

CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE
REVIEW REFERENCES

2.1 Surfactants

Surfactants (surface active agent) are substances having a contraction of the term surface-active agent. At low concentration, the surfactant has adsorbing property onto the surfaces or interface of the system and altering to a marked degree of the surface or interfacial free energies of those surfaces (Rosen, 2012). Surfactants have a characteristic molecular structure consisting of a structural group that has very much interaction for the water, known as a hydrophilic group, together with a group that has a strong attraction to oil, called that hydrophobic group consisting of an amphipathic structure. When the amphipathic molecule is dissolved in oil, the hydrophilic group distorts the structure of the oil, increasing the free energy of the system. When that occurs, the system responds in some fashion in order to minimize contact between the hydrophilic group and the oil. On the other hand, in the case of a surfactant dissolved in aqueous phase, the hydrophobic group distorts the structure of the water by breaking hydrogen bonds between the water molecules and by structuring the water in the vicinity of the hydrophobic group. In addition, surfactants are among the most versatile products of the chemical industry, appearing in such diverse products as the motor oils, pharmaceuticals, detergents, drilling chemicals, and flotation agents.

2.1.1 Conventional Surfactants

Typically, the structure of surfactant is derived into two parts; hydrophobic and hydrophilic groups. The hydrophobic group is usually a long-chain hydrocarbon (C₈-C₁₈), and less a halogenated or oxygenated hydrocarbon or siloxane; the hydrophilic group is an ionic or highly polar group depending on the nature of the hydrophilic group, surfactants are classified as;

2.1.1.1 Anionic Surfactant

The surface-active portion of the molecule is a negative charge. For example, RCOONa^+ (soap), $\text{RC}_6\text{H}_4\text{SO}_3^-\text{Na}^+$ (alkylbenzene sulfonate).

2.1.1.2 Cationic Surfactant

The surface-active portion of the molecule is a positive charge. For example, $\text{RNH}_3^+\text{Cl}^-$ (salt of a long-chain amine), $\text{RN}(\text{CH}_3)_3^+\text{Cl}^-$ (quaternary ammonium chloride).

2.1.1.3 Zwitterionic Surfactant

Both positive and negative charges may be present in the surface-active portion, for example, $\text{RN}^+\text{H}_2\text{CH}_2\text{COO}^-$ (long-chain amino acid), $\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{SO}_3^-$ (sulfobetaine).

2.1.1.4 Nonionic Surfactant

The surface-active portion bears no apparent ionic charge. For example, $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$ (monoglyceride of long-chain fatty acid), $\text{R}(\text{OC}_2\text{H}_4)_x\text{OH}$ (polyoxyethylenated alcohol) (Rosen, 2012).

2.1.2 Extended Surfactants

The extended surfactant molecule has intermediate polarity groups, such as polypropylene oxide (PO) and/or polyethylene oxide (EO), inserted between the hydrophilic head and the hydrocarbon tail. This unique molecular structure, the extended surfactants provide an enhanced interaction about both oil and water phases because they can stretch further into both oil and water, resulting in a smoother transition between the hydrophilic and hydrophobic regions at the interface. This results in microemulsion formation with ultralow IFT and high solubilization properties, especially for highly hydrophobic oils and vegetable oils (Phan, 2011). Extended surfactant systems have very low critical micelle concentrations (CMC) and critical microemulsion concentrations ($C_{\mu C}$) compared to those from other conventional surfactants. Such formulations have numerous potential applications in enhanced subsurface remediation, drug delivery, and detergency.

2.1.3 Renewable-Based Surfactants

Renewable-based surfactants are derived from natural sources such as plants, and animals where they are often referred to as polar lipids for example sugar-based surfactant. Surfactants derived from plants are widely used as same as petroleum based surfactants and employed in technical system to overcome solubility problems such as emulsifiers, dispersants, and surface modifications. Renewable-based surfactants can produce a low surface tension, characterized by low critical micelle concentration (CMC) values. The hydrophobic moiety in the renewable-based surfactants is composed of anionic or cationic derivatives of amino acids or peptides, and nonionic derivatives of di-or polysaccharides; the hydrophobic part is made from saturated, unsaturated, or hydroxylated fatty acid chains, or hydrophobic peptides. Although the higher production costs of renewable-based surfactants, their biodegradability, toxicity, and renewable resource based make them attractive in a number of industrial areas for example, agricultural applications, the food and beverage industries, industrial cleaning, textile manufacture, cosmetic formation (Rosen, 2012).

2.2 **Microemulsion**

Microemulsions are thermodynamically stable and do not coalesce over time. A concept of microemulsions includes any system containing oil and water domain coexisting in equilibrium. Microemulsions are divided into four categories as depicted in Figure 2.1-2.2.

1) Winsor Type I microemulsion, which contains excess oil, is oil droplets in continuous aqueous phase where the curvature of the surfactant membrane is concave relative to the oil phase (micelle). This Winsor Type I microemulsion usually applies in hard surface cleaning industries.

2) Winsor Type II microemulsions containing excess water phase, are water droplets in oil phase where the curvature of the surfactant membrane is convex (reverse micelle). There are wild uses in biofuel as alternative energy and dry cleaning applications.

3) Winsor Type III microemulsions are bi-continuous micelle that has a net curvature of oil and water near zero having both excess water and oil phases in equilibrium. Mostly, this microemulsion type is used in detergent application.

4) Winsor Type IV microemulsions are single phase system (high surfactant concentration) containing the same amount of oil and water co-solubilized in the system. These microemulsions are used as same as Winsor type III microemulsions.

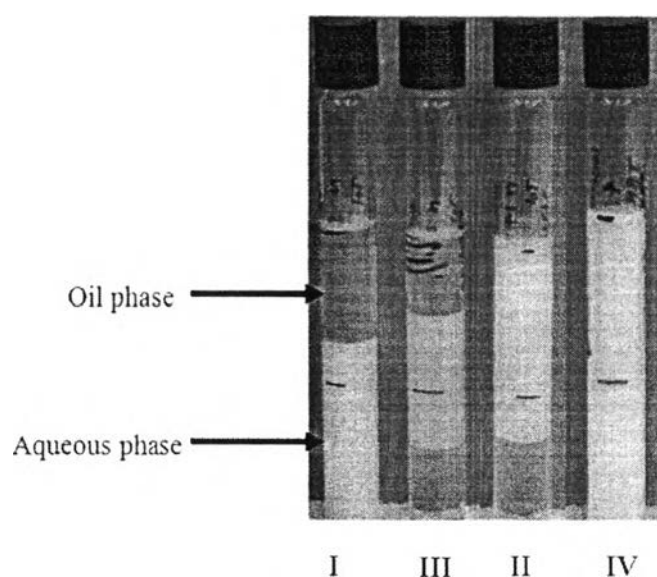


Figure 2.1 Demonstration of Winsor Type I, III, II, and IV microemulsion (Nguyen, 2011).

Microemulsion formation can be explained in phase behavior using fish diagram as shown in Figure 2.1. Figure 2.1 shows Winsor Type I to Type III to Type II microemulsions. Winsor Type I to Type III to Type II transition can be achieved by increasing electrolyte concentration (anionic surfactants), temperature (nonionic surfactants), surfactant hydrophobicity or decreasing oil hydrophobicity (lower HLB).

Winsor Type I microemulsion (oil-swollen micelles) is located on the left-hand side of the fish body of Figure 2.2. In this region, the surfactant is more hydrophilic and form micelles. The capacity of oil solubilization is not high as much as Winsor Type III microemulsions, but it is still significant increase as the system approaches the Winsor Type I to III boundary.

Winsor Type II microemulsions are illustrated on the right side of Figure 2.2. The surfactant in this region is more hydrophobic and formed reverse micelles containing water-droplet solubilized in oil phase. When reverse micelles approach Winsor Type I microemulsion phase boundary, the water soluble in the reverse micelles increases and IFT decreases.

Winsor Type III microemulsions are depicted in Figure 2.2 inside of the fish body. The surfactant is more water and oil soluble in middle phase microemulsions providing ultralow IFT.

Winsor Type IV microemulsions occur at high surfactant concentrations that surpass the amount of oil and water available, yielding a single phase Winsor Type IV microemulsions as depicted in Figure.2.2.

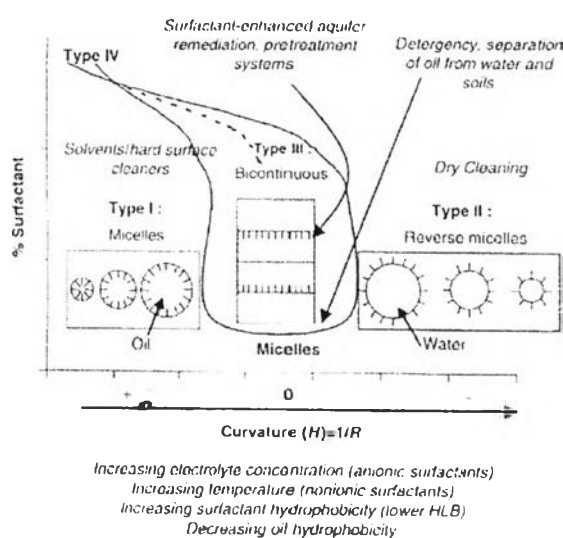


Figure 2.2 Microemulsion phase map. The solid line indicates the different microemulsion types (I, III, II, and IV). The inset figures show the changes in curvature as the microemulsion transition from Type I to Type III to Type II microemulsion (Acosta, 2007).

2.2.1 The Effect of Salinity and Temperature on Microemulsion Formation

The effect of temperature on solubilization capacity is shown in Figure 2.3. When the temperature of an aqueous micellar solution, W_D of a POE (polyethylene oxide) nonionic surfactant is increased, its solubilization of nonpolar

material, O increases due to the increasing dehydration of POE chains increases the hydrophobic character of the surfactants. If this occurs for POE nonionics of the proper structure in the presence of excess nonpolar material, the volume of the aqueous phase, W_D increases, and that of the nonpolar phase oil decreases as the temperature increases which indicate in Figure 2.3a and 2.3b. This is accompanied by a decrease in the tension γ_{OW} at the O/W interface. With further an increase in temperature, the POE chains become more and more dehydrated, the surfactant becomes more and more hydrophobic, and more and more nonpolar material oil is solubilized into the increasingly asymmetric micelles. When the vicinity of the cloud point of the nonionic is reached, the surfactant micelle, together with solubilized materials, will start to separate from W_D as a separate phase D . The O/W_D interface is now replaced by a D/W_D interface, whose interfacial γ_{DW} is close to zero. At this point, there is also an O/D interface, whose interface tension γ_{OD} is low. The volume of W_D continues to decrease and that of middle phase D increases; γ_{OD} continues to decrease and γ_{DW} increases (Figure 2.3c and 2.3d). A point is reached at which the micelles start to invert and dissolve in the excess O , carrying with them solubilized water and forming a reverse micellar solution O_D . This is accompanied by an increase in O_D and a decrease in D to a very small volume (Figure 2.3e). Eventually, all of D dissolves in O_D , leaving only W (Figure 2.3f). At this point, the DW interface disappears and γ_{DW} , still low, is replaced by γ_{OW} . With further increase in temperature, the surfactant becomes more hydrophobic, the solubilization capacity of the surfactant becomes more and more hydrophobic, the solubilization capacity of the inverted micelles decreases, more W separates out, and γ_{OW} increases (Figure 2.3g).

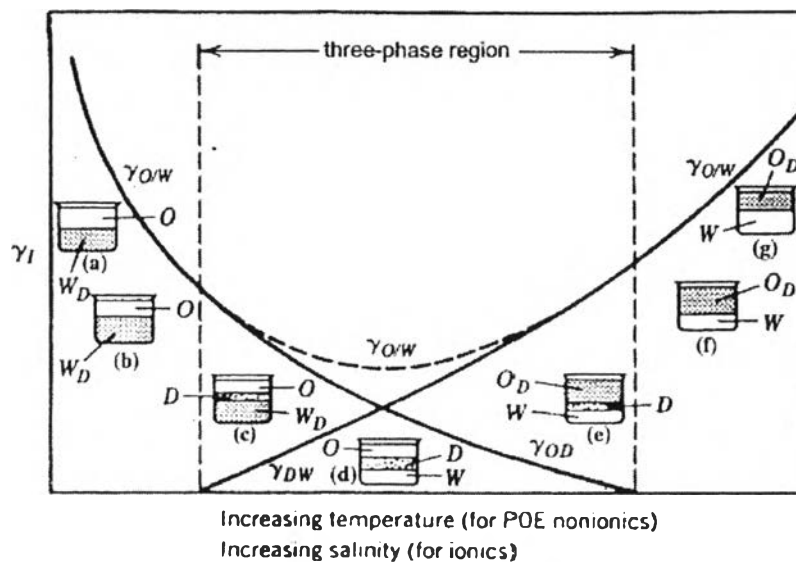


Figure 2.3 The effect of molecular environmental conditions on IFT and phase volume. Shaded phases indicate surfactant locations (Rosen, 2012).

2.3 Adsorption at The Liquid-Gas (L/G) and Liquid-Liquid (L/L) Interfaces

The direct determination of the amount of surfactant adsorbed per unit area L/G or L/L interface, although possible, is not generally undertaken because of the difficulty of isolating the interfacial region from the bulk phase for purposes of analysis when the interfacial region is small, and of measuring the interfacial area when it is large. Instead, the amount of material adsorbed per unit area of interface is calculated indirectly from surface or IFT measurement. As a result, a plot of surface (or interfacial) tension as a function of equilibrium concentration of surfactant in one of the liquid phases, rather than an adsorption isotherm, is generally used to describe adsorption at these interfaces. From such a plot, the amount of surfactant adsorbed per unit area of interface can readily be calculated by use of the Gibbs adsorption equation (Equation 2.1).

2.3.1 The Gibbs Adsorption Equation

The Gibbs adsorption equation, in its most general form

$$d\gamma = - \sum_i \tau_i d\mu_i \quad (2.1)$$

Where $d\gamma$ = the change in surface or IFT of the solvent
 τ_i = the surface excess concentration of any component of the system
 $d\mu_i$ = the change in chemical potential of any component of the system

2.3.2 Calculation of Effective Area Per Molecule (A_s)

For surface-active solutes, the surface excess concentration, τ_1 , can be considered to be equal to the actual surface concentration without significant error. The concentration of surfactant at the interface may therefore be calculated from surface or IFT data by use of the appropriate Gibbs equation. Thus for dilute solutions of a nonionic surfactant, or for a 1:1 ionic surfactant in the presence of a swamping amount of electrolyte containing a common non-surfactant ion using Equation 2.2,

$$\tau_1 = - \frac{1}{2.303RT} \left(\frac{\partial \gamma}{\partial \log C_1} \right)_T \quad (2.2)$$

and the surface concentration can be obtained from the slope of a plot of γ versus $\log C_1$ at constant temperature (where γ is in dyn/cm or ergs/cm² and $R = 8.31 \times 10^7$ ergs/mol/K, then τ_1 is in mol/cm²; when γ is in mNm⁻¹ or mJm⁻² and $R = 8.31$ J mol⁻¹ K⁻¹, τ_1 is in mol/1000 m²).

For solution of 1:1 ionic surfactant in the absence of any other solutes using Equation 2.3

$$\tau_1 = - \frac{1}{4.606RT} \left(\frac{\partial \gamma}{\partial \log C_1} \right)_T \quad (2.3)$$

The area per molecule at the interface provides information on the degree of packing and the orientation of the adsorbed surfactant molecule when compared with the dimensions of the molecule as obtained by use of molecular models. From the

surface excess concentration, the area per molecule at the interface, A_s in square angstroms is calculated from the Equation 2.4

$$A_s = \frac{10^{16}}{N\tau_1} \quad (2.4)$$

Where N = Avogadro's number and τ_1 is in mol/cm².

A typical γ - $\log C_1$ plot for a dilute solution of an individual surfactant (surfactants are often used at concentrations of less than $1 \times 10^{-2} M$) is shown in Figure 2.4. The break in curve occurs at the CMC, the concentration at which the monomeric form, in which the surfactant exists in very dilute solution, aggregates to form a surfactant cluster known as micelle. Above this concentration, the surface tension of the solution remains essentially constant since only the monomeric form contributes to the reduction of the surface or IFT. For concentrations below but near the CMC,

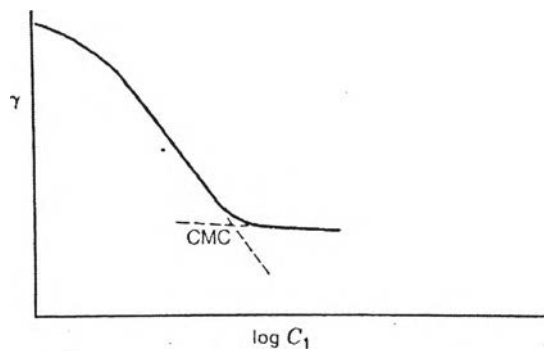


Figure 2.4 The surface tension (γ) versus surfactant concentration ($\log C_1$) (Rosen, 2012).

The slope of the curve is essentially constant, indicating that the surface concentration has reached a constant at maximum value. In this range, the interface is considered to be saturated with surfactant concentration, and the continued reduction in the surface tension is due mainly to the increased activity of the surfactant in the bulk phase rather than at the interface. For ionic surfactants in the presence of a

constant concentration of counterion, this region of saturated adsorption may extend down to one-third of the CMC.

2.4 Solubilization by Surfactant Solutions

One of the most important properties of surfactants that is directly related to micelle formation is solubilization. Solubilization may be defined as the spontaneous dissolving of a substance (solid, liquid, or gas) by reversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of solubilized material. Although both solvent-soluble materials may be dissolved by the solubilization mechanism, the importance of the phenomenon from the practical point of view is that it makes possible the dissolving of substances in solvents in which they are normally insoluble.

Solubilization into aqueous media is of major practical importance in such areas as the formulation of products containing water-insoluble ingredients where it can replace the use of organic solvents or co-solvents: in detergency, where solubilization is believed to be one of the major mechanisms involved in the removal of oily soil. Solubilization is distinguished from emulsification (the dispersion of one liquid phase in another) by the fact that in solubilization, the solubilized material called "solubilize" is in the same phase as the solubilizing solution and the system is consequently thermodynamically stable.

If the solubility of a normally solvent-insoluble material is plotted against the concentration of the surfactant solution that is solubilizing it, we find that the solubility is very slight until a critical concentration is reached at which the solubility increase approximately linearly with the concentration of the surfactant. That critical concentration is the critical micelle concentration (CMC) of the surfactant in the presence of the solubilize as shown in Figure 2.4. This indicates that solubilization is a micellar phenomenon, since it occurs only to a negligible extent at concentrations where micelles, if they exist at all, are found only in insignificant numbers.

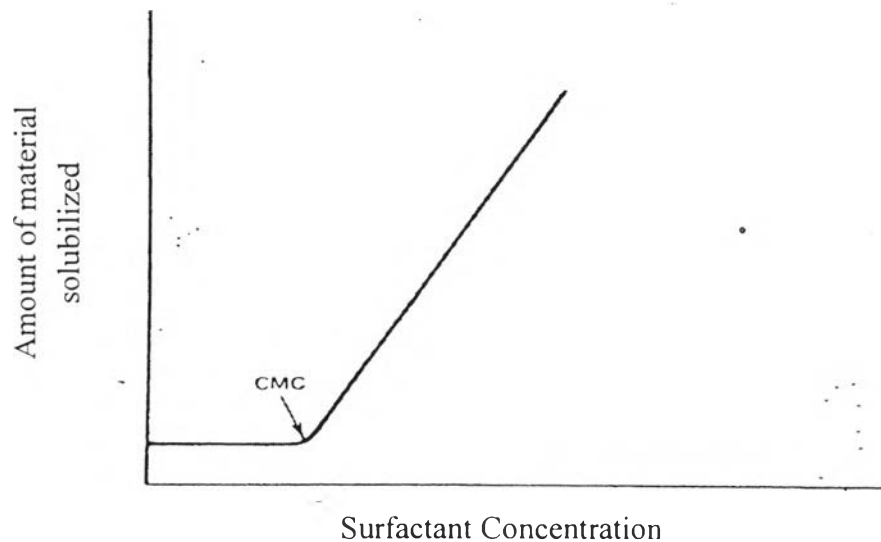


Figure 2.5 The solubility as a function of surfactant concentration (Rosen, 2012).

2.4.1. Solubilization in Aqueous Media

2.4.1.1 *Locus of Solubilization*

The exact location in the micelle at which solubilization occurs varies with the nature of the material solubilized and is of importance in that it reflects the type of interaction occurring between surfactant and solubilize. Solubilization is believed to occur at a number of different sites in the micelle as depicted in Figure 2.5: (1) on the surface of the micelle, at the micelle-solvent interface; (2) between the hydrophilic head groups; (3) in the so-called palisade layer of the micelle between the hydrophilic groups and the first few carbon atoms of the hydrophobic groups that comprise the outer core of the micellar interior; (4) more deeply in the palisade layer; and (5) in the inner core of the micelle.

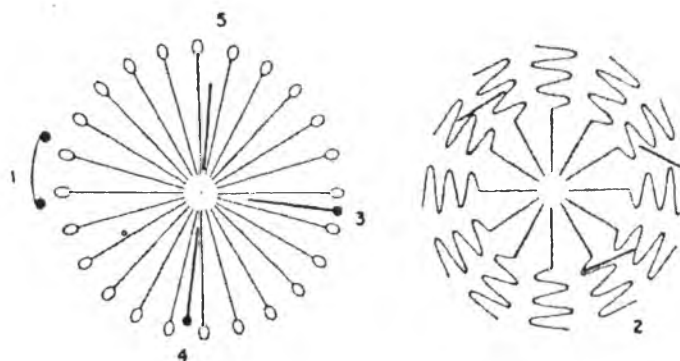


Figure 2.6 The location of solubilizate in a surfactant micelle (Rosen, 2012).

Small polar molecules in aqueous medium are generally solubilized close to the surface in the palisade layer or by adsorption at the micelle-water interface. The spectra of these materials after solubilization indicate that they are in a completely, or almost completely, polar environment. Short-chain phenols, when solubilized in POE nonionics, appear to be located between the POE chains (Schick, 1967). The localization of probes like ruthenium bi-pyridyl complexes has been addressed affirmatively in sodium dodecylsulfate (SDS) micelles, comicelled with nitroxide substituted surfactants of comparable chain length, in which the position of the nitroxide quencher group on the carbon chain was varied, by fluorescence spectroscopy (Kunjappu, 1990).

In concentrated aqueous surfactant solution, although the shape of the micelles may be very different from that in dilute solution, the locus of solubilization for a particular type of solubilizate appears to be analogous to that in dilute solution; that is, polar molecules are solubilized mainly in the outer regions of the micellar structures, whereas nonpolar solubilizates are contained in the inner portion.

2.4.2 Solubilization by Solutions of Surfactants

2.4.2.1 *Factor Determining the Extent of Solubilization*

Because of the importance of solubilization in the removal of oily soil by detergents and in the preparation of pharmaceutical, cosmetic, insecticide, and other types of formulation, a good deal of work has been done on

elucidating the factors that determine the amount of solubilize that can be solubilized by various types of surfactants. The situation is complicated by the existence of the different sites for the solubilization of different types of materials.

The solubilization capacity or solubilizing power of the micelle is defined as the number of moles of solubilize per mole of micellized surfactant as shown in Equation 2.5

$$MSR = \frac{S_w - S_{CMC}}{C_{surf} - CMC} \quad (2.5)$$

Where S_w is the molar solubility at the solubilize in the aqueous system, S_{cmc} is its molar solubility at the CMC, and C_{surf} is the molar concentration of the surfactant. It often remains constant for a particular surfactant over a wide concentration range above the CMC, although some surfactants show increasing solubilizing power at higher concentration. MSR also can be calculated from a plot between solubility (M) and surfactant concentration (M). In general, solubilization capacity is greater for polar solubilizes than for nonpolar ones, especially for spherical micelles (because of the larger volume available at the surface of the micelle than in the interior), and decreases with increase in the molar volume of the solubilize.

An alternative approach used to quantify the surfactant solubilization is based on the micelle-water partition coefficient (K_{mic}) as shown in Equation 2.6, which represents the distribution of organic compounds between surfactant micelles and the aqueous phase and may be expressed as follow

$$K_{mic} = \frac{X_{mic}}{X_a} \quad (2.6)$$

where X_m and X_a are the mole fraction of solute in the micelle and aqueous phase, respectively.

The value of X_m can be calculated from the MSR using Equation 2.7

$$X_{mic} = \frac{MSR}{1 + MSR} \quad (2.7)$$

The mole fraction of organic compound in the aqueous phase (X_a) can be calculated using Equation 2.8

$$X_a = C_a^* V_{w,mol} \quad (2.8)$$

Where C_a^* is the aqueous solubility of solute and $V_{w,mol}$ is the molar volume of water

There are several factors in the increase in solubilization capacity of micellization.

2.4.2.1.1 Structure of the Surfactant

For hydrocarbons and long-chain polar compounds that are solubilized in the interior of the micelle or deep in the palisade layer, the amount of material solubilized generally increases with increase in the size of the micelles. Therefore, any factor that causes an increase in either the diameter of the micelle or its aggregation number can be expected to produce an increase in the solubilization capacity for this type of material. Since aggregation numbers increase with increase in the degree of “dissimilarity” between solvent and surfactant, an increase in the chain length of the hydrophobic portion of the surfactant generally results in increased solubilization capacity for hydrocarbon in the interior of the micelle in aqueous media.

2.4.2.1.2 Structure of the Solubilizate

Crystalline solids generally present less solubility in micelles than do liquids of similar structure, the latent heat of fusion presumably opposing the change.

2.4.2.1.3 Effect of Electrolyte

The addition of small amounts of neutral electrolyte to solution of ionic surfactants to increase the extent of solubilization of hydrocarbons that are solubilized in the inner core of the micelle and to decrease that of polar compounds that are solubilized in the outer portion of the palisade layer. The effect of neutral electrolyte addition on the ionic surfactant solution is to decrease the repulsion between the similarly charged ionic surfactant head groups, thereby decreasing the CMC and increasing the aggregation number and volume of the micelles. The increase in aggregation number of the micelles presumably results in an increase in hydrocarbon solubilization in the inner core of the micelle. The decrease in mutual repulsion of the ionic head groups causes closer packing of the surfactant molecules in the palisade layer and a resulting decrease in the volume

available there for solubilization of polar compounds. This may account for the observed reduction in the extent of solubilization of some polar compounds.

2.4.2.1.4 Mixed Anionic-Nonionic Micelles

An investigating of the solubilization of Yellow OB by mixed micelles of anionics and a POE nonionic, $C_{12}H_{25}(OC_2H_4)_9OH$, indicated that increased solubilization of the dye occurs when there is interaction between the POE chain and the benzenesulfonate groups, rather than the phenyl or sulfonate groups alone.

2.4.2.1.5 Effect of Temperature

For ionic surfactants, an increase in temperature generally results in an increase in the extent of solubilization for both polar and nonpolar solubilizates, possibly because increased thermal agitation increases the space available for solubilization in the micelle. For nonionic POE surfactants on the other hand, the effect of temperature increase appears to depend on the nature of the solubilizate. Nonpolar materials such as aliphatic hydrocarbons and alkyl halides, which are solubilized in the inner core of the micelle, appear to show increased solubility as the temperature is raised, the increase becoming very rapid as the CP of the surfactant is approached.

2.5 Model Oil

Palm oil, one of the most widely used in food products, is extracted from the mesocarp of oil palm fruit. Basically, there are two main products of the palm oil industry; palm oil and palm kernel oil. Out of these, many products could be derived. Crude palm oil is normally processed by a physical refining process in which the oil is turned into golden yellow refined oil for further end-use applications.

The palm stearin and palm olein, for their versatile composition in fatty acids and triacylglycerols, are the raw material for interesterification producing a variety of products such as margarine, shortenings, cookies, ice cream, chocolates, cakes and others (Aini, 2007).

Palm stearin is the solid fraction and palm olein is the liquid fraction obtained by fractionation of palm oil after crystallization at a controlled temperature. Palm stearin is not used directly for edible purposes due to its high melting point ranging from 44 to 56 °C giving the product low plasticity and incomplete melting at body temperature (Aini, 2007).

Palm olein contains a high proportion of saturated fatty acids that contribute to oxidative stability. This is because, its low iodine value and melting point (max. 24 °C), pure palm olein cannot be used in shortenings. However, it can be used after some modification by interesterification with others fats or oils (Farmani, 2006).

There are different fatty acid compositions in palm oil as shown in Table 2.1.

Table 2.1 The composition of palm stearin and palm olein (Soares, 2009)

Derivative Palm Oils	Fatty Acids (%)				
	Myristic Acid (C14:0)	Palmitic Acid (C16:0)	Stearic Acid (C18:0)	Oleic Acid (C18:1)	Linoleic Acid (C18:2)
	Palm Olein	0.8 ± 0.4	38.0 ± 0.2	5.0 ± 0.8	45.4 ± 0.2
Palm Stearin	2.4 ± 0.3	64.4 ± 0.1	4.5 ± 0.1	23.8 ± 0.1	4.9 ± 0.0

For extended surfactant formulation, Witthayapanyanon *et al.* (2006) studied the formation of three anionic extended surfactant types which were branched $C_{14-15}H_{29-31}-(PO)_8-SO_4Na$, branched $C_{12-13}H_{25-27}-(PO)_{14}-(EO)_2-SO_4Na$, and linear $C_{12}H_{25}-(PO)_{14}-(EO)_2-SO_4Na$ with petroleum hydrocarbons and vegetable oils (canola and palm oils). These formations compared to conventional anionic surfactant (AOT) with IFT reduction. The salinity scans at 10 mM surfactant found that the optimum salinities (S^*) of branched $C_{14-15}H_{29-31}-(PO)_8-SO_4Na$ /triolein/NaCl, and branched $C_{12-13}H_{25-27}-(PO)_{14}-(EO)_2-SO_4Na$ /triolein/NaCl were 0.13 M, and 0.21 M, respectively, providing minimum dynamic IFT close to 0.01 mN/m. A minimum optimum salinity for linear $C_{12}H_{25}-(PO)_{14}-(EO)_2-SO_4Na$ /triolein/NaCl was observed at 0.09 M NaCl and also reached the lowest IFT value close to 0.001 mN/m. On the other hand, AOT/triolein/NaCl could not reach a minimum IFT at all NaCl concentrations. The results were the addition of PO and EO groups in anionic extended surfactants the increased interaction between surfactant and triglyceride molecules or these groups match the polarity of the glycerol ester of triolein. The other scans were surfactant concentration with fixed salinity at the optimum salinity (S^*) considering systems of branched $C_{14-15}H_{29-31}-(PO)_8-SO_4Na$ /triolein/NaCl, and linear $C_{12}H_{25}-(PO)_{14}-(EO)_2-SO_4Na$ /triolein/NaCl. The $C_{\mu}C$ value of branched $C_{14-15}H_{29-31}-(PO)_8-SO_4Na$ /triolein/NaCl, which was 1000 μM , was much less than linear $C_{12}H_{25}-(PO)_{14}-(EO)_2-SO_4Na$ /triolein/NaCl which was 4365 μM . Therefore, branched $C_{14-15}H_{29-31}-(PO)_8-SO_4Na$ is more effective, but this surfactant provided a slightly more IFT value. Moreover, the surfactant concentration above the $C_{\mu}C$ formed gel phase instead of middle phase because IFT value increased. Therefore, branched $C_{14-15}H_{29-31}-(PO)_8-SO_4Na$ /triolein/NaCl was the best candidate for microemulsion formation providing ultralow IFT with various oil types, the sequences of varying oil types were triolein having a highly negative EACN (equivalent alkane carbon number), whereas vegetable oils have positive values. These meant that triolein was significantly more hydrophobic than vegetable oils, so triolein required less optimum salinity (S^*) to reach ultralow IFT.

For structure of anionic extended surfactants, Phan *et al.* (2011) investigated the effect of linear and branched anionic extended surfactants on dynamic IFT, and microemulsion formation with triglycerides. These experiments performed at

surfactant concentration of 0.1 %wt., and temperature of 25 ± 1 °C. The effect of surfactant structure having 3 different types; $C_{12-13}H_{25-27}-(PO)_4-SO_4Na$ (100% branched), $C_{12-13}H_{25-27}-(PO)_4-SO_4Na$ (100 % linear), and a mixture of branched and linear alkyl of C_{12} and C_{13} (50 % linear and 50 % branched). For tricaprylin, optimum salinity (S^*) decreased with an increase in the percentage of branching in tail. Linear $C_{12-13}H_{25-27}-(PO)_4-SO_4Na$ had optimum salinity (S^*) of 23 % NaCl, but optimum Salinity (S^*) for branched $C_{12-13}H_{25-27}-(PO)_4-SO_4Na$ was 11 % NaCl. Nevertheless, linear $C_{12-13}H_{25-27}-(PO)_4-SO_4Na$ could not achieve ultralow IFT ($IFT < 10^{-3}$ mN/m). As a result, 100 % branched alkyl chain of extended surfactant influenced IFT value. The effect of PO group was studied with two pairs of branched $C_{12-13}H_{25-27}-(PO)_4-SO_4Na$ versus branched $C_{12-13}H_{25-27}-(PO)_4-SO_4Na$, and branched $C_{14-15}H_{29-31}-(PO)_4-SO_4Na$ versus branched $C_{14-15}H_{29-31}-(PO)_8-SO_4Na$. The results of increasing PO groups decreased both optimum salinity (S^*) and IFT values because PO groups were a part of hydrophobic tail of the surfactants. Furthermore, the short-chain saturated triglycerides tricaprylin C8:0 (EACN=16) was able to achieve ultralow IFT ($IFT < 10^{-3}$ mN/m) with PO groups were more 4 groups. Subsequently, microemulsion formations (Winsor Type I and II microemulsions) only occurred in tricaprylin. In contrast, canola oil (EACN=18) could reach ultralow IFT using PO groups of 8. This could form Winsor Type I, II, and III microemulsions for both tricaprylin and canola oil at 7 and 10 % NaCl, respectively. But, the solubilization parameters (SP^*) for canola oil (3.3-3.4 mL/g) was considerably less than tricaprylin (5.5-6 mL/g).

For triglyceride structures, Phan *et.al* (2010) examined the effect of triglyceride molecule structure on hydrophobic oil. Their study compared optimum salinity (S^*) with varying triglycerides having different chain lengths and degree of unsaturations using branched $C_{14-15}H_{29-31}-(PO)_8-SO_4Na$ anionic extended surfactant of 0.15 %wt. The optimum salinities (S^*) of tricaprylin (C8:0) and trinonanoin (C9:0) were slightly different (7.25 and 7.5 % NaCl) despite a total increase of three carbons in the trinonanoin molecule compared to tricaprylin. The optimum salinities (S^*) of trimyristolein (C14:1), tripalmitolein (C16:1), and triolein (C18:1) were 9.25, 10.5, and 11.25 % NaCl, respectively. And so, an increase of carbons in each fatty acid chain resulted in an increase in optimum salinity (S^*). According to, increasing

the carbon length of triglycerides increased the optimum salinity (S^*) required and thus correlated to increasing EACN values. Dynamic IFT values of tricaprylin (C8:0) and trinonanoin (C9:0) were approximately the same (0.0061 and 0.0041 mN/m). On the other hand, IFT values of trimyristolein (C14:1) and triolein (C18:1) increased from 0.0058 to 0.0106 mN/m. The optimum salinity (S^*) and IFT values increased from 11.25 % NaCl and 0.011 mN/m for triolein (C18:1) to 12.5 % NaCl and 0.048 mN/m for trilinolein (C18:2) and to 14 % NaCl and 0.15 mN/m for trilinolenin (C18:3). The increasing number of double bonds increased in optimum salinity (S^*) required because triglycerides act as hydrophobic which required a higher optimum salinity (S^*). The pair of saturated and unsaturated triglycerides with the same fatty acid chain length (C11) was compared to the optimum salinity (S^*) and IFT values of triundecanoin (C11:0) and tridecanoin (C11:1) both measured at 35 °C were 7.25 and 8.5 % NaCl, and 0.0012 and 0.0078 mN/m, respectively. This is implied that double bonds increase hydrophobicity that required higher optimum salinity and increased IFT value.

For optimum detergency formulation, Phan *et al.* (2010) examined suitable detergent formulation using a branched $C_{14-15}H_{29-31}-(PO)_8-SO_4Na$ anionic extended surfactant at different salinities with canola oil at 25 ± 1 °C and low surfactant concentration. Winsor Type I, II, and III microemulsions were observed a wide range of surfactant concentrations and salinities. At low surfactant concentration, middle phase of Winsor Type III microemulsions was obviously observed at 0.39 %wt surfactant concentration. For wash solutions, $C_{14-15}H_{29-31}-(PO)_8-SO_4Na$ concentration of 1000 ppm without NaCl could not reach dynamic ultralow IFT (IFT=2.2 mN/m) but could achieve ultralow IFT (0.009-0.30) at various salinities (2-16 % NaCl). These dynamic IFT values were much less than commercial liquid detergent products (1.9 mN/m). Salinity concentrations of 0-6 %, 8-10 %, and 14-16 % NaCl provided Winsor Type I, Type II, and Type III microemulsions, respectively. The lowest ultralow IFT was 10 % NaCl as Winsor Type III microemulsion. Maximum detergent efficiencies of 94.7 % and 92.8 % were located at 14 % and 16 % NaCl, respectively in Winsor Type II region instead of Winsor Type III system. Winsor type III system gave undesirable detergent efficiency as low as 63.1 % at optimum salinity (10 % NaCl). For detergency efficiencies with various surfactant

concentrations in the range of 125-2000 ppm showed little impact on the detergency efficiencies in Winsor Type I and Type III regions. It was found that 4 % NaCl, the detergency efficiency kept quite high at 125 ppm surfactant concentration. These were significant decreases in detergency efficiencies on Winsor type II microemulsion at surfactant concentrations of 125 and 250 ppm (69 % and 86 %) although the IFT values remained stable.

For mixed surfactant systems, Tanthakit *et.al* (2010) examined palm oil removal from a polyester/cotton blend using mixing of branched anionic extended surfactant ($C_{14-15}H_{29-31}-(PO)_3-SO_4Na$) and nonionic secondary alcohol surfactant ($C_{12-14}O_9(EO)_5$). A mixture of 25 parts ($C_{14-15}H_{29-31}-(PO)_3-SO_4Na$) and 75 parts ($C_{12-14}O_9(EO)_5$) was the suitable formulation. The total of oil removal of the selected formulation reached a plateau at near 0.2 % ($C_{\mu}C=0.06$ %) of total surfactant concentration with a maximum oil removal of 84% compare to the other single surfactant concentrations and the commercial detergency. Winsor Type III can form with the range of salinities from 1.22 % to 3.7 5% NaCl but the optimum salinity (S^*) was at 2 % NaCl to remove a maximum of oil. The effect of washing temperature on the percentage of oil removal slightly increased with increasing temperature from 20 to 50 °C, but the percentage of oil removal decreased between 50 and 60 °C. To study the amount of rinse cycles was found that the accumulative oil removal went up to 97.5 % after four cycles. In contrast, the brightness and detergency decreased because fiber of soiled swatch was damaged after second rinse from agitation during washing. Another studied effect of detergency was presoaking step. The selected formulation for soaking step increased oil removal from 83 % (no soaking) to 92 %. This had detergent efficiency almost as same as second wash cycle. Therefore, soaking was better than increasing the number of rinse cycle. Considering contact angle for the selected formulation gave higher oil contact angles in Winsor Type III and shorter oil droplet detachment times corresponding to higher detergency but this system cannot remove oil totally on the fused fabric due to happening snap-off rather than roll-up.

For renewable-based surfactants, Acosta *et.al* (2005) studied bio-compatible microemulsion formulation using lecithin (nonionic bio-surfactant) and hexyl polyglucoside and sorbitan monooleate (SO) acted as hydrophilic and lipophilic

linker, respectively. This work used isopropyl myristate (IPM) as a representative. The fixed mixture of 4 %w/v lecithin, 4 %w/v sorbitan monoleate (SO), 0.9 %w/v electrolyte (0.9 %w/v), and increment amounts of hexyl polyglucoside can achieve microemulsion Type II, III, I transition. These systems also provided low IFT (<0.1 mN/m). Moreover, increasing the temperature from 27 to 40 °C, electrolyte concentrations and pH illustrated a slight shift in the phase map toward lower hexyl polyglucoside-to-lecithin ratio and increase the minimum concentration of lecithin required to achieve Winsor Type IV system. This means that decreasing the system efficiency. These systems were also able to form microemulsion with a wide range of oils, from polar chlorinated hydrocarbons to hydrophobic oils such as squalene because SO was more surface active than alcohol and the longer extended tail of lecithin attributed the greater solubilization. These lecithin and hexyl polyglucoside and sorbitol monoleate systems were substituted chlorinated solvents in dry-cleaning and as solvent delivery systems for pharmaceutical application.

For supersolubilization region study, Tongcumpou *et.al* (2003) investigated the relationship between microemulsion phase behavior and detergency for oily soils. This work used hexadecane and motor oil as model oils. To form microemulsion system, in this work used mixed surfactants of alkyl diphenyl oxide disulfonate [ADPODS (highly hydrophilic)], dioctyl sodium sulfosuccinate [AOT (intermediate character)], and sorbitan monoleate [SO (highly hydrophobic)]. This mixed surfactant could produce substantial solubilization and reached ultralow IFT. The microemulsion phase transition was observed for both hexadecane and motor oil. Furthermore, the use of mixed surfactant containing both anionic and nonionic surfactants led to systems that were durable with respect to temperature compared to single-surfactant systems. Interfacial tensions (IFT) were not substantially worse than at optimal condition for a middle-phase system, so quite low IFTs could be achieved without middle-phase microemulsion formation. On the other hand, these formulations developed the fairly high salinity (e.g., 5 %w/v NaCl) needed to attain optimal middle-phase systems.

For solubilization test, Acosta *et.al* (2008) studied the relationship between curvature and hard surface cleaning performance. This work used mixed anionic surfactant system of 0.1 M between 20 % SDS and 80 % SDHS to evaluate the

cleaning efficiency of saturated triglycerides (shortening) for Winsor Type I microemulsion. For the hard surface cleaning experiments, 0.2 g of melted shortening (Armour Lard died with Sudan Red III) were deposited on the bottom of 15 mL flat bottom tubes and then left until the lard solidified at room temperature. The tubes were placed in a near-horizontal position in a Burrell wrist-action shaker operated at 4 cycles/s for 15 mins. At the end of shaking, the surfactant solution containing any emulsified fat was removed and the tube was gently rinsed with deionized water. The remaining shortening in the tube was removed using limonene. The result showed that the fat removal continuously increased as the inverse of the HLD increased. The highest percentage of fat removal significantly increased from 5 % to 25 %.

For solubility of different surfactant solutions and fatty acids, Lim *et.al* (2005) studied the solubility of palmitic acid as a semi-solid representative and oleic and linoleic acids as liquid representatives at 23 °C for 7 days with different surfactant types. The solubility of different fatty acids in palm oil showed interesting result because there was different in locus of solubilization. palmitic solubility presented the highest molar solubilization ratio (MSR) value (just about 0.17) of mixed secondary ethoxylated alcohols [$C_{11-15} (EO)_{5.2}OH$ and $C_{11-15}EO_{7.3}OH$] in a weight ratio of 3:1. The solubilization capacity of palmitic acid decreased as HLB of nonionic increased. This implied that nonpolar saturated palmitic acid is preferentially solubilized in the hydrophobic cores of nonionic micelles. However, linoleic and oleic acid had much more MSR of 0.75 and 0.57 with glycolic acid ethoxylate lauryl ethers [$CH_3(CH_2)_{11-13}O(CH_2CH_2O)_{4.5}CH_2COOH$] and primary ethoxylated alcohol [$C_{12-15}EO_{7.3}OH$]. Oleic acid is located in the core if the micellar or in deeper palisade compared to linoleic acid, while, higher polarity of oleic acid lead to be solubilized in the shallow palisade of the micelles as well. Therefore, the solubilization space of oleic acid in a micelle is enlarged and the solubility is improved. Solubilization is difficult mechanism because it depends on several variables such as the loci of solubilization or surfactant structure and its HLB number.