



## CHARTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Surfactants

Surfactants are a diverse group of chemicals designed to have cleaning or solubilization properties. They generally consist of a polar head group (either charged or uncharged), which is well solvated in water, and a non-polar hydrocarbon tail, which is not easily dissolved in water. Hence, surfactants combine hydrophobic and hydrophilic properties in one molecule. They are widely used in household cleaning detergents, personal care products, textiles, paints, polymers, pesticide formulations, pharmaceuticals, mining, oil recovery, and the pulp and paper industries. (Zoller, 2004)

A surfactant (a contraction of the term surface-active agent) is a substance that, when presents at low concentrations in an aqueous system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surfaces (or interfaces). The term interface indicates a boundary between any two immiscible liquid phases; the term surface denotes an interface where one phase is a gas, usually air and another can be a liquid or a solid. (Rosen, 2004)

Surfactants are amphipathic molecules which consist of a non-polar hydrophobic portion, usually a straight or branched hydrocarbon or fluorocarbon chain containing 8–18 carbon atoms, which is attached to a polar or ionic portion (hydrophilic). The hydrophilic portion can, therefore, be nonionic, ionic or zwitterionic. Figure 2.1 shows a typical structure of a surfactant. The hydrocarbon chain interacts weakly with the water molecules in an aqueous environment, whereas the polar or ionic head group interacts strongly with water molecules. (Tadros, 2005)

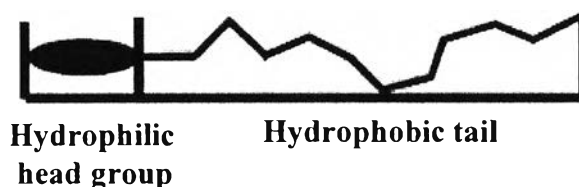
According to the nature of the hydrophilic group, surfactants are classified into four main types as follows:

1. *Anionic*: the hydrophilic portion of the molecule bears a negative charge; for example,  $\text{RCOO}^-\text{Na}^+$  (soap),  $\text{RC}_6\text{H}_4\text{SO}_3^-\text{Na}^+$  (alkylbenzene sulfonate).

2. *Cationic*: the hydrophilic portion bears 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).

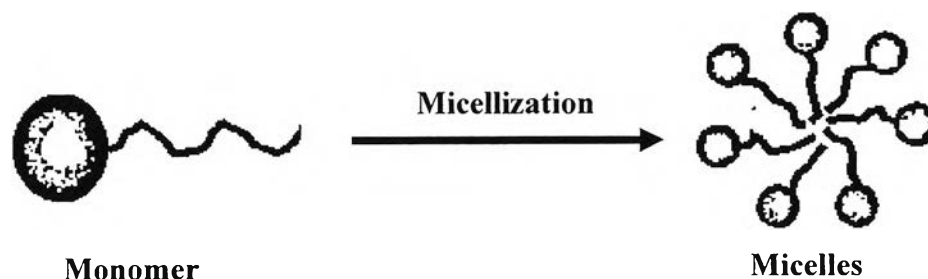
3. *Zwitterionic*: both positive and negative charges may be present in the surface-active portion; for example,  $\text{RN}^+\text{H}_2\text{CH}_2\text{COO}^-$  (long-chain amino acid),  $\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^-$  (Sulfobetaine).

4. *Nonionic*: the hydrophilic portion bears no apparent ionic charge; for example,  $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$  (monoglyceride of long-chain fatty acid),  $\text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)_x\text{OH}$  (polyoxyethylenated alkylphenol).



**Figure 2.1.** The basic molecular structure of a surface-active material (Tadros, 2005).

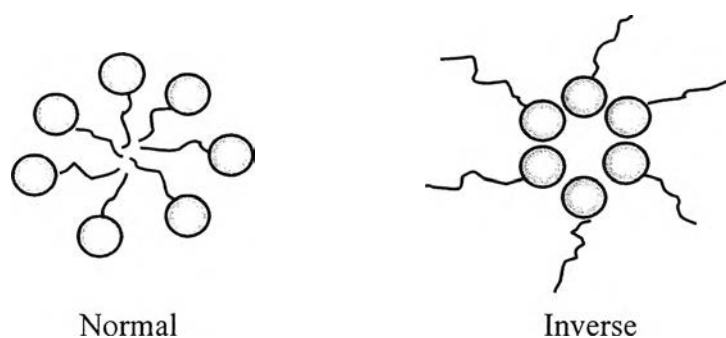
A single molecule of a surfactant is called a monomer and at a sufficient concentration in an aqueous solution, the monomer or surfactant molecules will nucleate to form aggregates called micelles. This process is called micellization, as shown in Figure 2.2, and the lowest total surfactant concentration at which micelles are present is called the critical micelle concentration (CMC).



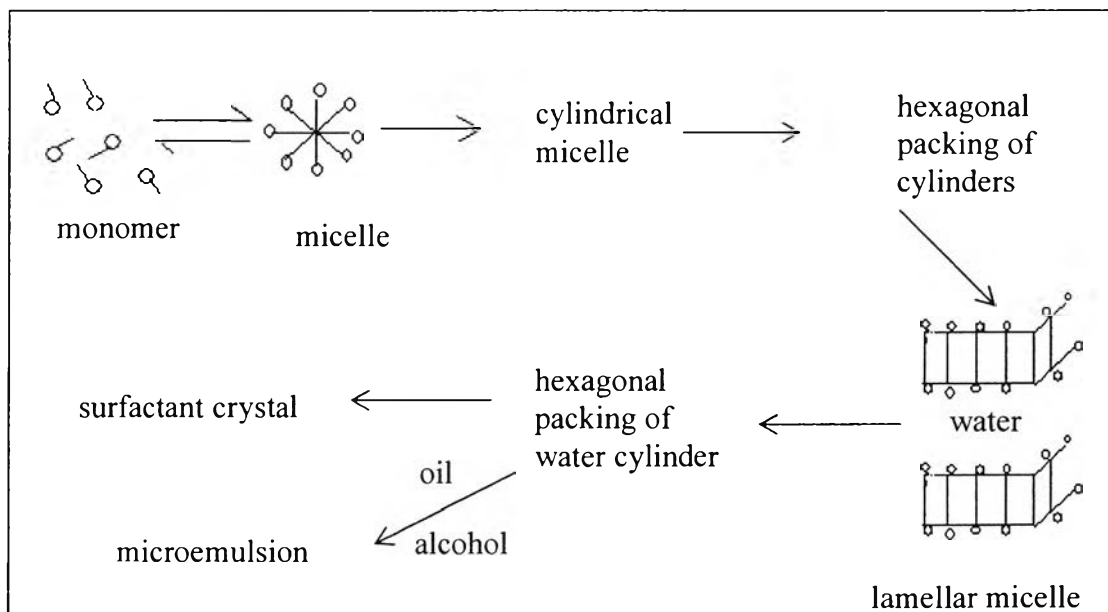
**Figure 2.2** Schematic of a monomer, micelles, and micellization.

There are two types of micelles which are normal and inverse (or reverse) micelles. In water or aqueous solution, normal micelles are formed with the hydrophobic part in the interior and the hydrophilic part in the external. On the other

hand, inverse micelles are formed in a non-polar solvent with the hydrophilic part in the interior and the hydrophobic part in the exterior. A schematic of a normal and inverse micelles is shown in Figure 2.3. The formation of various association structures with increasing surfactant concentration is shown in Figure 2.4. It is likely that surfactant molecules may form spherical, cylindrical, hexagonal, lamellar, or reverse micelle structures, depending on the physicochemical conditions, such as surfactant structure, surfactant concentration, pH, temperature, and the presence of various electrolytes.



**Figure 2.3** Schematic of normal micelle and inverse micelle.

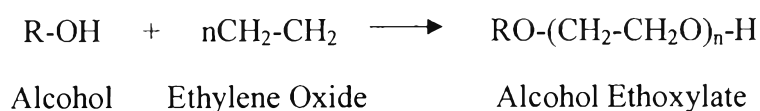


**Figure 2.4** Schematic of surfactant association structures (Sharma *et al.*, 1991).

If an oil is present in the system, these association structures can solubilize the oil, and can produce a clear, thermodynamically stable system. Depending on the nature of the oil and the oil-to-water ratio, the oil can be a continuous or disperse phase in the system (Sharma *et al.*, 1991). Furthermore, the solubilization increases as the number of micelles in the solution increases (Clarence *et al.*, 1985).

## 2.2 Alcohol Ethoxylates (AEs)

Ethoxylated alcohols, the most widely used nonionic surfactants, are prepared by the reaction of ethylene oxide with aliphatic or aromatic alcohols (see Figure 2.5). Most commercially available ethoxylated alcohols contain a relatively broad distribution of degrees of ethoxylation. Ethoxylated alcohols are "amphiphiles" containing hydrocarbon tails which prefer oil environments and ethoxylated alcohol groups which prefer water environments. However, short-chain amphiphiles such as C<sub>4</sub>E<sub>1</sub> are inefficient at mixing oil and water and only form weakly structured solutions. Longer chained amphiphiles such as C<sub>12</sub>E<sub>5</sub> are true surfactants which efficiently mix oil and water, and also form distinct droplets and bicontinuous microemulsion microstructures (Holmberg *et al.*, 2002).



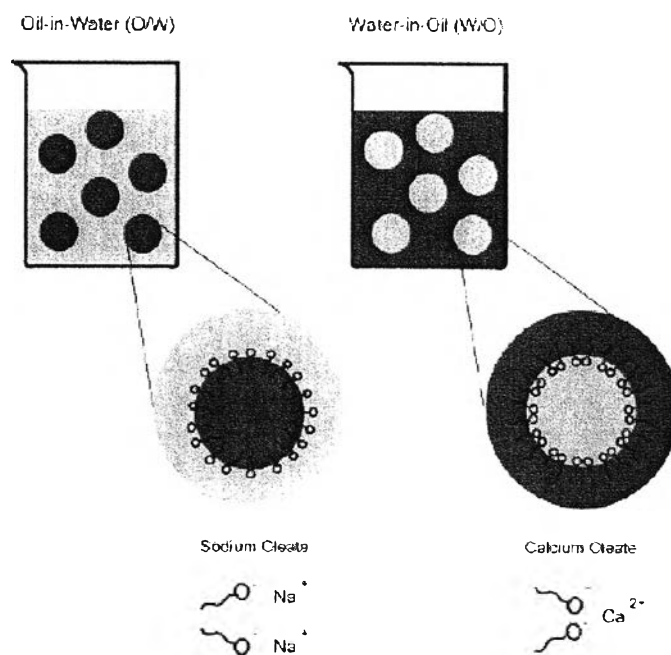
**Figure 2.5** Ethoxylation Reaction.

The alcohol ethoxylate structure can be optimized for performance since the average hydrophobe, hydrophile, and distribution of the ethoxymers can be varied. Alcohol ethoxylates biodegrade more rapidly than alkylphenol ethoxylates. They are also more tolerant of high ionic strength and hard water than anionic surfactants. They also have excellent compatibility with enzymes in laundry formulations. Somewhat better than the corresponding alkylphenol ethoxylates for emulsification. They are more water-soluble than LAS (linear alkyl benzene sulfonate), for use in

high active, heavy-duty liquid detergents free of phosphates. They are more effective in detergency than LAS under cool washing conditions and on synthetic fabrics. Alcohol ethoxylates are excellent detergents for removal of oily soil and are often used in laundry products, especially liquids. They are also excellent emulsifiers and suspending agents in numerous industrial applications, where they compete with alkylphenol ethoxylates. However, high concentrations of alcohol ethoxylates in laundry powders often “bleed” from the powder, giving poor powder properties. Because alcohol ethoxylates are composed of a distribution of ethoxymers, some unethoxylated alcohol remains in commercial products. If it presents in sufficient quantity, this can impart an objectionable odor to the ethoxylates (Rosen, 2004).

### **2.3 Microemulsions**

Microemulsions are composed of two mutually immiscible liquid phases, one spontaneously dispersed in the other with the assistance of one or more surfactants with or without cosurfactants. While microemulsions of two nonaqueous liquids are theoretically possible (e.g., fluorocarbon–hydrocarbon systems), almost all of the reported work is concerned with at least one aqueous phase. The systems may be water continuous (o/w) or oil continuous (w/o) (see in Figure 2.6), which are governed by several variables including the surfactant systems employed, temperature, electrolyte levels, the chemical nature of the oil phase, and the relative ratios of the components (Myers, 1999).



**Figure 2.6** Illustration of the oriented-wedge theory of emulsion type (Schramm, 2005).

Microemulsions, like micelles, are considered to be lyophilic, stable, colloidal dispersions. In some systems, the addition of a fourth component, a cosurfactant, to an oil/water/surfactant system can cause the interfacial tension to drop close to near-zero values, easily on the order of  $10^{-2}$ – $10^{-3}$  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).

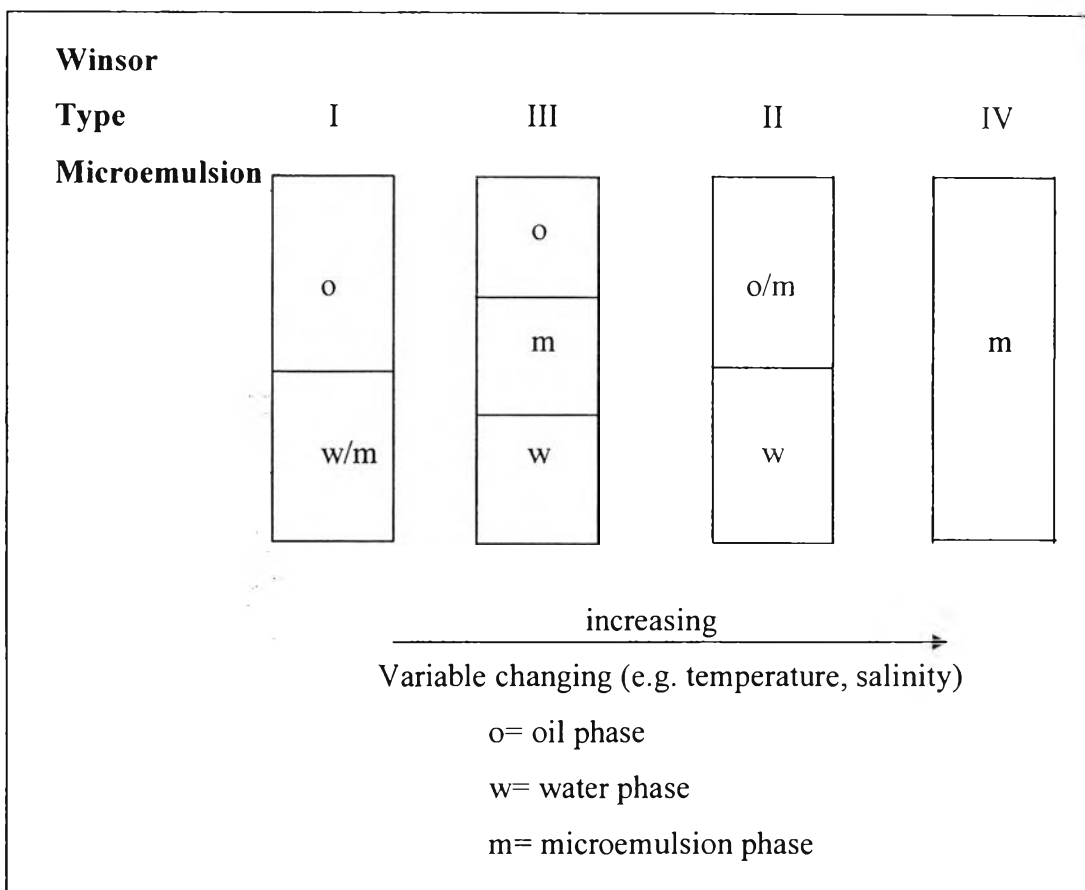
The most studied phase equilibria of microemulsions are probably the Winsor-Type microemulsions. There are four types of microemulsions, as shown in Figure 2.7:

1. Winsor Type I: an oil-in-water microemulsion in equilibrium with an excess oil phase

2. Winsor Type II: a water-in-oil microemulsion in equilibrium with an excess water phase

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

4. Winsor type IV: a single phase or microemulsion phase



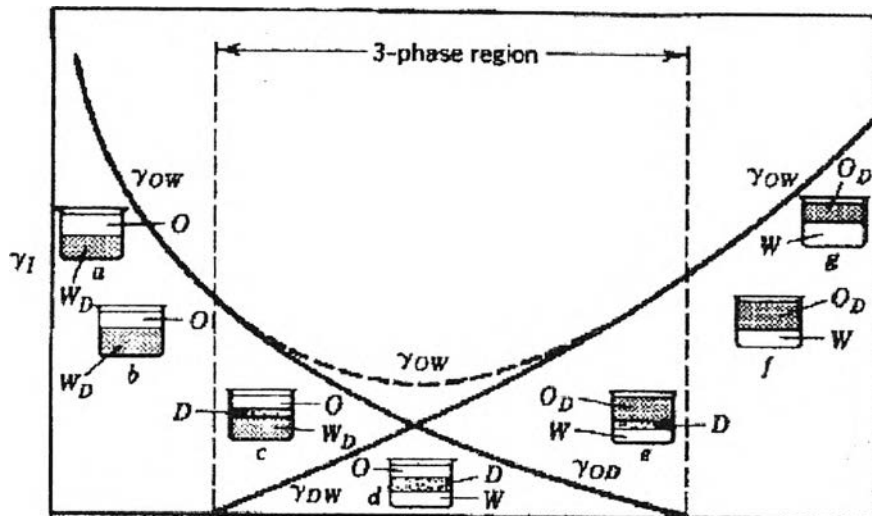
**Figure 2.7** Microemulsion phase behavior for a model system (Winsor, 1968).

A transformation in the system of Winsor Type I-III-II can be achieved by progressively changing temperature, salinity, the molecular structure of the surfactant and cosurfactant, the oil-to-water ratio, or the structure of oil in a homologous series. This studied phase diagram is normally carried out by increasing salinity for an ionic system (known as a salinity scan) and the temperature for a single nonionic surfactant system, as illustrated in Figure 2.7.

For a given chemical system, phase-type diagrams can be constructed that show the regimes in which each type of microemulsion will exist. These can be used

to understand and predict the effects of, for example, increasing salinity or decreasing HLB, which tend to shift the emulsion type directionally from Type I to Type III to Type II. Type III microemulsions can be thought of as bi-continuous, as opposed to drop-like or lamellar. It is thought that phase inversion from a water-in-oil microemulsion to an oil-in-water microemulsion takes place by transition through a bi-continuous structure in which the aqueous and oleic phases are mutually intertwined. The transition of Winsor Type I-III-II influences the two interesting properties of microemulsion, solubilization and interfacial tension (IFT), due to the changing of the microstructure. Figure 2.8 shows the relationship between the type of microemulsion and the interfacial tension. The region on the left hand side of the figure is Winsor Type I where an oil-in-water (O/W) microemulsion exists along with an excess oil phase. IFT between the excess oil phase and the micellar solution ( $\gamma_{o/m}$ ) decreases with increasing salinity or temperature. When the middle phase is formed, the microemulsion becomes a bi-continuous structure in equilibrium with excess oil and excess water phases. The IFT between the excess oil and excess middle phases ( $\gamma_{o/m}$ ) and between the excess water and the middle phases ( $\gamma_{w/m}$ ) further decreases. The point in the Type III region where the IFT between the excess oil and the middle phases ( $\gamma_{o/m}$ ) equals the IFT between the excess water and the middle phases ( $\gamma_{w/m}$ ) is known as the minimum IFT or optimum state.





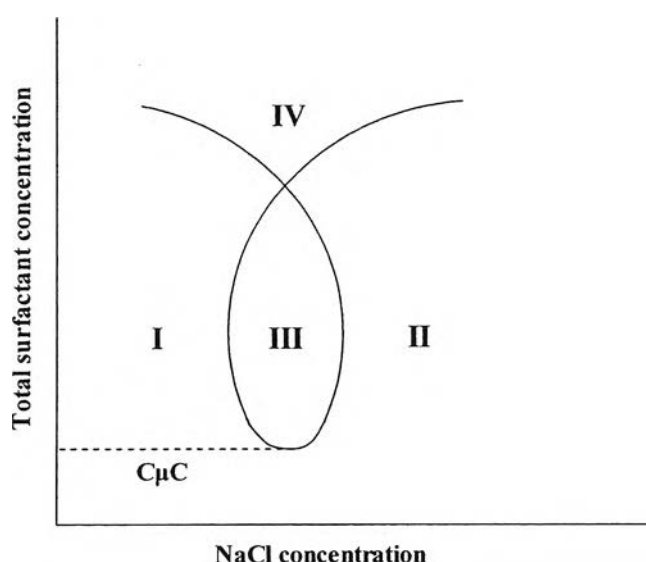
**Figure 2.8** Transition of the microemulsion structure and the interfacial tension as a function of salinity or temperature scan.

Applications of microemulsions 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 both 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.

The application potential of microemulsions was recognized at an early stage and has triggered a buildup of knowledge about the phase behaviour of oil-water-surfactant systems. At low surfactant concentrations, there is a sequence of equilibria between phase in equilibrium with an excess oil phase (Winsor Type I, or lower phase microemulsion), with an excess water phase (Winsor Type II, or upper phase microemulsion) or with both excess phases (Winsor Type III, or middle phase microemulsion). For nonionic surfactants, the I-III-II transition may occur by raising the temperature while for ionic surfactant systems containing an electrolyte, i.e. a quaternary system, the transition may be induced by increasing salinity (Holmberg *et al.*, 2002).

## 2.4 Fish Diagram

The fish diagram has been used to describe the phase behavior of microemulsion systems for decades. As shown schematically in Figure 2.9, the fish diagram looks like a lower case Greek gamma with a Winsor Type I microemulsion at low salinity or temperature, a Type III inside the closed loop and Type II at high salinity or temperature. A Winsor Type IV microemulsion occurs at high surfactant concentration and corresponds to the whole solution being a single homogeneous surfactant-rich phase. The phase diagram is shown as symmetrical in Figure 2.9, but could be tilted to the left or right. The lowest surfactant concentration at which the Type III microemulsion forms is known as the critical microemulsion concentration or  $C_{\mu C}$ , as shown in Figure 2.9; since the volume of the middle phase is too small to be visually observed at the  $C_{\mu C}$ , the surfactant concentration that first produce the ultralow IFT which is only attained when a Type III microemulsion is present. If the phase diagram is rotated  $90^\circ$ , it looks like a fish. If a studied system consists of oil, water and nonionic surfactant, the role of salt or cosurfactant is replaced by temperature.



**Figure 2.9** Schematic representation of normal fish phase diagram. Roman numerals refer to the Winsor Type microemulsion existing at that condition.

## 2.5 Oils

### 2.5.1 Motor Oil

Motor oil is complex in composition and has high hydrophobicity. It generally consists of at least five main components: n-paraffin, isoparaffin, cycloparaffin, 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. Wu *et al.* (2000) studied and reported the EACN value of motor oil to be 23.5.

### 2.5.2 Palm Oil

Palm oil is produced as the second largest world production of vegetable oils and it is widely used as cooking oil and in food industry because of its competitive price. Therefore, it is considered to be a good representative as a model oily soil on clothes, and kitchenware. Palm oil consists of fatty acids, which are mainly composed of 44.3% palmitic acid, 38.7% oleic acid, 4.6% stearic acid, 10.5% linoleic acid, 1% myristic acid and 0.9% other (Wang, 1999). It contains the same amount of saturated and unsaturated fatty acids and it is considered as polar oil because of the presence of fatty acids. The polar property of palm oil makes its phase behavior different from typical petroleum-based hydrocarbons and the bulky structure of the fatty acids contained in the palm oil makes it more difficult to be solubilized.

### 2.5.3 n-Octane

n-octane is a straight-chain alkane with the chemical formula  $\text{CH}_3(\text{CH}_2)_6\text{CH}_3$  and it is used as simple molecular structure of oil. The EACN of n-octane is 8.

Piispanen *et al.* (2004) synthesized sugar-based surfactants, characterized and compared some of their surface properties with those of commercial nonylphenol ethoxylates. The surfactant solubilities in water, ethanol, and dodecane were studied. The properties of these compounds as emulsification agents in various systems composed of the surfactant with water/isopropyl myristate, water/rapeseed oil, and water/dodecane were studied. The aqueous solubility of the studied surfactants was found to follow the general trend expected from their hydrophilic-lipophilic balance according to Griffin (HLBG). The ester or amine group as the connecting unit between the hydrophile and the hydrophobe produces a more water-soluble surfactant than the corresponding amide derivative. Some effective emulsifiers were found in this study. For instance, the surfactants with a dehydroabietic nonpolar group appear to be promising emulsifiers. Most sugar-based surfactants were able to form macroemulsions of up to around 2 wt.% of oil. The reference surfactants, NP-6, NP-10, and NP-20, with HLBG values of 11.6, 13.8, and 16.3, respectively, were all found to emulsify all three tested oils over short time scales. However, only NP-6 gave reasonably stable emulsions and only with the most nonpolar oil. Some of the surfactants tested were found to perform poorly, they may perform well at higher surfactant concentrations or in combination with other surfactants or polymers. For ethylene oxide-based surfactants, temperature is an important variable. The stability of many of these emulsions was very high, extending for months.

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” ( $\gamma_B, \delta_B$ ) ( $\gamma_B$  = the mass fraction of the surfactant and alcohol at the head of the fish,  $\delta_B$  = the mass fraction of alcohol in the surfactant and alcohol mixture at the head of the fish) and “tail” ( $\gamma_E, \delta_E$ ) ( $\gamma_E$  = the mass fraction of the surfactant and alcohol at the tail of the fish,  $\delta_E$  = the mass fraction of alcohol in the surfactant and alcohol mixture at the tail of the fish) points of the phase diagram are obtained by using the HLB plane equation. The  $\gamma_E$  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 indicates 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  $\gamma_E$  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  $\varepsilon$ – $\beta$  ( $\varepsilon$  is the mass fraction of alcohol in the whole system,  $\beta$  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 Type I→III→II 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,  $\beta_E$  and  $\varepsilon_E$ , reveal the minimum amounts of surfactant and alcohol to form single-phase microemulsion, respectively, therefore,  $\beta_E$  and  $\varepsilon_E$  can be used to estimate the solubilization power of the microemulsion system. The smaller the value of  $\beta_E$  and  $\varepsilon_E$ , the larger the solubilization power of the microemulsion system. The order of the solubilization power of three anionic surfactants studied is: SDBS  $\gg$  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.

Yang *et al.* (2007) studied the three-phase behavior of quaternary systems comprising *N*-lauroyl-*N*-methylglucamide (MEGA-12)/alcohol/alkane/water using  $\varepsilon$ – $\beta$  ( $\varepsilon$  is the mass fraction of alcohol in the whole system,  $\beta$  is the mass ratio of

surfactant in the whole system) fishlike phase diagrams. From the  $\varepsilon$ - $\beta$  fishlike phase diagrams a series of phase inversions Winsor I (2)  $\rightarrow$  III (3)  $\rightarrow$  II ( $\bar{2}$ ) were observed, the “fish head” of this kind of phase diagram was downward and the “fish tail” was upward. The HLB plane equation of the  $\varepsilon$ - $\beta$  phase diagram was deduced based on the tetrahedral phase diagram. A series of physicochemical parameters related to the phase behavior were calculated using the HLB equation and the mass balance equations. The coordinates of the “fish tail” ( $\beta_E$  and  $\varepsilon_E$ ) of the  $\varepsilon$ - $\beta$  phase diagram showed the minimum amounts of MEGA-12 and alcohol, respectively, for forming a single-phase microemulsion. They were also used to evaluate the maximum solubilization capacity of the system. The effects of alcohols, alkanes, and salt concentrations on the phase behavior and the solubilization capacity could be revealed from their  $\varepsilon$ - $\beta$  phase diagrams. In this paper, the order of the maximum solubilization capacity for different alcohols investigated was 1-hexanol  $>$  1-pentanol  $>$  1-butanol, and for alkanes is *n*-octane  $>$  *n*-decane  $>$  *n*-dodecane. The NaCl concentration was found to have a little influence on the phase behavior.

Mitra and Paul (2005) investigated the phase behavior of Brij-56/1-butanol/*n*-heptane/water at 30 °C with  $\alpha$  [weight fraction of oil in (oil + water)] = 0.5, wherein a Winsor Type I $\rightarrow$ III $\rightarrow$ II phase transition occurred 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 Winsor Type I $\rightarrow$ III $\rightarrow$ II phase transition occurred at a higher  $X$ . An addition of an ionic surfactant, sodium dodecylbenzene sulfonate, destroys the three-phase body and decrease the solubilization capacity of the system at different  $\delta$  (weight fraction of ionic surfactant in total surfactants). No three-phase body was formed for the Brij-56/ionic surfactant(s)/1-butanol/*n*-heptane/water system; instead a wide channel of single-phase region was formed. Increasing temperature increased the solubilization capacity of the Brij-56 system, whereas it showed negligible effect on the Brij-56/SDBS mixed system. An addition of salt (NaCl) was found to induce three-phase body formation in the Brij-56/SDBS system, and the solubilization capacity of both single and mixed surfactant systems increased. The monomeric solubility of 1-butanol in oil phase ( $S_1$ ) was decreased,

whereas the interfacial concentration of 1-butanol ( $S_1^s$ ) increased with the addition of NaCl, which in turn increases the solubilization capacity of these systems.

Lee and Lim (2005) examined the morphologies of two-phase emulsions in the ternary 2-butoxyethanol/*n*-decane/water system at various temperatures and water-to-oil ratios (WORs). The two-phase emulsion morphologies depended on temperature, WOR, and amphiphile concentration, and the results were presented in a temperature–amphiphile concentration coordinate system or a “fish” diagram. The observations made in this work contradicts the predictions by the phase-inversion-temperature (PIT) concept. At  $\text{WOR} < 1$ , a vertical inversion line was observed at  $T < T_{lc}$  (lower critical endpoint temperature), dividing the two-phase region into the subregions of B/T (W/O) and T/B (O/W) emulsions. At  $T > T_{uc}$  (upper critical endpoint temperature) and at low amphiphile concentrations, only B/T emulsions appeared, irrespective of temperature. At  $\text{WOR} > 1$ , the situation was reversed; T/B emulsions at  $T < T_{lc}$ , T/B and B/T emulsions at  $T > T_{uc}$ , and T/B emulsions at low amphiphile concentrations, irrespective of temperature. At  $\text{WOR} = 1$ , two horizontal inversion lines, one each at  $T < T_{lc}$  and  $T > T_{uc}$ , were observed. The morphologies of the two-phase emulsions were B/T or T/B emulsions at low amphiphile concentrations, and at higher amphiphile concentrations T/B at  $T < T_{lc}$  and B/T at  $T > T_{uc}$ . All these findings along with three-phase emulsion data result in complete emulsion morphology diagrams in the temperature–amphiphile concentration space or fish diagram.

Acosta (2008) studied the net–average curvature (NAC) model which is the equation of state to fit and predict the phase behavior of microemulsions ( $\mu\text{Es}$ ) formulated with nonionic ethoxylated surfactants and commercial nonylphenol ethoxylate (NPEj) surfactants with a range of alkanes (Cn). The NAC model requires three basic parameters: the characteristic curvature of the nonionic surfactant ( $C_{cn}$ ), and the scaling length parameter ( $L$ ). Five example applications of the NAC model are presented and discussed: (I) fit/prediction of phase inversion temperature (PIT) values, (II) prediction of phase transition temperatures and characteristic lengths, (III) fit/prediction of interfacial tensions, (IV) prediction of “fish” phase diagrams, and (V) prediction of the composition of bicontinuous systems. The NAC model was able to predict within 30% the value of phase volumes and transition temperatures

for CiEj systems. In all cases, a good agreement was found when the length parameter ( $L$ ) was estimated as 1.4 times the extended length of the surfactant tail.

Ratanarojanatam *et al.* (1997) investigated the effect of mixed surfactants, sodium dodecyl sulfate (SDS) and nonylphenol polyethoxylate (NP(EO)<sub>10</sub>), on the removal of  $\sigma$ -dichlorobenzene (ODCB). The Winsor Type III system gave a higher percentage of ODCB removal than Type II or Type I. For the system containing a surfactant concentration of 7% and a weight fraction of SDS of 0.8, the highest ODCB removal (91%) was obtained, corresponding to the surfactant removal of 65%.

To enhance the formation of microemulsions with ODCB, Chavadej *et al.* (2004) focused on the use of mixed anionic and nonionic surfactants; sodium dodecyl sulfate (SDS) and nonylphenol polyethoxylate (NP(EO)<sub>10</sub>). The optimum condition was achieved at 5% total surfactant concentration with the fraction of SDS of 0.5. From the results of froth flotation experiment, under the Winsor Type III microemulsion condition, the system had a higher oil removal than those under the Winsor Type I or II microemulsion condition. The highest oil removal of 91% was achieved at 7% total surfactant concentration and a weight fraction of SDS of 0.8. Moreover, the selectivity of oil-to-water in the overhead froth was much higher than that of the feed under the Winsor type III microemulsion condition. In addition, the maximum oil removal was achieved when the system was in the Winsor Type III microemulsion region.

Chavadej *et al.* (2004), studied the relation of Winsor type III microemulsion and the removal of ortho-dichlorobenzene (ODCB) by using mixed surfactant systems, sodium dodecyl sulfate (SDS) and nonylphenol polyethoxylate (NP(EO)<sub>10</sub>). Froth flotation experiments were studied at 3 wt.% and 5 wt.% total surfactant concentrations. The results in this study confirmed that the highest oil removal corresponded to the formation of Winsor Type III microemulsion. In addition, the combination of two phases of the Winsor Type III microemulsion system was studied to identify which phase was the main source of the removed oil. The results revealed that most the removed oil came from the excess oil phase instead of the middle phase. Moreover, the optimum salinity was found to be 0.5%.



Feng and Aldrich (2000) investigated the removal of diesel from aqueous emulsions by using batch flotation. The stability of these emulsions was characterized and factors such as pH and salinity affecting the stability of the emulsion were investigated. In addition, the effects of anionic and cationic surfactants, original diesel content, air flow rate, surfactant dosage, and the air distributor sinter were investigated. It was concluded that when pH increased, the diesel-water emulsion stability constant ( $K_s$ ) increased as a result of the emulsion unstable, leading to rapid destruction of the emulsion, and enhancing the diesel removal efficiency. The emulsion was gradually destabilized by the increase in the amount of NaCl. The oil could be removed more effectively with the cationic surfactants, octadecyl amine chloride (ODAC) and cetyl trimethyl ammonium chloride (CTMAC), but less with the anionic surfactant, SDS. Under the optimal conditions, up to 99% of the diesel could be removed.

Phoochinda *et al.* (1999) focused on the effect of NaCl added to the mixed surfactants SDS and NP(EO)<sub>10</sub> on the microemulsion formation and the efficiency of flotation for removing ODCB from water. It was found that small amounts of NaCl added to the mixed surfactants could improve the microemulsion formation. However, precipitation and liquid crystals that limit the solubilization capacity of the solution appeared at a high NaCl concentration. The mixed surfactant concentrations of 3 and 5 wt% were selected for the froth flotation experiment. The prepared solutions, i.e. water excess and middle phases (w-m), water excess and oil excess phases (w-o), and water excess, middle and oil excess phases (w-m-o) were transferred to a flotation column to determine oil removal efficiency. The results showed that ODCB removal in the w-m-o system was much higher than the m-o and w-m systems. The effect of NaCl in the w-m-o system was studied and showed that adding 0.5 wt% NaCl increased ODCB removal. The effect of each phase was also studied. The results showed that when the volume of the oil phase decreased and the volume of the water phase increased in the w-o system, ODCB removal decreased. When the volume of the middle phase increased and the volume of the water phase decreased in the w-m system, ODCB removal increased.