CHARTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Surfactants

Surfactants play an important role in today's life of nearly every human being. In our daily life surfactants are involved in many applications or products. They are used in various applications ranging from e.g. the mining industry to the nutrition industry. The largest market for surfactants is the household and personal-care product markets.

The personal-care sector comprises of toilet soaps, hair-care products, skin-care products and oral care products.

Anionics are the most important class of surfactants regarding volume followed by the nonionics. Cationics and amphoteric surfactants are less important. Surfactants are generally available from two different sources: petrochemicals and oleochemicals. The feedstocks for petrochemicals are crude oil and natural gas, for oleochemicals the fats and oils.

The source of oils and fats are various vegetable and animal raw materials. The vegetable oils soybean, palm, rape seed, and sunflower are the most important ones regarding volume. Fats and oils are triglycerides i.e. esters of fatty acids and glycerol. The composition of the fatty acid is different in the various fats and oils and is decisive for the further usage. Generally, there are two different types of fatty acids: 1. The lauric oil that contains high amounts of lauric and medium chain fatty acids like myristic acid, e.g. coconut oil and palm kernel oil. 2. The long chain fatty acids, e.g. steric acid, that are incorporated in e.g. tallow and palm oil.

Based on fats and oils the three types of oleochemical raw materials are available: fatty acids, fatty acid methyl ester and fatty alcohol. The latter one plays the most important role as a raw material for manufacturing of surfactants (Behler *et al.*, 2000).

2.2 Nonionic Surfactants

The most common nonionic surfactants are those based on ethylene oxide, referred to as ethoxylated surfactants. Several classes can be distinguished: alcohol ethoxylates, alkyl phenol ethoxylates, fatty acid ethoxylates, monoalkaolamide ethoxylates, sorbitan ester ethoxylates, fatty amine ethoxylates and ethylene oxide-propylene oxide copolymers (sometimes referred to as polymeric surfactants).

Another important class of nonionics is the multihydroxy products such as glycol esters, glycol (and polyglycol) esters, glucosides (and polyglucosides) and sucrose esters. Amine oxides and sulphinyl surfactants represent nonionics with a small head group (Tadros, 2005).

2.3 Alcohol Ethoxylates (AE)

A new developed manufacturing process now enables the production these products in a single reaction step through ethoxylation of a fatty chain alcohol such as dodecanol. Several generic names are given to this class of surfactants, such as ethoxylated fatty alcohols, alkyl polyoxyethylene glycol, monoalkyl poly(ethylene oxide) glycol ethers, etc. A typical example is dodecyl hexaoxyethylene glycol monoether with the chemical formula $C_{12}H_{25}(OCH_2CH_2O)_6OH$ (sometimes abbreviated as $C_{12}E_6$). In practice, the starting alcohol will have a distribution of alkyl chain lengths and the resulting ethoxylate will have a distribution of ethylene oxide chain lengths.

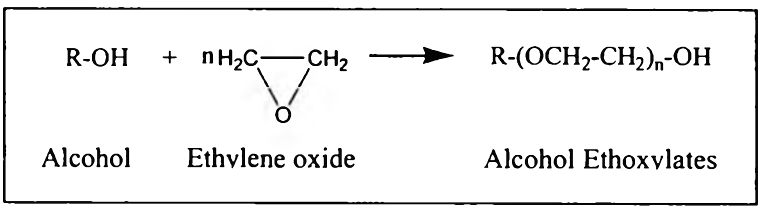

Figure 2.1 Reaction of ethoxylated alcohols.

The critical micelle concentration (CMC) of nonionic surfactants is about two orders of magnitude lower than the corresponding anionics with the same alkyl chain length. The solubility of the alcohol ethoxylates depends both of the alkyl chain length and the number of ethylene oxide units in the molecule. Molecules with an average alkyl chain length of 12 C atoms and containing more than 5 EO units are usually soluble in water at room temperature. However, as the temperature of the solution is gradually raised the solution becomes cloudy (due to dehydration of the polyethylene oxide chain) and the temperature at which this occurs is referred to as the cloud point (C.P.) of the surfactant. At a given alkyl chain length, C.P. increases with increasing EO chain of the molecule. C.P. changes with changing concentration of the surfactant solution and the trade literature usually quotes the C.P. of a 1% s olution.

2.4 Motor Oil

Motor oil is complex in composition and has high hydrophobicity. It generally consists of at least five main components: *n*-parafin, isoparafin, cycloparafin, aromatic hydrocarbon, and mixed aliphatic and aromatic ring (Tungsubutra and Miller, 1992). In addition to these main components, several additives are commonly added to the oil to act as rust inhibitor, oxidation inhibitor, detergent-dispersant, viscosity-index improver, pour-point dispersant, and antifoam. The EACN (equivalent alkane carbon number) is a parameter used to characterize the hydrophobicity of different oils. It is an equivalent number of carbons in the complex mixed oil as compared to single component alkane oil. The higher the EACN, the higher the hydrophobicity of the mixed oil is. Wu *et al.* (2000) studied and reported the EACN value of motor oil to be 23.5.

2.5 Microemulsions

Microemulsions are macroscopically homogeneous mixtures of oil, water and surfactant, which on the microscopic level consist of individual domains of oil and water separated by a monolayer of amphiphile. Microemulsions should not be regarded as emulsions with very small droplet size; micro- and macroemulsions are fundamentally different. Whereas macroemulsions are inherently unstable systems in which the droplets eventually will undergo coalescence, Microemulsions, like micelles, are considered to be lyophilic, stable, colloidal dispersions (Holmberg *et al.*, 2002). In some systems the addition of a fourth component called cosurfactant to an oil/water/surfactant system can cause the interfacial tension to drop to near-zero values, easily on the order of 10^{-3} – 10^{-4} mN/m, allowing spontaneous or nearly spontaneous emulsification to very small drop sizes, typically about 10–100 nm, or smaller. The droplets can be so small that they scatter little light, so the emulsions appear to be transparent. Unlike coarse emulsions, microemulsions are thought to be thermodynamically stable: they do not break on standing or centrifuging. The thermodynamic stability is frequently attributed to a combination of ultra-low interfacial tensions, interfacial turbulence, and possibly transient negative interfacial tensions (Schramm, 2005).

The systems of microemulsions may be water continuous (O/W) or oil continuous (W/O) as shown in Figure 2.2. In the Oil-in-Water (O/W) microemulsions, there is a continuous phase of water containing unconnected droplets of the oil phase. The O/W microemulsions will exhibit the ability to wet hydrophilic surfaces on contact and will exhibit electrical conductivities characteristic of an aqueous phase. On the other hand, The W/O microemulsions will exhibit the ability to wet hydrophobic surfaces on contact and will exhibit electrical conductivities characteristic of the oil phase. When the volume of oil and water in the microemulsions are approximately equal, the microemulsions may have a bicontinuous structure. (Holmberg *et al.*, 2002)

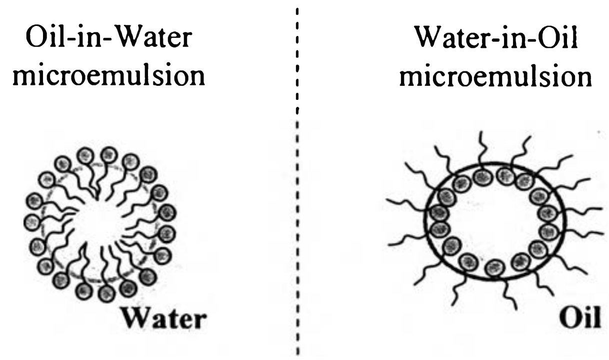

Figure 2.2 Illustration of the Oil-in-Water (O/W) and the Water-in-Oil (W/O) microemulsions.

The most studied phase equilibria of microemulsions are probably the Winsor Types microemulsion. There are four types of microemulsion, as shown in Figure 2.3:

1. Winsor Type I microemulsion: Oil-in-Water microemulsion in equilibrium with excess oil.

2. Winsor Type II microemulsion: Water-in-Oil microemulsion in equilibrium with excess water.

3. Winsor Type III microemulsion: middle phase microemulsion in equilibrium with an excess of both water and oil.

4. Winsor Type IV microemulsion: single phase microemulsion.

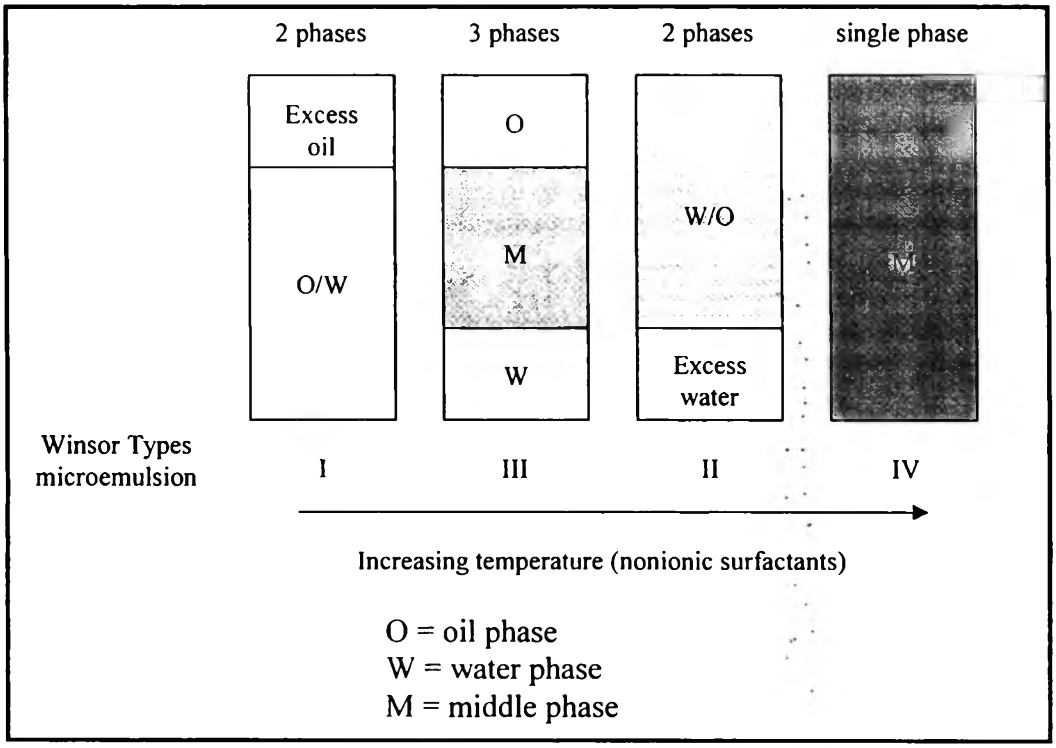

Figure 2.3 Winsor classification and phase sequence of microemulsions encountered as temperature for nonionic surfactant.

For nonionic surfactant, a transformation in the system from Winsor Types I to III to II microemulsion can be achieved by progressively changing temperature, the molecular structure of the surfactant and cosurfactant, the oil-to-water ratio, or the structure of oil in a homologous series.

For a given chemical system, phase-type diagrams can be constructed that show the regimes in which each type of microemulsions will exist. These can be used to understand and predict the effects of, for example, increasing salinity or temperature, which tend to shift the microemulsions type directionally from Type I to III to II. Type III microemulsion can be thought of as bi-continuous in which the aqueous and oil phases are mutually intertwined.

The transition of Winsor Types I-III-II microemulsion influences the two interesting properties of microemulsions which are solubilization and interfacial tension (IFT), due to the changing of the microstructure. Figure 4 shows the relationship between the type of microemulsions and the interfacial tension.

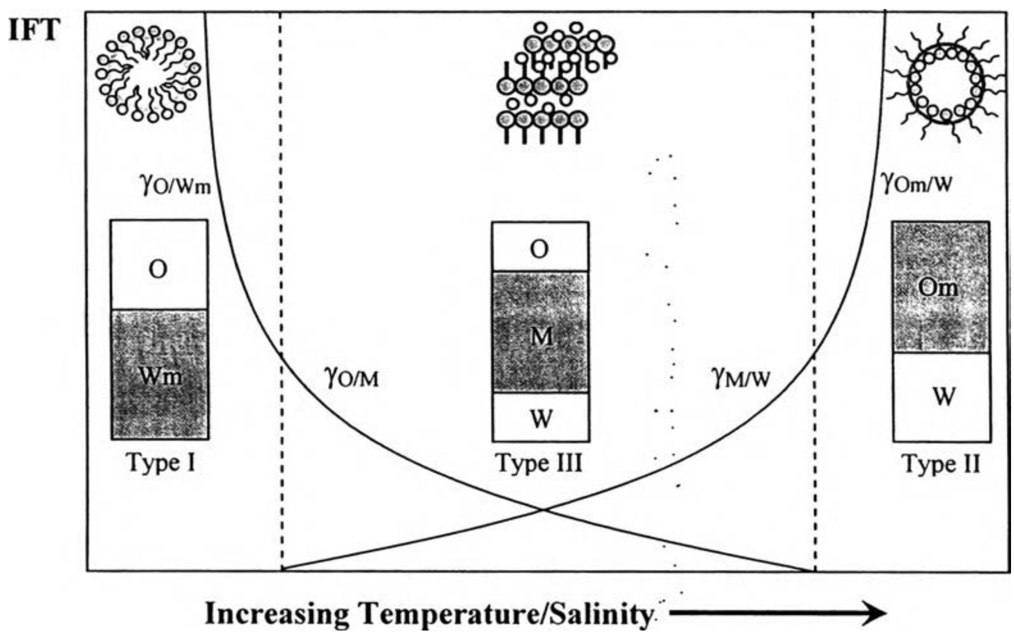

Figure 2.4 Phase behavior showing interfacial temsion (IFT) as a function of scanning variables. Where O is oil; W is water; M is middle phase; Wm is Oil-in-Water (O/W) microemulsions; Om is Water-in-Oil (W/O) Microemulsions.

The region on the left hand side of Figure 2.4 is a Winsor Type I microemulsion where Oil-in-Water (O/W) microemulsions exist along with an excess oil phase. IFT between the excess oil phase and the micellar solution ($\gamma_{o/m}$) decreases with increasing temperature or salinity. When the middle phase is formed, the microemulsions become a bicontinuous structure in equilibrium with excess of both oil and water phases. IFT between the excess oil and the middle phase ($\gamma_{o/m}$) further decreases with increasing temperature of salinity while IFT between the excess water and the middle phases ($\gamma_{w/m}$) is increased. The point in the Type III region where $\gamma_{o/m}$ equals to $\gamma_{w/m}$ is known as the minimum IFT or optimum state.

Microemulsion applications span many areas including enhanced oil recovery, soil and aquifer decontamination and remediation, foods, pharmaceuticals (drug delivery systems), cosmetics, and pesticides. The widespread interest in microemulsions and use in these different industrial applications are based mainly on their high solubilization capacity for hydrophilic and lipophilic compounds, their large interfacial areas, the ultra-low interfacial tensions achieved when they coexist with excess aqueous and oil phases, and their long-term stability.

Cox *et al.* (1984) determined the effect of surfactant composition on performance in order to determine the optimum nonionic for hard-surface cleaning. The hard-surface cleaning performance of various nonionic homologs was evaluated as a function of carbon chain length, ethylene oxide (EO) content, blending and concentration. The result shows that carbon chain length to be very important to hard-surface cleaning performance of grease, wax, and particulate soils dramatically increases as carbon-chain length decreases, probably as a result of an increase in solvency properties as carbon chain length is decreased. EO content is also important, particularly if nonionics with longer carbon chain lengths are used. Surfactant concentration (dilution) has little effect on the optimum ethylene oxide content but significantly affects the optimum carbon chain length of the hydrophobe. Overall results show the optimal nonionic for hard-surface cleaning to consist of a blend of C6, C8, and C10 alcohols ethoxylated to a 50% EO level at a variety of use concentrations.

A series of ethoxylates, propoxylates and mixed alkoxylates based on *n*-hexanol were investigated by Moy *et al.* (2000) to determine the effect of alkoxylation on key physical properties (cloud point, viscosity) which were performance-tested in hard surface and glass cleaning formulations. In order for a product to be considered a good glass cleaner, it must loosen and dissolve oily soils and dry quickly without streaking or leaving residues. The results show that the alkoxylate type, degree of alkoxylation, and catalyst choice are important to cleaning performance. The C6 propoxylates based on the "peaked" technology showed good hard surface cleaning and low glass streaking. The mixed EO/PO alkoxylates also showed good hard surface cleaning. Therefore, these products can function as components of hard surface cleaning formulations. They are readily biodegradable, have little to no odor and have low volatile organic content due to their low free alcohol content. These products are good candidates for further evaluations.

Smith *et al.* (2004) studied the formulating cleaning products with microemulsions on variety of different surfactant systems. Typically, a mixture of anionic and nonionic surfactant is used along with a short chain alcohol to help solubilize the oil phase and prevent liquid crystal formation leading to high viscosity gels. While short chain alcohols are effective, they contribute to the volatile organic solvent content (VOC) of the product and may pose flammability problems. Thus, a VOC free surfactant mixture was developed for this work. The mixture consists of sodium xylene alcohol (SXS) and a blend of anionic and nonionic surfactants. A blend of high and low HLB alcohol ethoxylates is used to fine tune the Winsor ratio to allow for use with a variety of different oils. SXS is used to help solubilize the low HLB nonionic, prevent liquid crystal formation and lower the viscosity of the microemulsion at high oil levels. Anionic surfactant is used to minimize the temperature sensitivity of nonionic microemulsion systems. The result shows that the efficiency of the surfactant system was found to increase with increasing concentration of nonionic in the blend. Work was performed to better understand the phase behavior of single phase microemulsions. The phase boundary was determined by titrating mixtures of pine oil and water at different ratios with the universal surfactant blend until the mixture turned from cloudy to clear. Microemulsions prepared at the edges of the diagram tend to show a faint bluish tint whereas the bicontinuous microemulsions appear less turbid. This suggests that O/W and W/O microemulsions are composed of discreet particles or swollen micelles whereas the bicontinuous microemulsions have a sponge-like structure.

Moreover, worked was performed to measure the cleaning performance of the single phase microemulsions. The ratio of oil to water in most of the systems is close to unity, favoring the formation of bicontinuous microemulsions. In general, the higher the molecular weight of the solvent, the greater the surfactant requirement. Attempts to prepare microemulsions using olive oil were not successful, and triglycerides are high molecular weight and may require a different surfactant blend ratio to obtain good surfactant efficiency.

2.6 Fish Diagram

The fish diagram has been used to describe the phase behavior of microemulsion systems for decades. As shown schematically in Figure 2.5, the fish diagram looks like a lower case Greek gamma with Winsor Type I microemulsion at low cosurfactant concentrations, Winsor Type III inside the closed loop and Type II at high cosurfactant concentrations. Winsor Type IV microemulsion occurs at high surfactant concentrations and corresponds to the whole solution being a single homogeneous surfactant-rich phase. The lowest surfactant concentration at which Winsor Type III microemulsion is known as the critical microemulsion concentration (CμC); since the volume of the middle phase is too small to be visually observed at the CμC, the surfactant concentration that first produce the ultra-low IFT which is only attained when Winsor Type III microemulsion is present.

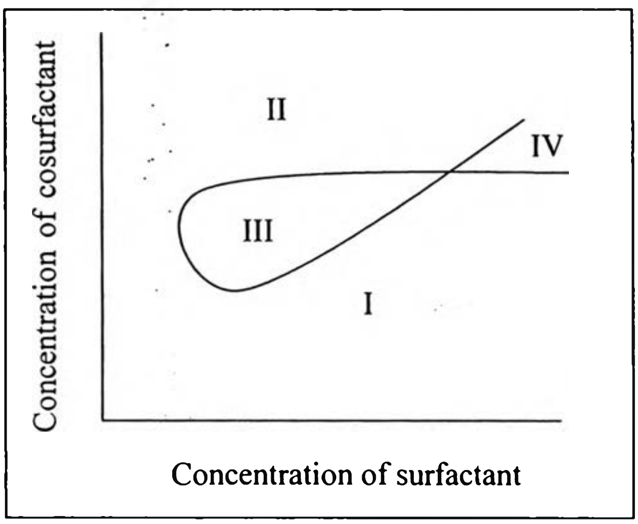

Figure 2.5 Schematic representation of normal fish phase diagram. Roman numerals refer to the Winsor Type microemulsion existing at that condition.

Yang *et al.* (2008) studied the three-phase behavior of quaternary systems comprising *N*–lauroyl–*N*–methylglucamide (MEGA–12)/alcohol/alkane/water by using ε–β fishlike phase diagrams, where ε and β is the mass fractions of the alcohol and surfactant in the system, respectively. The effects of different alcohols, alkanes, and NaCl concentrations in the aqueous phase on the phase behavior and solubilization capacity were investigated; then it can be discussed from their ε–β fishlike phase diagrams. In this paper, the order of the maximum solubilization capacity for different alcohols investigated is 1-hexanol > 1-pentanol > 1-butanol, and for alkanes is *n*-octane > *n*-decane > *n*-dodecane. NaCl concentrations have a little influence on the phase behavior.

Chai *et al.* (2003) studied the fishlike phase diagrams for the quaternary system of alkyl polyglucoside (APG: $C_{8/10}G_j$ or $C_{12/14}G_j$)/alcohol/alkane/water mixtures at 40 °C. Alcohol in these microemulsion systems acts as both a cosurfactant and a cosolvent. The distorted shape of the fish body region is believed to be a direct consequence of the competition, between the incorporation of *n*-butanol molecules into the interfacial film and its solubility in the bulk oil phase. The coordinates at the "head" (γ_B, δ_E) and "tail" (γ_E, δ_E) points of the phase diagram are obtained by using the HLB plane equation. The γ_E values reveal the minimum total concentration of APG for getting a single microemulsion system while the ratio of water to oil is equal 1. The mass fraction of alcohol in the hydrophile–lipophile balanced interfacial layer (A^S) value of $C_{8/10}G_{1.31}$ is larger than that of $C_{12/14}G_{1.43}$, which shows that $C_{12/14}G_{1.43}$ molecules are less hydrophilic and less alcohol is needed to balance the hydrophile–lipophile film. $C_{12/14}G_{1.43}$ has smaller γ_E value; therefore its solubilization is larger than that of $C_{8/10}G_{1.31}$. Additionally, the effects of alkanes and alcohols on the phase behavior are also investigated. The result shows that both have notable influence on the fishlike phase diagram, the composition of the optimum middle phase (C_S, C_A and A^S). It was found that the alcohols with longer hydrocarbon chain, oil molecules with smaller ones can increase the solubilization of the microemulsions.

Chai *et al.* (2007) studied the middle-phase behavior for the quaternary system of sodium dodecyl sulfonate (AS) (sodium dodecyl sulfate, SDS; sodium dodecyl benzene sulfonate, SDBS)/alcohol/oil/water with a novel ε–β (ε is the mass fraction of alcohol in the whole system, β is the mass ratio of surfactant in the whole system) fishlike phase diagram at 40 °C. The composition of the hydrophile–lipophile balanced interfacial layer was determined. A series of phase inversions of Winsor Types I ($\underline{2}$)→III (3)→II ($\bar{2}$) were observed from the fishlike phase diagram clearly, and some important physicochemical parameters of the microemulsion were calculated precisely. The coordinates at the "fish tail" point of the phase diagram, β_E and ε_E, reveal the minimum amounts of surfactant and alcohol to form single phase microemulsion, respectively; therefore, β_E and ε_E can be used to estimate the solubilization power of the microemulsion system. The smaller the value of β_E and ε_E, the larger the solubilization power of the microemulsion system. The order of the solubilization power of three anionic surfactants studied is: SDBS >> SDS > AS. The oils with short carbon chain lengths and the alcohols with long carbon chain lengths are of high solubilization power of their microemulsions, inorganic salt (NaCl) facilitates the microemulsion inversion Winsor I→III→II.

Mitra and Paul (2005) investigated the phase behavior of Brij-56/ 1-butanol/*n*-heptane/water at 30 °C with α [weight fraction of oil in (oil + water)] = 0.5, wherein a $\underline{2} \rightarrow 3 \rightarrow \bar{2}$ phase transition occurs with increasing W_1 (weight fraction of 1-butanol in total amphiphile) at low X (weight fraction of both the amphiphiles in the mixture) and a $\underline{2} \rightarrow 1 \rightarrow \bar{2}$ phase transition occurs at higher X. Addition of an ionic surfactant, sodium dodecylbenzene sulfonate, destroys the three-phase body and decreases the solubilization capacity of the system at different δ (weight fraction of ionic surfactant in total surfactant). No three-phase body is formed for Brij-56/ionic surfactant(s)/1-butanol/*n*-heptane/water system; instead a wide channel of single-phase region is formed. Increasing temperature increases the solubilization capacity of the Brij-56 system, whereas it has negligible effect on the Brij-56/SDBS mixed system. Addition of salt (NaCl) induces three-phase body formation in the Brij-56/SDBS system, and the solubilization capacity of both single and mixed surfactant systems increases with addition of NaCl. The monomeric solubility of 1-butanol in oil phase (S_1) is decreased, whereas the interfacial concentration of 1-butanol (S^{s}_{1}) increases with the addition of NaCl, which in turn increases the solubilization capacity of these systems.

The phase behavior of microemulsions of motor oil with alcohol ethoxylates was studied by Tongkak (2009). The microemulsions for single nonionic surfactant system without cosurfactant consists of alcohol ethoxylate (AE3)/different oils/water at 30 °C and α (the mass fraction of oil to water plus oil) = 0.5. In order to study effects of oils, *n*-octane, motor oil and palm oil with different polarity increasing in the order: *n*-octane < motor oil < palm oil were studied. The volume of both oil phase and water phase did not change and no middle microemulsion phase was formed with all of oils. From this result, the hydrophilic–lipophilic balance of these systems did not balance to form microemulsions because of high hydrophilicity of AE3. However, the Water-in-Oil (W/O) microemulsion phase (Winsor Type II microemulsion) could occur in high concentrations of AE3 around 10% w/v with only *n*-octane because *n*-octane had smaller molecule to penetrate the surfactant palisade layer and alcohol ethoxylate (AE3) was enough oil soluble surfactant to solubilize *n*-octane. The microemulsions for single nonionic surfactant system (AE3) with cosurfactant (*n*-butanol) at 30 °C and $\alpha = 0.5$ formed microemulsions with motor oil and *n*-octane. The microemulsion formation with only motor oil could occur in Oil-in-Water or O/W (Winsor Type I microemulsion), middle (Winsor Type III microemulsion) and Water-in-Oil (Winsor Type II microemulsion) microemulsions and the fish diagram was constructed. The microemulsion formation with *n*-octane still occurred in only W/O microemulsion.

Tongkak was also studied the effect of EO groups of alcohol ethoxylates on microemulsion formation. The results show that surfactant which has higher EO group has higher hydrophilic increasing in the order: AE3 < AE5 < AE7 < AE8 < AE9. Furthermore, the fish diagram of AE3/motor oil/water with cosurfactant (*n*-butanol) was constructed at three different temperatures. The temperature showed a significant effect on the microemulsion phase transformation and the critical microemulsion concentration (CμC) value which decreased with increased temperature.

2.7 Solubilization Parameters (SP)

The SP is defined as the volume of oil solubilized (SPo) or of water solubilized (SPw) per weight of total surfactants in the microemulsion phase.

2.8 Cloud Point Temperature

Aqueous solutions of polyoxyethylene nonionics, if the oxyethylene content is below about 80%, become turbid on being heated to a temperature known as the cloud point, following which there is separation of the solution into two phases. The phases appear to consist of an almost micelle-free dilute solution of the nonionic surfactant at a concentration equal to its critical micelle concentration (CMC) at that temperature and a surfactant-rich phase separation is reversible, and on cooling of the mixture to a temperature below the cloud point, the two phases merge to form once again a clear solution. Phase separation occurs because of the difference in density of the micelle-rich and micelle-poor phases.

The temperature at which clouding occurs depends on the structure of the polyoxyethylene nonionic surfactant. For a particular hydrophobic group, the larger the percentage of oxyethylene in the surfactant molecule, the higher the cloud point, although the relation between oxyethylene percentage and cloud point is not linear (Rosen, 2004).