic and non-ionic surfactants with the same hydrophobic part.
- Counter ion properties: Replacing the counter ion of ionic surfactants to a higher valence or polarized ion decrease the CMC. The size of the counter ion is also decisive, higher hydrodynamic diameter results higher CMC value.
- Effect of organic molecules: The organic molecules influence the CMC value and the properties of the solution containing micelles. According to their impact they can be divided into two groups: (1) molecules (long or medium-chain alcohols) which are absorbed in the external part of the micelle, they decrease the energy of the micelle formation resulting the decrease of CMC, (2) components which increase the CMC value, probably by modifying the structure of water.
- Effect of temperature: The decrease of CMC of ionic surfactants with the increase of the temperature can be explained by the dehydration of monomers.
- Effect of pressure: Experience has shown that until 150 MPa the CMC increases, at higher pressure decreases [8;9]

#### 4. SIZE AND SHAPE OF MICELLES

In addition to CMC, the micelle shape and size, the aggregation number, the electrostatic surface potential, the polarity and the microviscosity are essential properties in micelle formation.

The micelles are dynamic structures with a liquid core thus it is difficult to define them as structures with rigid, well-defined shape. Nevertheless, it may be useful to determine an average micelle form and size.

The experimental determination of the shape of smaller micelles near CMC is difficult to define therefore it is often described as spherical form. Whereas in the centre of the aggregate can not be holes so the micelle radius is equal to the length of the hydrocarbon chain.

The micelle shape formed by non-ionic and ionic surfactants is scientifically quite controversial [10].



**Fig3.** Schematic illustration of the three most commonly observed geometrical shapes of surfactant micelles [11]

#### 5. TESTING METHODS OF SURFACTANTS

Demanding analytical and impact assessment methods are needed for the development of modern surfactants, so the composition, the effect and other properties of surfactants are examined by analytical tools which may be suitable for the quality testing of raw materials, in-process products and final products. A commonly used combined method is not known thus the best option is a unique combination of the properly selected methods.

This list describes the most commonly used methods by the authors. Standard and non-standard analytical methods are used for structural and quality characterization:

1. Composition analysis of surfactants:
  - a. gel permeation chromatography method
  - b. NMR method
  - c. HPLC and mass spectrometry, parallel analysis

2. Determination of physical and chemical properties of surfactants:
  - a. acid number
  - b. saponification number
  - c. solubility in water
  - d. HLB value
  - e. viscosity
3. Analysis of the stability of surfactant mixtures:
  - a. chemical stability
  - b. biological stability
  - c. mechanical stability

Water-insoluble acidic and saponifiable components regularly occur in various petroleum products without additives. Their quantity is growing mainly because of usage and contamination. However most of the additives, especially the surfactants, give an alkaline reaction. The new and used oil products contain acidic components, like organic and inorganic acids, esters, phenols, lactones, resins, salt of noble metals and other acidic additives.

In the new and used oil products alkaline components also appear, like organic and inorganic bases, amino compounds, salts of weak acids, alkaline salts of polyacids, salts of heavy metals and other alkaline additives [12;13].

### **5.1 Determination of Acid Number**

The acid number shows the total (water soluble and insoluble) content of acidic additives. The test is performed as follows: the additive or surfactant is dissolved in toluene, then after the complete dissolution it is titrated by KOH solution until the change of colour in the presence of phenolphthalein indicator [14].

### **5.2 Determination of saponification number**

Saponification number is expressed in milligrams of potassium hydroxide which is required for the saponification of all free and bonded acid (ester) in 1 g sample.

The saponifiable components, the free and bonded acids (esters, lactones, anhydrides, etc.) and the alkali reactive additives are determined. As sulfur, phosphor, halogen and other compounds of elements which are doped to petroleum products can consume alkaline or acid, the results show the impact of these materials as well [14].

### **5.3 The viscosity**

The viscosity of the fluids is a mechanical property that is created in flow. The viscosity characterizes the frictional losses occurring in the fluid flow phenomena during the hydrodynamic and hydrostatic lubrication. One part of the crude oil and petroleum products behaves as a Newtonian fluid at the measurement temperature, so the viscosity is a characteristic data of the fluid depending only on the temperature and the pressure but not on the voltage and the shear rate. During the volume lasting deformation of Newtonian fluids the viscosity is constant. In the case of non-Newtonian fluids the viscosity is a function. Each viscosity value depends on the circumstances of the measurement and on the device which is used for its determination. It can not be used as a basis of calculations because only the viscosity measured in absolute physical units is applicable. The flow properties of high molecular weight petroleum products or doped with high molecular weight polymers can not be interpreted by Newton's law.

The viscosity and the apparent viscosity are not sufficient to characterize the non-Newtonian fluids. The non-Newtonian fluids (whose viscosity is not substantially dependent on time) can be sufficiently characterized by flow curves. If the shear rate drop ( $dv/dy$ ) and shear stress (%) values are plotted in log-log graph, and the same scale interval is used, the Newtonian behaviour is characterized by a line of 45°. If the line has different inclination, the tested fluid has anomalous behaviour and the product structure can be deduced [15;16].

### 5.4 Solubility in oil

1% of the sample is dissolved in model oil (SN-350 base oil) then the turbidity of the oil is measured by spectrophotometer. 0.2 g of emulsifier is added to 20 g of model oil and it is stirred for 1h and at 60°C. The samples are filled to clean, dry cuvettes after cooling down to room temperature, then the light scattering (turbidity) is measured by spectrophotometer at 500 nm wavelength. The clear oil (0%) and the standard opal body (100%) are used as a reference [17].

### 5.5 Solubility in water

The water number is widely used to determine the composition, for quality control and for product selection in the industries dealing with surfactants. The RSN (Relative Solubility Number) is an important indicator in the selection of stabilizers and emulsifiers. The water number is the volume of distilled water in milliliter necessary for permanent turbidity in benzene/dioxane solution, containing 1g of surfactant and 30 ml of solvent. It shows the relative solubility of surfactant in water and in oil. Higher numerical value means higher water-solubility, lower numerical value shows higher oil-solubility [18; 19; 20].

### 5.6 Experimental determination of HLB value

The method developed by Greenwald, Brown and Fineman is used to determine the hydrophilic-lipophilic nature of the surfactants. It can provide information about the effectiveness of the emulsifier, the estimated HLB value and if the surfactants are dominated by hydrophilic or lipophilic groups. According to literature, the correlation between the HLB and the water number is linear [19; 21; 22].

## 6. PROPERTIES OF AQUEOUS SOLUTIONS OF SURFACTANTS

The solutions of surfactants include some properties which characterize only certain groups, for example the dissociation, the hydrolytic degradation or micelle formation and the critical micelle concentration. These aggregates are called associative colloids. The polar groups turn to the water while the non-polars are linked to each other. Consequently the interfacial energy reduces and the mutual contact of the maximum number of water molecules is possible.

In the solutions of ionic surfactants this phenomenon occurs at a specific critical concentration (usually 0.1-0.5%). The nature of the solution becomes colloidal, the conductivity, the osmotic pressure, the surface and interfacial tensions show maximum.

However, the non-ionic, amphiphilic compounds may also form micelles, uncharged colloidal aggregates, but their formation is less clarified. These also have been created in diluted solutions and their properties change in a lesser extent than in ionic emulsifiers. The anomaly appearing in the solutions of surfactants is caused by the micelle formation. The surfactants behave ideally at low concentration, but beyond a certain point, they show a significant change.

The more general and main properties are the wet ability, the dispersibility, emulsification, the detergency and the foam ability. These characteristics can not be well-separated. An emulsifier has wetting effect, the detergents must be good emulsifiers and the foam ability is closely related to the detergency, although it is not an absolute requirement.

### 6.1 The Surface and Interfacial Tension

The molecules of liquids are under an interaction of various attractive forces, intermolecular forces have the same effect to the molecules inside the fluid in all directions therefore they compensate each other. Conversely on the surface of liquid each molecule is only subjected to attractive force which is directed to the interior of the liquid or tangentially to the surface. In the vapour or gas phase the attractive forces on the surface are lower than between the liquid molecules because of the limited density of gas phase. Thus, the energy content of surface molecules is higher than the inner molecules, and depends on the internal energy, the volume, the temperature and the surface area. The increase of liquid surface uses energy, which otherwise is released during the decrease of surface.

The surface tension is the force, affecting on 1 cm long surface perpendicularly, which is required for the isothermal and reversible formation of 1cm<sup>2</sup> surface. Thus the surface tension is the ratio of the work to increase the liquid surface and the growth of the surface.

When the liquid is in a container, a contact angle is formed. The size of the angle depends on the material of the wall, the nature of its surface, the liquid and whether the liquid has previously wetted the wall. The contact angle characterizes the wetting efficiency of liquid to the solid surface.

If a liquid is in contact with another immiscible liquid, the interfacial tension, similarly to the surface tension, is created because the resultant of tensile forces on the interface of molecules is not zero [10].

## **6.2 Determination of Surface Tension**

The interfacial tension is one of the most important properties of the aqueous solution of surfactants. The stalagmometric, the bubble pressure, the Du Noüy methods and the spinning drop method are the most common ways to measure the surface tension.

### *6.2.1 Stalagmometric Method*

The method is based on the formation of drops whose size depends on the surface tension and the density when the liquid disseminate slowly from a pipette (stalagmometer) with a well-defined aperture. The growing drop falls down from the disk of  $d$  diameter when the weight is equal to the surface force:  $d\pi\gamma$  (1 dyn =  $10^{-5}$  N).

### *6.2.2 Bubble pressure method*

The capillary pressure of the bubble's interior is measured in the liquid by this method. If an air bubble is formed by overpressure in a tube vertically extending to the liquid –beside of the hydrostatic pressure determined by the density of the liquid and the insertion depth of the pipe- an overpressure is generated depending on the size of the bubble and the surface tension which increases to maximum when the bubble grows. It is reached when a hemisphere is formed depending on the diameter of pipe (wider pipe more, thinner pipe less flattened). When the bubble rises above a maximum, the pressure decrease, the bubble becomes unstable and breaks off.

### *6.2.3 Du Noüy method*

The surface and interfacial tension can be determined by Du Noüy method. If a cleavable body (e.g. stretched wire or wire ring) is contacted with the surface of liquid and it is pulled up, during the draw between the liquid and the wire, a fluid film is formed which exerts tensile force to the cleavable body due to the surface tension. The Lecomete de Noüy tensiometer is a torsion balance, in which the force exerted by an adjustable torsion fiber and counteracts the retracting force of the liquid. The torsion fiber is connected to 4 scale where the surface tension can be read in dyn/cm (1 dyn/cm =  $10^{-3}$  N/m) by the use of a ring belonging to the device. In this case the cleavable body is a wire ring made of platinum-iridium and it is soldered perpendicularly to a stirrup. The shape of the ring is very important in terms of the measurement. It must be perfectly flat, circular and without distortion. The ring on suspended stirrup is fixed by a parallelogram rod that holds the ring in a horizontal position. This is connected to a torsion balance. The relevant information of the ring is the circumference and the radius of the wire [11;14].

### *6.2.4 Spinning drop method*

The surface tension is measured in a rotating tube containing dense liquid. A drop of a less dense liquid or gas bubbles are injected into the liquid. Centrifugal force is generated because of the rotation, the liquid drop begins to deform elongated and only stops when the surface tension and the centrifugal forces are balanced. The surface tension can then be derived from the form of the drop.

## **6.3 Efficiency Analysis of Aqueous Solutions of Surfactants**

### *6.3.1 Wettability*

Wetting is when a solid surface is in contact with a solution by displacing air. The wettability is higher when a surfactant solution reduces greatly the surface tension of the liquid and the interfacial tension between the solid and the liquid. The surfactant is adsorbed on the surface of liquid and solid as well.

The wetting effect can reach maximum by increasing the concentration of the solution of surfactants. After reaching this concentration, further increase of concentration will not cause significant change.

The unconventional oil shales and gas reservoirs have an increasing role in hydrocarbon production. The shale rock consists of complex nano- and micro-sized pores, mainly clay minerals,

carbonate/silica particles and other organic materials. The shales are artificially fractured to improve the low permeability and the connection between the pores. In addition, the presence of nano- and micropores results high capillary pressure. Surfactants are often used as additives of fracturing fluids to change the wettability on the oil/water interface of oil shale. Mirchi et al has studied the effect of pressure, temperature, surfactant concentration and brine in oil/water/rock systems under reservoir conditions. It was found that the brine has no significant effect on the CMC, however the increase of water salinity decreases the CMC. IFT value can be reduced by anionic surfactants, non-ionic surfactants reduce only slightly. The lowest adhesion work was achieved slightly above CMC, so the high surfactant concentration is not necessarily required [23].

### 6.3.2 Dispersibility

The dispersion is the shredding of a solid or liquid material within another material. During the shredding the total surface of the particles increases. The solids in liquid form suspension, the fluids form emulsions.

The dispersed part is characterized by the degree of dispersion. The liquid containing the dispersed material is the dispersion medium.

The surfactant molecules are adsorbed on the surface of dispersed molecules and thus they form a protective sheath around the particles. During the adsorption the hydrophobic moiety of the surfactant is directed toward the dispersed material, the hydrophilic part extends into the water and due to the hydration forms a water protective sheath.

The electric charge has great importance in the stability of these systems, because the similarly charged particles repel each other and thus prevent the aggregation of the dispersed particles.

### 6.3.3 Emulsification

The emulsion is the mixture of two immiscible, not indefinitely soluble liquids, where the particles of one liquid are finely divided in the other.

The completely clear, two-component (binary) systems form emulsions as long as the system is under mechanical stress. If the vegetable oil is shaken with clear water, the fine oil droplets are dispersed in the water and the fluid becomes cloudy. However, the two liquids separate soon and the entire quantity of oil floats on the water surface. Nevertheless, if the appropriate surfactant is added previously to the water or oil, and then shaken with the oil, the oil remains longer in emulsion.

Practically, the permanent emulsion is only a third substance which forms as a result of an emulsifier. Thus, the permanent emulsions are at least three-component, ternary systems.

The interface of liquids in the emulsions is about 50-100 thousand times higher than the surface of the emulsified liquid (in cube). The emulsified particles are in constant motion, and try again to merge to droplets for the smaller interfacial tension. Emulsions are more stable, if the interfacial tension between the two fluids is lower. This interfacial tension is reduced by emulsifiers, and on the other hand they surround the disperse particles by an adsorption layer.

There is an energy difference between the two sides of the adsorption layer on the interface. The adsorption film bends in the direction of less work, so toward the more lipophilic liquid. The adsorption layer formed on the oil-water interface becomes concave toward the aqueous medium if hydrophilic surfactant is added, because it is less work. In this type of emulsions the dispersion medium is the water. If the emulsifier is lipophilic, then the situation is the reverse. This case refers to the emulsions prepared only with one hydrophilic or lipophilic emulsifier.

The cholesterol, the wool-fatty-alcohol etc. are lipophilic, the soap, the sodium-cetyl-sulfate etc. are hydrophilic film forming emulsifiers.

The spontaneous emulsification occurs without external mechanical effect and forms stable emulsion. The spontaneous emulsified material is incorporated in the larger micelles of surfactants and therefore the interface between the hydrophobic material and the water shrinks [24].

The amino silicones are one of the most widely used functional silicones to change the surface properties. They are often used in a form of microemulsion. The droplet size of the silicone, the surface charge, the conformation, the pH and the temperature play the most important role to achieve

the suitable properties. Purohit et al have investigated the droplet size of silicone emulsions in high concentrated solutions by DLS and electroacoustic techniques. It was found that the most of the silicon droplets are in submicron range, especially nanoparticles. The size of the micelles started to decrease for dilution [25].

Oil in water nanoemulsions were produced using non-ionic surfactants and amphiphilic anionic polyelectrolytes by Galindo-Alvarez et al. The initial diameter of droplets and the rate of aging were investigated under different storage parameters (storage temperature, oil and stabilizers of different origins). The nanoemulsions are not thermodynamically stable and one of the most important characteristics is the kinetics of aging. Aqueous solutions of polymers and surfactants have shown special rheological properties and are able to stabilize colloids. The mixture of polymer and surfactants has significantly slowed the aging of nanoemulsions. This phenomenon can be explained by the changes of surface properties which are caused by the polymer-surfactant associates on the oil-water interface [26].

The emulsions are systems of two immiscible liquid where one is dispersed in the other. They can be made miscible by the addition of a third component, called surfactant or emulsifier. The stability of emulsions of liquid paraffin and castor oil was studied with various surfactants, like sodium stearate, glycerol monostearate, dioctyl sodium sulfosuccinate and benzalkonium chloride at a concentration of 1-8%, 300-600°C and for 42 days by Naik. S et al. 3% of glycerol monostearate and 5% of sodium dioctyl sulfococinate have showed good stability under these conditions, whereas the surface tension and the particle size remained unchanged [27].

The stability of emulsions depends significantly on the type and the ratio of emulsifiers. Kamba et al have found that increasing the concentration of surfactant, the separation time has also increased, so the emulsion was more stable. The mixture of soap and surfactant has resulted a more stable emulsion. The microscopic pictures showed that the emulsions containing lecithin the stabilizing force was stronger, because the size of emulsion particles is smaller [28].

#### *6.3.4 Detergency*

The washing serves to remove the contaminants from the solid surface. The detergency is different from the emulsification process, the emulsified contaminants (especially fat) is in a laminar difformed state, thus the shredding is only one way and must be perpendicular to the surface layer.

The surfactant dissolved in the detergent is adsorbed on the surface of the body, the contact angle increases and the penetration of washing liquid between the fat layer and the surface becomes possible, as well as the fat layer transforms to droplets and forms emulsion with the washing liquid.

A surfactant having good detergency must be water soluble (hydrophilic), reduce highly the surface and interfacial tension and in addition must have good wettability.

#### *6.3.5 Foamability*

If a gas is dispersed in a liquid medium, colloidal gas dispersion, foam is formed. Good foamability can be reached by surfactants which reduce the surface tension. The lower is the surface tension, the easier the production of film, the formation of bubbles and the tendency of foaming. The surfactant is adsorbed on the gas-liquid interface of the foams and a liquid coat is formed around the gas bubble which is connected by the surfactant. Due to mechanical stress (stirring, shaking), the gas bubbles move to the liquid surface and a foam is produced.

The liquid films of fluids with low friction are torn quickly and do not provide long-lasting foams because the liquid leaks down quickly and a vertical film is formed. The durability of foam can be increased to some extent by the growth of viscosity and the internal friction of the fluid (e.g. glycerol added to the soap solution). The foam is not constant it will be burst, eliminated eventually. The foamability is not in a linear correlation with the surfactant concentration [29].

The presence of a surfactant is necessary for the formation of stable foam which ensures the formation of liquid film. Mixtures of n-dodecyl- $\beta$ -d-maltoside (C12G2 or G2) with hexaethyleneglycol monododecyl ether (C12E6 or E6), dodecanol (C12E0 or E0), and dodecyl trimethylammonium bromide (C12TAB or TAB) were studied and analyzed by Angarska et al where the hydrophobic part was the same while the head moiety was different. The velocity of film formation was observed. It was found that the velocity of film formation decreases with the increase of radius [30].



### 7. STABILITY ANALYSIS OF SURFACTANTS

#### 7.1 Chemical Stability

The chemical stability is a key property for the commercial but also for the own-developed surfactants.

The aging tests are one of the most important measurements to investigate the chemical stability. It provides information about the storage lifetime. Depending on the application the low and the high temperature storage can also be indicative.

Another method to determine the chemical stability is the degree of separation. In this case the phase separation of emulsion or disperse system has been investigated. This is performed by transmitted light which is supplemented by density, particle size and particle distribution measurements [28].

#### 7.2 Mechanical Stability

The importance of mechanical stability is in the practical application. However this property is relatively difficult to determine (in terms of size and type a variety of mechanical stress can occur to the material) therefore a unified, accepted method which is applicable for all type of surfactants is not exist [31].

#### 7.3 Biological Stability

The harmful effect of organic materials in water can be different. The conventional organic contaminants are injurious in higher concentration and adverse effect especially on the oxygen balance. Biodegradation of the components of petroleum products occurs in different ways. Although some hydrocarbons are toxic, another part is tolerated and degraded by the aquatic ecosystem. Usually the paraffins decompose more easily than the aromatics and the straight carbon-chain groups can be divided more easily than the branched ones. The C10-C18 compounds can be oxidized most readily. The methane, ethane, propane is only metabolized by specific species, while the compounds of more than C30 carbon number are completely insoluble and totally resistant to biodegradation [32].

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