CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Structural Features and Behavior of Surfactants [5]

Surfactant or surface-active agent has a characteristic molecular structure consisting of a structure group that has strong attraction for the solvent called the hydrophilic (lyophilic) group and a very little attractive for the solvent, called the hydrophobic (lyophobic) group. The chemical structure of grouping suitable as the hydrophilic and hydrophobic portions of the surfactant molecule, which vary with the nature of the solvent and the conditions of use. In a polar solvent such as water, ionic or highly polar groups may act as hydrophilic (water-loving) groups, whereas in the nonpolar solvent is usually a long-chain hydrocarbon they may act as hydrophobic (water-hating) groups. Depending on the hydrophilic group surfactant are classified as anionic, cationic, zwitterionic, and nonionic.

Anionic surfactant is a surfactant molecule whose polar group is negatively charged, such as alkylbenzene sulfonate $(RC_6H_4SO_3^-Na^+)$. Cationic surfactant is a surfactant molecule whose polar group is positive charged, such as quaternary ammonium chloride $(RN(CH_3)_3^+Cl^-)$. Zwitterionic surfactant is a surfactant molecule whose polar group contains both negatively and positively charged groups, such as long-chain amino acid $(RN^+H_2CH_2COO^-)$. Nonionic surfactant is a surfactant molecule whose polar group is not electrically or no appear ionic charged, such as monoglyceride of long-chain fatty acid $(RCOOCH_2CHOHCH_2OH)$.

Surfactant monomer is a single molecule of surfactant and at sufficiently concentration in solution, monomer or surfactant molecules will nucleate to form

aggregates called micelles. This process is called micellization that is illustrated in Figure 2.1.

Figure 2.1 Schematic diagram of monomer, micelles, and micellization [6]

At the lowest total surfactant concentration at which micelle are present is critical micelle concentration (CMC). In aqueous media the surfactant molecule are oriented with their polar heads toward the aqueous phase and their hydrophobic group away from it. Whereas in nonpolar media, the structure of micelle is similar but reversed, with the hydrophilic heads comprising the interior region surrounded by an outer region containing hydrophobic groups and nonpolar solvent. The surfactant solution with concentration above the CMC can dissolve considerably large quantities of organic materials than surfactant solutions with concentration below the CMC.

2.2 Introduction of Emulsion System

An emulsion is a significantly stable suspension of particle of liquid of a certain size within a second, immiscible liquid. Two immiscible, pure liquids can not form an emulsion. For a suspension of one liquid in another to be stable enough to be classified as an emulsion, a third component must be present to stabilize the system. The third component is called emulsifying agent and it is usually a surface-active

agent. An emulsion can be distinguished among three different types of emulsions based upon the size of dispersed particles as [5].

1. Macroemulsion
2. Microemasion
3. Miniemulsion

Macroemulsion is opaque emulsion with particles > 400 nm (0.4 μm). There are two types based on the nature of dispersed phase i.e. oil-in-water (O/W) emulsion and water-in-oil (W/O) emulsion. The oil-in-water type is a dispersion of a water-immiscible liquid or solution, always called the oil (O), regardless of its nature in an aqueous phase (W). The oil is a discontinuous or inner phase, water is a continueous or outer phase. O/W emulsions are produced by emulsifying agents that are more soluble in water than in the oil phase, whereas W/O emulsions are produced by emulsifying agents that are more soluble in the oil than in the water.

Microemulsion is transparent dispersion containing two immiscible liquids with particles of 10-100 nm (0.01-0.1 μm) diameter. They differ markedly from both macroemulsion and miniemulsion because these two types are dependent upon intense agitation for their formation. Microemulsion may be oil-in-water (O/W) emulsion or water-in-oil (W/O) emulsion, or both. An aspect of microemulsion remains controversial, such as the nature of the interface (discrete or bicontinuous) between the dispersed particles, the nature of continuous phase (swollen micellar solution) and whether they contain one type of dispersed particle or micelle, or more. Fig 2.2 shows types of microemulsion upon scanning salinity for ionic and scanning temperature for nonionic surfactants. The three-phase system of microemulsion consists of middle (surfactant) phase, a nonpolar phase (O) and an aqueous phase (W). If the concentration of surfactant is increased, the middle phase incorporates both the O and W phases into a single (microemulsion) phase or type-IV microemulsion. For nonionic surfactants, when the temperature increased, its solubilization of nonpolar material O

increases due to increase of dehydration of nonionic surfactant chain and increases the lipophilicity of the surfactant.
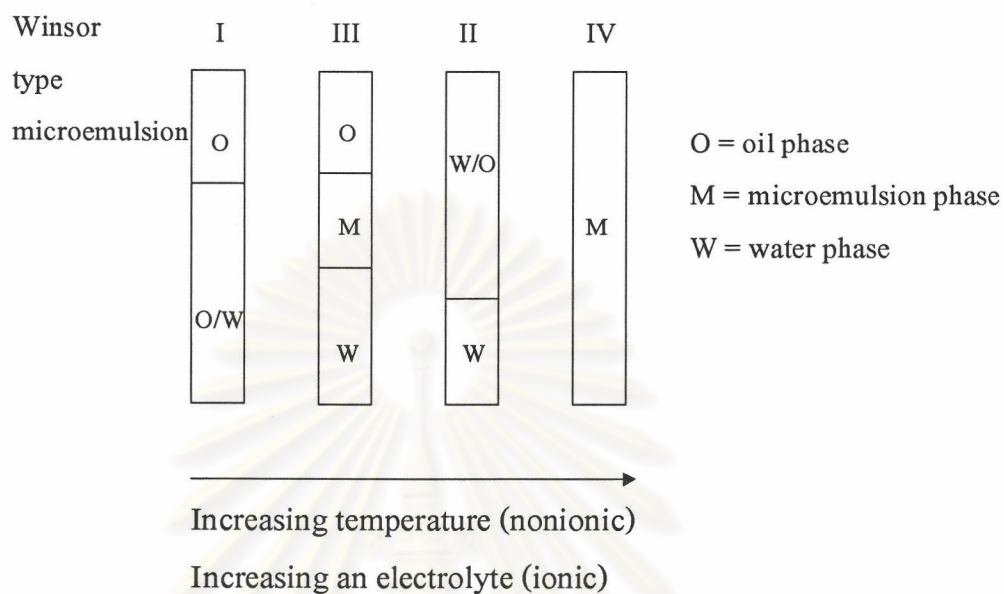

Figure 2.2   Schematic diagram of Winsor types I, III, II, and IV microemulsion [7]

Further increase in temperature, a nonionic surfactant becomes more dehydrated and more lipophilicity, consequently a nonpolar material O is solubilized into nonionic surfactant chain, increasingly asymmetric micelles. In the vicinity of the cloud point of the nonionic surfactants, micelles together with solubilized material separate into three phases, i.e. excess O, middle and excess W phases. If the temperature is further increased, the system becomes a single phase as shown in Figure 2.2. For ionic surfactants of proper structure, the addition of electrolytes, such as NaCl, with its consequent reduction of the electrical interactions of the ionic head groups can cause the surfactant to change from hydrophilicity to lyophilicity. With increasing salinity such systems may show changes in phase, solubilization and interfacial tension the same way as nonionic surfactant with temperature change.

Miniemulsion is blue-white semiopaque emulsion of 100 -400 nm (0.1-0.4   μm) droplet size. The emulsifiers are a mixture of an ionic surfactant and a cosurfactant,

where the latter is generally a long-chain alcohol. The chain length of the cosurfactant is at least 12 carbons, in contrast to the considerably shorter length used in microemulsion.

2.3 Wax Emulsion and Emulsifier

A wax emulsion may be defined as a stabilized dispersion of solid wax particles in water. A certain chemical called emulsifiers stabilize the dispersion or emulsion. Although, wax has valuable properties such as water repellency, it is solid at ambient temperature and difficult to apply on solid surface. On the other hand, wax emulsion flows at ambient temperature and is easy to use. Wax is naturally water immiscible. It is necessary to use an emulsifier, to keep the wax dispersed in the water phase. Emulsifiers or surface active agents, which can impart a charge or polarity to the surface of the wax particles, create repulsion among the wax particles when come into contact or prevent agglomeration and separation from the water phase but remain dispersed as discrete particles. Emulsifier may be chosen to give either negative or positive charges to the particles. If a potential is applied across a dispersion of negatively charged wax particles, they will flow to the anode. Such a dispersion or emulsion is said to be anionic. Similarly, positively charged particles will move to the cathode and the dispersion is cationic. A third type of an emulsifier however does not impart a charge but surrounds the wax particle with polar groups. An electrical potential will have no effect on such dispersion and so it is called a nonionic dispersion. Obviously, anything with upsets or changes the electrical balance will cause the wax particles to agglomerate and precipitate from the emulsion.

Anionic emulsion, the surface-active portion of the molecules bears a negative charge, such as alkylbenzene sulfonate ($RC_6H_6SO_3^-$ Na^+) though stable in alkali (high pH) condition, is not stable in an acidic condition where the pH below 7. They do not have excellent shear stability, can be stabilized over relatively long periods of time,

and have a tendency to foam with even mild agitator, but are not tolerant against electrolytes and hard water.

Cationic emulsion, the polar portion bears a positive charge, such as salt of long-chain amine ($RNH_3^+Cl^-$), quaternary ammonium chloride($RN(CH_3)_3^+Cl^-$) which are acid stable, will break in alkali condition at pH greater than 7. At relatively low viscosity, they display good stability in hard water and have only moderate stability against electrolytes.

Nonionic emulsion, the polar portion bears no apparent ionic charge, such as monoglyceride of long-chain fatty acid ($RCOOCH_2CHOHCH_2OH$), polyoxyethylenated alkylphenol ($RC_6H_6(OC_2H_4)_xOH$) are relatively unaffected by charge and may be stable in both acidic and alkali media over a pH range of at least 4-9.

Zwitterionic emulsion, both positive and negative charges may be present in the surface-active portion, such as long-chain amino acid.

2.4 The Counterion of Ionic Surfactants : Degree of Binding to the Micelle

The critical micelle concentration in aqueous solution reflects the degree of binding of the counterion to the micelle. In an aqueous system, increase binding of counterion to surfactant head group causes decrease in the CMC of the surfactant. The extent of binding of the counterion increases with increase in polarizability and valence, and decreases with increase its hydrate radius [5]. The degree of binding of the couterion to the micelle also depend on the surface charge density of the micelle. The greater the surface charge density i.e., the smaller the surface area per head group, the greater the degree of binding of the counterion. The surface area per head group, decrease with increase the length of the alkyl chain of the surfactant and increase with increase in the bulkiness of the head group.
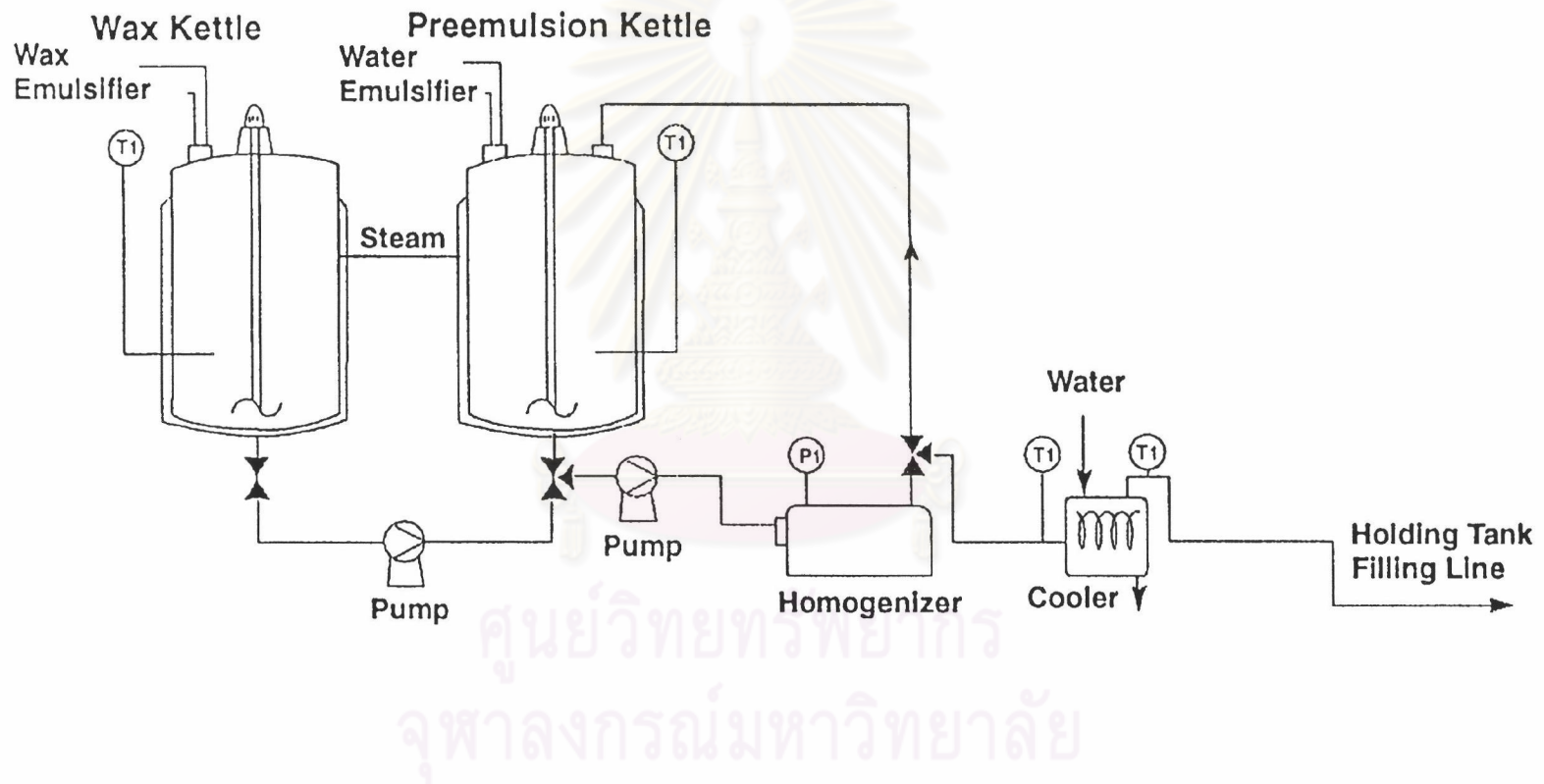
Figure 2.3 Schematic diagram of wax emulsion manufacture

2.5 Effect of Electrolyte on Surfactant Solubilization

Addition of small amount of neutral electrolyte to a solution of ionic surfactant appears to increase the extent of solubilization of hydrocarbon that are solubilized in the inner core of micelle [8] and to decrease that of polar compounds that are solubilized in the outer portion of the palisade layer. It can be explained due to neutral electrolyte decrease the repulsion between the similarly charged ionic surfactant head group, thereby decrease the critical micelle concentration (CMC), increase the aggregation number and volume of micelle. 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 group causes closer packing of the surfactant molecule in the palisade layer and results in decrease in the volume available there for solubilization of polar compound.

2.6 Effect of Temperature on Surfactant Solubilization [9]

For ionic surfactants an increase in the temperature, 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 surfactants the effect of temperature increase appears to depend on the nature of solubilizate. Nonpolar materials are solubilized in the inner core of micelle, appear to show increase solubility as the temperature is raised, the increase becoming very rapid at the cloud point.

2.7 The Destabilization and Separation of Emulsion System [10]

In the destabilization, such as two-phase emulsion goes through several consecutive and parallel steps the final stage of separation layer is reached. The first step, the droplets move due to diffusion or stirring and if the repulsion is too weak, they become aggregated to each other, flocculation has taken place. The single droplets are now replace by twins (or multiple) separated by a thin film. This step is important

because the stabilization process now passes from the realm of particles in random motion in a medium to describe the phenomena in a thin liquid film of colloid dimensions. The thickness of thin film is reduce due to the van der Waals attraction, and when a critical value of its dimension is reached, the film bursts and the two droplets unite to a single droplet. Coalescence is occurred. Figure 2.4 shows that the destabilization of an emulsion passes through the several stages, flocculation, coalescence and creaming before the final phase separation is occurred.
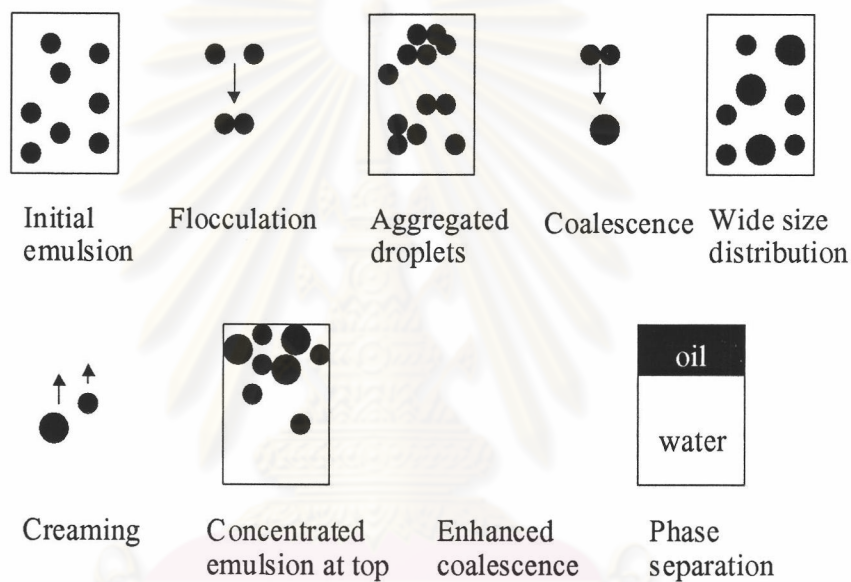

Figure 2.4   Schematic diagram of destabilization and phase separation
process of an emulsion **[10]**

In parallel with these phenomena, the droplets rise through the medium (creaming) on sink to the bottom (sedimentation) due to difference in density of the dispersed and continuous phase. This process is enhanced by the fact that larger droplets or aggregates move faster through the medium; in dilute suspensions, the velocity is proportional to the square of the radius. As consequence, lager droplets pass the smaller ones, causing sedimentation-induced flocculation. The final result is a highly concentrated emulsion at the top or bottoms of the container and the increased number

of droplets per volume increase the flocculation rate in the most decisive manner. The flocculation and coalescence process lead to larger and larger droplets until finally a phase separation has occurred.

2.8 Literature Reviews

Many work of wastewater treatment is interested at the presence, especially wastewater from oil industries. The process of the oil removal is consisted of physical separation and chemical treatment by adding with an electrolyte, cationic and anionic polymer and consequently oil phase separated from water. Other work used surfactant in a froth flotation process to remove the oil from wastewater.

Z h u *et al.* [11] investigated emulsified oils wastewater treatment with polymers. Wastewater was withdrawn from two holding ponds of metal industry. In this work the effectiveness of different polymer addition was studied through a chemical addition (CA), gravity separation (GS), process for oil and grease (O/G) and total suspended removal. In a dual polymer system, cationic polymer (W-2923) was used to break the emulsion and anionic polymer (POL-Z-E-2706) was used to enhance coagulation. In a single polymer system cationic polymer (KLAR-AID 2400) was used as a coagulant. The experiments, jar test method were performed for selecting chemical type, dosage and treatment conditions. Batch mixing tank experiment was conducted after the completion of a series of jar test. The results showed that the effluent O/G concentration range from 3 to 52 mg/L for a dual polymer system and from 1 to 35 mg/L for a single polymer system. The optimum removal occurred in a relatively narrow dosage range. A longer settles time was required for a single cationic polymer. Both dual polymer and single cationic polymer systems were sensitive to pH, however, the dual system was more sensitive.

Benito *et al.* [12] studied integrated process for the removal of emulsified oils from effluents in the steel industry. The researcher investigated two-staged treatment of emulsified oils. The process consist of either a coagulation or flocculation stage

removed the oil layer and followed by treatment of resulting water phase by ultrafiltration. Two types of emulsified oil studied were Qaukerol that is water miscible oil and Tinol which is an animal fat and becomes solid at temperature below $30^{\circ}C$. Inorganic flocculants were DK-1014 and DK-1018 and contained prehydrolyzed aluminium salts. Organic flocculant, N-7723, which contains ZnCl2, CaCl2, and NaOH in its formulation, was a quaternary polyamine. Ultrafiltration membranes were polysulfone (PM30) and a copolymer of polyacrylonitrile and polyvinyl chloride (XM300). The results of pH adjustment (pH = 10) leaded to destabilization of suspended particles of Tinol, and addition of $CaCl_2$ did not effect the suspension. The flocculant N-7723 gave better results than the inorganic compound. The addition of NaOH in the integrated treatment of the regular effluent gave 90% oils removal and 75% COD. The treatment of the washing effluent using DK-1014 flocculant and subsequent ultrafiltration could remove 90% oil and gave the COD values exceed regulatory standards. The high COD values obtained when the effluents were treated at $60\ ^{\circ}C$. In contrast COD value obtained for N-7723 was probably due to the presence of an excess flocculant dissolving in water.

Pondstabodee *et al.* [13] studied effect of microemulsion formation on cleanup of oily wastewater by froth flotation. The oil as ortho-dichlorobenzene was used for studies the efficiency of oil removal from water by batch froth flotation experiments. Three types of surfactant, sodium dodecyl sulfate (SDS), sodium salt of mono- and dihexadecyldiphenyloxide disulfonate (DADS) and cetylpyridinium chloride (CPC), and NaCl as electrolyte were used for study microemulsion phase behavior. The equilibrium phase behavior showed the Winsor Type I to Type III transition as inferred from the phase boundary measurements. The removal of oil increased with increasing salinity, decreasing oil/water ratio and increasing surfactant concentration. The percentage of oil and surfactant removal tends to increase with decreasing oil to water ratio.

Wungrattanasopon *et al.* **[14]** used foam flotation to remove tert-butylphenol from water. Cetyl pyridinuim chloride (CPC) and sodium dodecyl sulfate (SDS) were used for adsorptive a bubble flotation processes in batch mode to remove tert-butyl phenol (TBP) from water. The percentage of TBP removed showed a maximum around the critical micelle concentration (CMC) with SDS as the collector and maximum at a concentration a little lower than CMC with CPC as the collector.

Phoochinda **[6]** studied removal of emulsified oil from wastewater using froth flotation. A mixture of sodium dodecyl sulfate (SDS) and nonylphenol ethoxylate (NP $(EO)_{10}$) were used for studied microemulsion formation of ortho-dichlorobenzene (ODCB). The effect of NaCl in water, middle and oil phase system has been studied and showed that adding 0.5 wt % of NaCl increased ODCB removal. The concentration more than 1.0 wt % of NaCl decreased ODCB removal. The phase volume of middle phase increased and volume of water phase decreased in the water-middle phase system. The efficiency ODCB removal was investigated in flotation column experiment.

Binks *et al.* **[15]** studied stability of oil-in-water emulsion in a low interfacial system. The emulsions, a mixture of heptane and water stabilized by sodium bis (2-ethylhexylsulfosuccinate) were prepared from pre-equilibrated phases in Winsor I system. For up to 0.035 M NaCl, the creaming rate decrease with salt concentration, with no visible sign of coalescence. Above 0.035 M NaCl and approaching the phase inversion salt concentration of 0.055 M, the creaming rate quite markedly and coalescence become appreciable. At high NaCl concentration, due mainly to the low interfacial tension, the drops can deform and the attraction between them become significant, flocculation occurred which lead to coalescence instability.

Paton *et al.* **[16]** studied colloidal flocculation of micellar solution of anionic surfactants. They reported that α-olefin sulfonates $C_{14}C_{16}$ (AOS) and laulyl sulfate (SDS) micellar solution was flocculated at the present of Al^{3+} ions. The concentration of $Al_2(SO_4)_3$ are 0.035 M for AOS, and 0.023 M for SDS lead to flocculation of

surfactant micelle. SDS micelle was flocculated faster than AOS micelle. The behavior of AOS and SDS micellar solution were precipitated in the present of cation, following a mechanism by which initially cation bind themselves to the micelle surface. A higher cation concentration unbound cation precipitate with surfactant monomer.