# CHAPTER III

# FUNDAMENTALS

## 3.1 Surfactant

Surface active agents or surfactants are known as amphiphilic molecules. They have both polar and non-polar characteristics in the same molecule. Therefore, a surfactant molecule has both hydrophilic (water-loving) and hydrophilic (water-hating) components. Symbolically, a surfactant molecule can be represented as having a polar "hydrophilic head" and a non-polar "hydrophobic tail"

Surfactant could be categorized into the following classifications according to the nature of the hydrophilic group:

- Anionic: hydrophilic head is negatively charged.

- Cationic: hydrophilic head is positively charged.

- Nonionic: hydrophilic head is polar but not charged.

- Zwitterionic: molecule has both potential positive and negative groups; charge depends on pH of the medium.

The amphiphilic nature of surfactant molecules causes them to accumulate at interface of liquid. Furthermore, surfactant molecules can self-assemble into dynamic aggregates known as micells. The surfactant concentration at which the first micelle is formed is known as the critical micelle concentration (CMC). Beyond the CMC, any surfactant added to aqueous solution does not increase the number of surfactant monomers in aqueous solution, but rather will contribute to the formation of addition micelle.

## 3.2 Microemulsion System[16]

As mentioned above, microemulsions are isotropic, thermodynamically stable dispersions of oil, water, surfactant and often cosurfactant (with is generally alcohol). Microemulsion can be characterized as oil-in-water (O/W), water-in-oil (W/O) or bicontinuous system. Oil-in-water is microemulsion in equilibrium with an excess oil phase with the surfactant molecules existing in the aqueous phase in form of normal micelles. On the other hand, water-in-oil (W/O), microemulsion that coexists with an excess water phase and the surfactant molecules which aggregate in the oil phase in the form of reverse micelle.

Microemulsions have been used as chemical reactors because of their special interfacial properties allowing an intimate contact, at nanoscale level, of hydrophilic and hydropho-bic domains. In microemulsions, the size of droplets is in a range of 10-100 nanometers. When interactions among droplets occur, some droplets will coalesce and then spontaneously break apart. There must be a balance of forces present to drive the coalesced micro-emulsion droplets into splitting again. Overtime, the average droplet size of a micro-emulsion will remain constant. This results in a mixing of the contents inside the microemulsion droplets.

## 3.3 Nature of microemulsion droplet

There are generally asked "What a microemulsion droplet looks like", and what its dynamic behavior is? It is helpful to think of a microemulsion droplet as an intermediate between a micelle and an emulsion droplet. Some researchers even suggest that a W/O

microemulsion droplet to be a hydrated reverse micelle. One can consider an emulsion droplet to be a rather static structure, a large droplet of water suspended in a continuous phase of oil, with the oil/water interface stabilized by a monolayer of surfactant. On the other hand, a micelle is a very dynamic structure. It is a bit deceiving to see drawings of micelles in journals, because this representation is by necessity static, and micelles are actually dynamically changing and loosely bound aggregates. There is an equilibrium and a constant exchange between surfactant monomers and surfactant in the micelle aggregation. Micelles may have lifetimes as short as milliseconds, while emulsion droplets have long lifetimes, without the disintegration we see in micelles, but potentially with the occurrence of some coalescence over time. Given these two extremes of micelles and emulsion droplets, what will be our model for microemulsion droplets? It is know that the contents of mixed microemulsions do mix, this allows reactions to occur using microemulsion droplets as tiny microreactors. Because the water droplet is very small, we know that there exist two significant states of water, the "free" water in the interior of the droplet, and the water at the interface, associated with the surfactant molecules. Since we know that some fraction of microemulsion droplet collisions result in coalescence, yet the mean droplet size in the microemulsion remains constant over time, there must be a driving force to break up these aggregations again. Positive interfacial tension is the driving force for decreasing interfacial area of a giving droplet, so there must be some "negative" interfacial tension present to force an increase in interfacial area and the resulting breakup of microemulsion droplets that are too large. At the optimum droplet size, the forces are balanced and the interfacial tension must approach zero. We can envision a microemulsion as a dynamic entity, a tiny droplet surrounded by a monolayer

or aggregate of surfactant, sometimes combining with its neighbors, and subsequently breaking apart, sometimes exposing the water phase to the oil phase.

**Microemulsion nonionic surfactants.** For oil-in-water (O/W) microemulsions made with ionic surfactants, the primary force preventing coalescence is electrostatic charge repulsion. These microemulsions display the greatest ability to solubilize one phase within another. For W/O microemulsions, and microemulsions made with nonionic surfactants, there is only steric hindrance preventing coalescence of the droplets. This is a weaker force than electrostatic repulsion, so these microemulsions display les solubilization ability. Steric hindrance is affected only by the part of the surfactant molecule exposed to the continuous phase, for example, the hydrophobic region in a W/O microemulsion. Repulsion is enhanced by the of this region, as well as disorder introduced by such features as double bonds, which introduce bends and interfere with orderly packing of the surfactant molecules at the interface.

## 3.4 The Reactant exchange in microemulsion[17]

As mentioned above, microemulsions have been used as chemical reactors because of their special interfacial properties allowing an intimate contact, at nanoscale level, of hydrophilic and hydrophobic domains. There are many parameters which effect on a size and a morphology of nanoparticles synthesized in microemulsion. How does each micelle move, and how often micelle can contact to the other? If one assumes that microemulsion domains are formed by spherical droplets, the characteristic droplet's collision time in microemulsions can be easily calculated assuming that the droplets diffuse through a

continuous medium with viscosity, $\eta$. Then, the collision rate constant is given by

$k_D=(8/3)k_BT/\eta \approx 10^9$ $M^{-1}$ $s^{-1}$ for a typical low viscosity solvent. Because usually the

droplet's volume fraction $\Phi \approx 0.1$, i.e., [droplet] $\approx 10^{-3}$ M for a typical droplet's size $\approx 10$

nm, the encounter rate constant $k_{en} \approx 10^6$ $s^{-1}$. Thus, the average collision time (encounter

time) is $\tau_{en} \approx 1$ $\mu$s.

It is known that all droplets' collisions are effective for material exchange. This can be

taken into account introducing an encounter rate factor, $\gamma$, which for a particular material

(reactant), depends on the film flexibility. For rigid films like AOT microemulsions, $\gamma \approx$

$10^{-3}$ – that is, only 1 in each 1000 collisions is effective for the reactants' exchange.

However, for flexible films, this value can reach up to $\gamma \approx 10^{-1}$. Yhen the microemulsion

exchange characteristic time $\tau_{ex}$ is in the range $\approx 10$ $\mu$s$< \tau_{ex}<1$ ms.
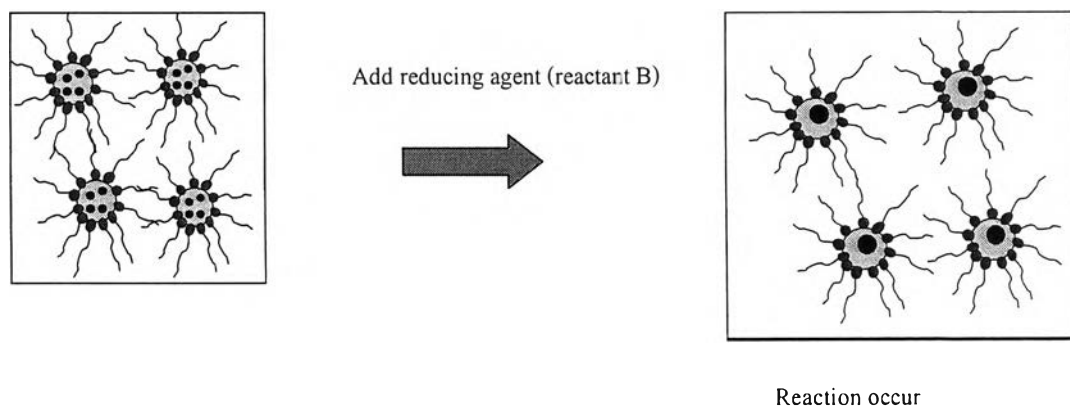
## 3.5 Preparation of nanoparticles in micromulsion[18]

In generally, two different methods could be employed for preparing the nanoparticles
in microemulsion.

1) By mixing two microemulsions, one containing the precursor and the other the

   precipitating agent (Figure 3a)

2) By adding the precipitating agent directly to the microemulsion containing

   the precursor. (Figure 3b)

Surfactant

Oil

Water + Reactant #1

Water + Reactant #2

Nanoparticles

**(a)** mixing of two microemulsions
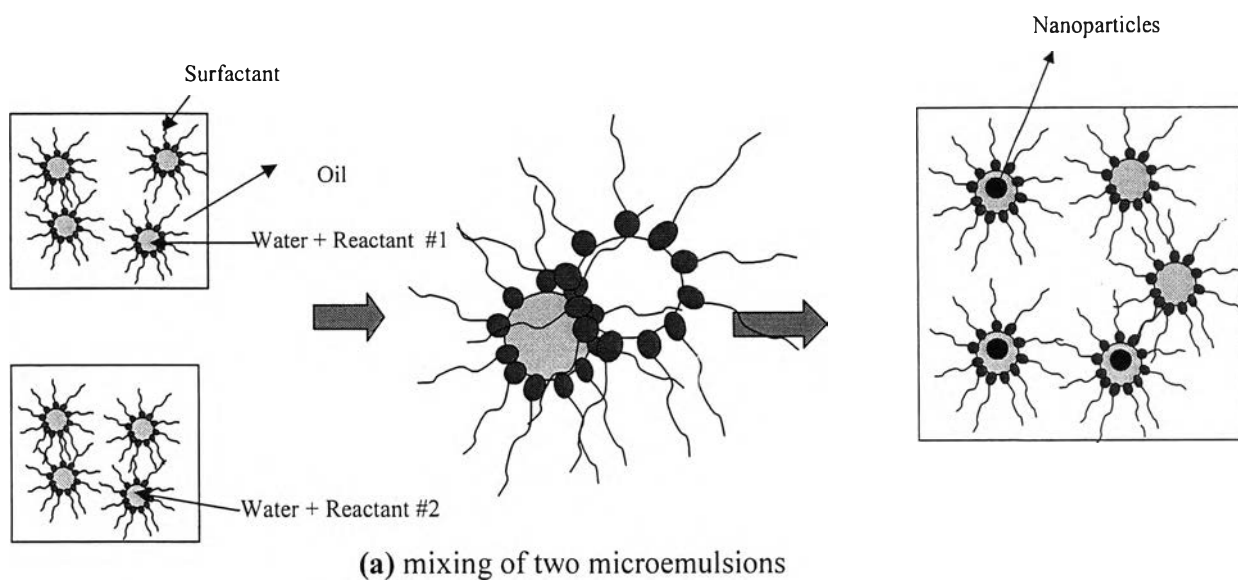
Microemulsion containing reactant A

Add reducing agent (reactant B)

Reaction occur

**(b)** direct addition of precipitating (reducing) agent to the microemulsion

**Figure 3.1** Preparation nanoparticles in microemulsion [18, 19]

## 3.6 Crystal structure of Zinc sulfide (ZnS)[20]

Zinc sulfide crystallizes in two different forms: Wurtzite and Zinc Blende. The ionic radius of the zinc(II) ion is 0.74 angstroms and that of the sulfide ion is 1.84 angstroms. If the sulfide ions originally adopt a hexagonal closest-packed structure, the ZnS crystal is Wurtzite (Figure 3.2a) If the sulfide ions originally adopt a cubic closest-packed structure, the ZnS crystal is Zinc Blende (figure 3.2b)
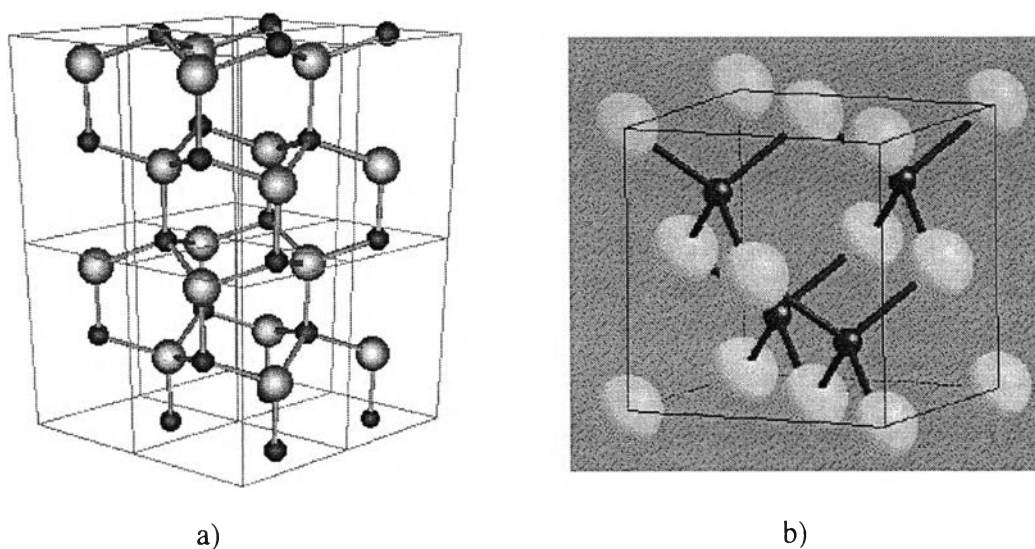


a)          b)

**Figure 3.2**    Crystal structure of Zinc sulfide: a) Wurtzite and b) Zinc Blend (Larger atoms are Sulfide)