CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Enhanced oil recovery

Generally, crude oil production process can be categorized for three stages. The first is primary oil recovery stage, crude oil is produced from reservoir by natural energy of the reservoir (mainly refer as pressure). The natural energy present in a given reservoir depends on rock and fluid properties, geologic structure and geometry of the reservoir (such as gas-cap drive, natural water-drive, fluid and rock expansion, solution-gas drive and gravity drainage). Typically, average amount of crude oil produced from this stage is 20% of the original oil in phase (OOIP). Because of reservoir natural energy will decrease after crude oil has been produced.

Secondary oil recovery stage is normally applied after primary recovery was completely operated. The secondary stage is purpose on reservoir pressure maintenance by compatible methods such as waterflooding or gas injection. In petroleum industry, the term of secondary oil recovery is mainly referred as waterflooding method as shown in Figure 2.1. However, water flooding process has some limitation to produce crude oil such as solubility between water-crude oil and reservoir surface wet-condition. Generally, 30% of OOIP is an average amount of crude oil production is expected from this stage.
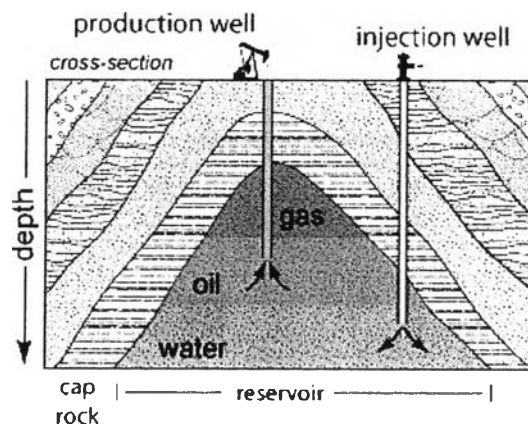

Figure 2.1 Schematic of water flooding process. (Source: http://www.gg.uwyo.edu)

After the two first stages were completely operated, a significant amount of crude oil (40-60% OOIP) is still remaining in the reservoir due to many factors. In order to recover the remaining crude oil, tertiary oil recovery stage is required to operate.

The tertiary oil recovery stage is also referred as enhanced oil recovery (EOR) or improved oil recovery stage. In this stage, crude oil may be produced because of the mechanisms involved in injection of hydrocarbon gases, carbon dioxide, nitrogen, hydrocarbon solvents, liquid chemical, thermal energy, and combination of two or more of different techniques. Selections of these methods are depend on the characteristics of the reservoir and availability of injection fluid.

Every crude oil production stages are aim to recover crude oil from the reservoir much as possible as. However, decision to operate those stages is mainly depend on technology available, benefit valuable and/or crisis situation. Summary of overall crude oil recovery mechanism is shown in Figure 2.2.
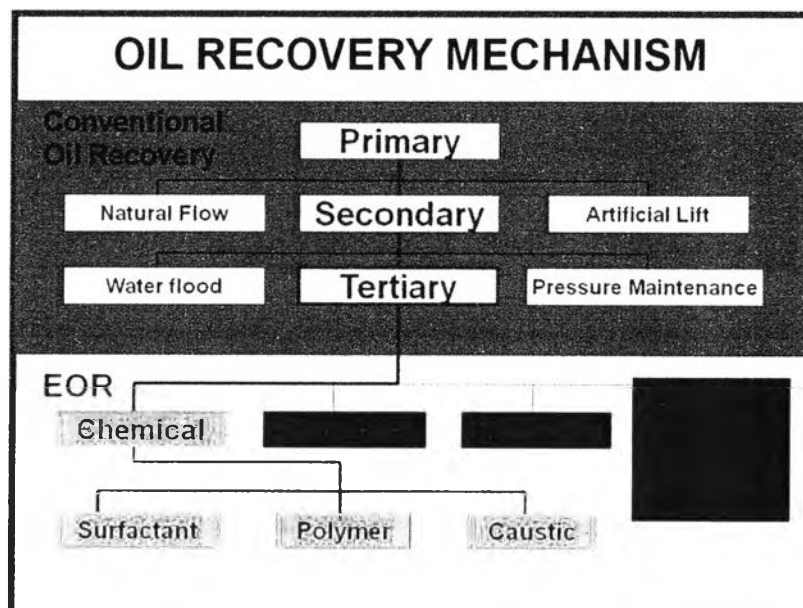

Figure 2.2 Oil recovery mechanism. (Source: http://ugmsc.wordpress.com)

2.1.1 Chemical Enhanced Oil Recovery

Chemical enhanced oil recovery is one of technique in tertiary oil recovery stage that has been studied for many years and gained more interest in recent years. This technique involves in the injection of various chemicals into the reservoir to achieve one or more effects, their aim to improve oil recovery such as interfacial tension reduction between immiscible fluid and/or wettability alterations of reservoir.

Chemical enhanced oil recovery can be categorized as polymer flooding, surfactant flooding and alkaline flooding processes (Figure 2.2). Polymer flooding process is mainly aim to shut-off the high permeability areas of the reservoirs (Seright and Liang, 1994). Feature of polymer flooding is characteristic to increase viscosity of the injected fluid. That causes the sweep areas in the reservoir is increased (Chauveteau and Sorbie, 1991; Yang et al, 2006). Surfactant and alkaline flooding processes are focuses to decrease ultra-low interfacial tension between water-oil phases also include of wettability alteration of the reservoir rock. Increases of relative permeability ratio and displacement efficiency are obtained from surfactant and alkaline flooding processes.

The feature characteristic of surfactant flooding is able to use in low permeability reservoirs (0.1 - 100 mD) where difficult to inject pure water and polymer flooding. Not only in case of very low permeability but also in case of high temperature and/or high salinity. This process can also be used where the amount of divalent cations is too high to use alkali. However, combination of the processes for advantage synergism to obtain the highest efficiency to recover the crude oil is possible to operate.

Generally in chemical enhanced oil recovery process, surfactant flooding, polymer flooding and water flooding were operated to produce crude oil together. Figure 2.3 shows the various zones and phase position in a typical of chemical flooding.
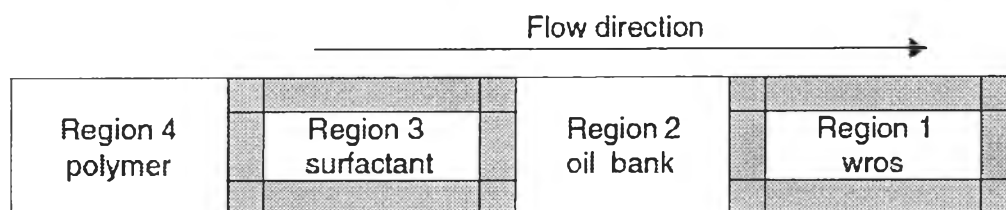
Figure 2.3 Phase position in a typical chemical flooding.

Region 1: water flooded residual oils saturation, only water is flowing.

Region 2: an oil bank is formed, both oil and water are flowing.

Region 3: surfactant slug forming the low IFT region, two or three phase flow of oil, brine, and microemulsion depending on the actual phase behavior.

Region 4: polymer solution for mobility control, single phase flow of water (Austad T. and Milter J., 2000)

The first purpose of using surfactants flooding is lowers interfacial tension (IFT) between crude oil and injected water. Another purpose is reservoir surface wet-condition alteration from oil-wet to water-wet. While polymer slug will improving viscosity for the surfactant slug and also improve mobility control of whole phases. Finally, displacing or driving force of whole slug is performed by the injected water.

Table 2.1 several series of surfactants to meet the needs of the various processes and conditions

	ORS Surfactants	Super Surfactants	GreenSurf	Smart Surfactant
EOR Applications	ASP	SP, ASP	SP, ASP	Visco-elastic surfactant that provides low IFT and viscosity
TDS Tolerance	30,000 ppm	>100,000 ppm	>200,000 ppm	>200,000 ppm
Ca, Mg tolerance	~400 ppm	> 1000 ppm	> 2000 ppm	> 2000 ppm
Temperature Stability	> 100°C	> 100°C	> 100°C	90°C
Water softening	Yes	SP - No ASP - Yes	SP - No ASP - Yes	No
Source	Petro based	Petro and bio based	Bio based	Bio based
Co-surfactant required	No	No	No	No
Co-solvents required	No	No	No	No
Salinity optimization required	No	No	No	No
IP Status	Patented	Patented	Patent pending	Patented

2.2 Surfactants

Surface active agents or surfactants are amphiphilic molecule that able to dissolve in water and oil phase. Because there contain both hydrophilic (polar, head group) and hydrophobic (non-polar, tail group) in the same molecule. Figure 2.4 is show the general structure of surfactant molecule.
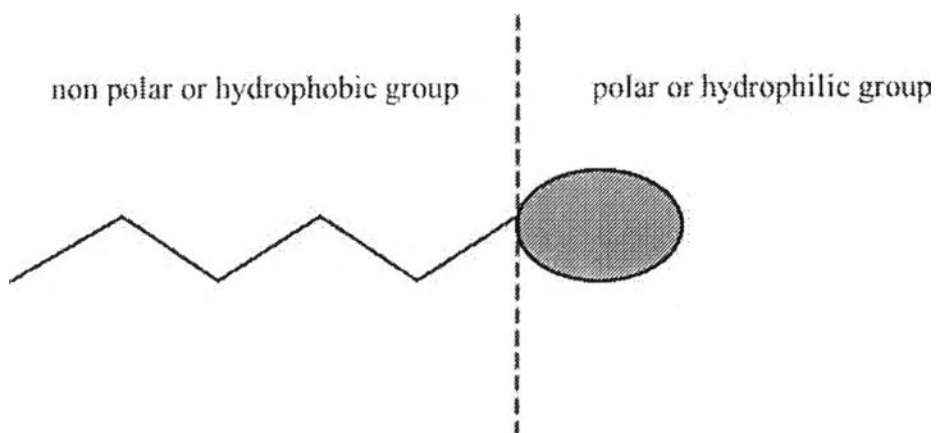
non polar or hydrophobic group   polar or hydrophilic group

Figure 2.4 Structure of surfactant molecule.

However, surfactant molecule is possible to contain one or more hydrophilic and hydrophobic groups. Different of chain length, size and/or type of each group are also effect to the surfactant properties. In usually, surfactants are broadly categorized depend on charge of the head group for 4 types. There are anionic surfactant (negatively charge), cationic surfactant (positive charge), amphoterics or zwitterionic surfactant (both positive and negative charge) and non-ionic surfactant as shown in Table 2.2.

Table 2.2 Classification of surfactants type

Anionics	⊖ x ⊕	Sulfates, sulfonates, phosphates, carboxylates, stearate
Cationics	+ x ⊖	Quaternary ammonium organics, pyridium, imidazolinium, Piperidinium and sulfononium compounds
Amphoterics	+ -	Aminocarboxylic acids
Non-ionics	●	Alkyl-, Alkyl-aryl, acyl-, acylamindo-, acyl-aminepolyglycol, amd polyol ethers Alanolamides.

Configuration of surfactant molecule is mainly depends on surfactant concentration. If the concentration is lower than the critical micelle concentration (CMC), surfactant monomers are in the surfactant rich phase and also form as monolayer at the surface. If the concentration is equal or higher than the critical

micelle concentration (CMC), the surfactant will align as micelle which is allow one fluid can dissolve into the micelle as shown in Figure 2.5.
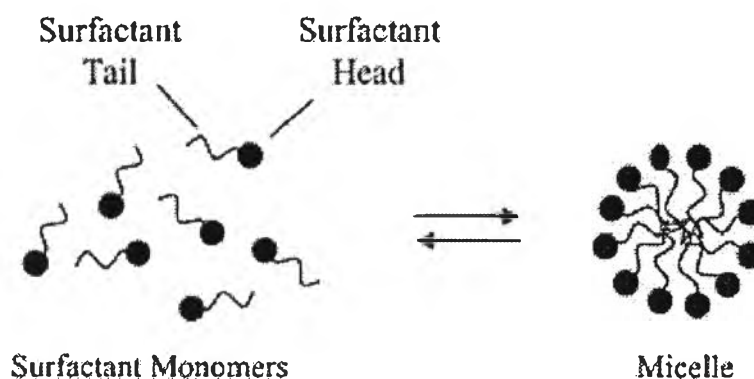

Figure 2.5 Schematic illustration of the reversible monomer-micelle thermodynamic equilibrium.

Micelle formation will act as linkage at the interface between two immiscible fluids. Therefore, surfactants have the potential to change surface properties, interface properties and/or lowering the interfacial surface energy that cause the two immiscible fluids can mix together which is the main purpose of surfactant.

In order to obtain very low interfacial tension (IFT) between water and oil phases, high surface coverage of surfactant at the interfacial surfactant is required. Thus, the surfactant molecules must have strong lateral intermolecular association without forming precipitate and gels.

2.2.1 Surfactant in Enhanced Oil Recovery

Surfactant flooding process is the process that injects surfactant slug into the reservoir to lower the interfacial tension between crude oil and water front. Although the use of surfactants to remediate organic contaminants in the subsurface is a relatively new area of application, their use in subsurface systems dates back to 1963 when petroleum sulfonates were patented for widespread use in enhanced oil recovery efforts (Pope and Wade, 1995). In oil recovery process, surfactants are

believed to play a key role of altering the wettability of the surface (Khan and Marques, 1997). Chain length of the surfactant is also importance to adsorption effect. A longer chain length surfactant led to more adsorption on the solid. (Patrick Shuler et al, 2009). Lower adsorption at the reservoir could be obtained from below CMC of some surfactants (E.A. Spinler et al, 2000).

2.3 Microemulsion phase behavior

Microemulsion is a small-scale of emulsions that considered in thermodynamic equilibrium of a micellar phase containing surfactant, aqueous and oil (Bourrel and Schechter, 1988). Observation of microemulsion phase behavior is the fastest and the most effective method to determine and screen hundreds of surfactant which are able to form as micelle. Microemulsion phase behavior can be categorized for 3 types according the Winsor phase behavior theory (Figure 2.6).
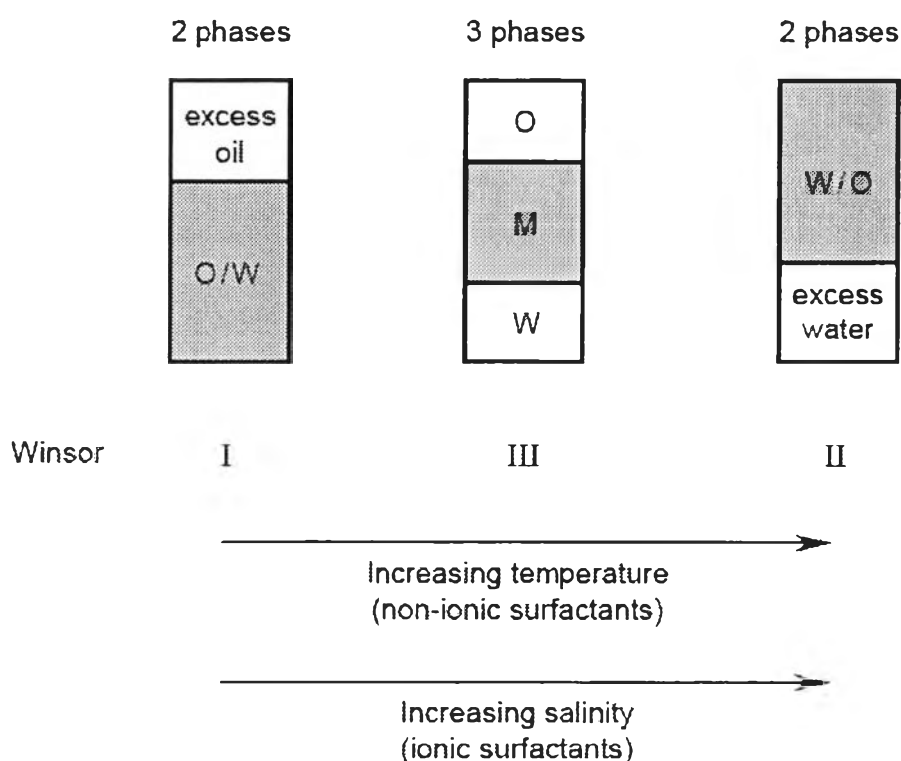

Figure 2.6 Classification of microemulsion phase behavior according to Winsor behavior and also show the relationship between salinity and temperature.

- Winsor type I is an oil-in-water microemulsion, the surfactant is preferentially dissolved in water and has remain the excess oil phase. That mean the surfactant-rich water phase coexists with the oil phase where surfactant is only present as monomers at small concentration.

- Winsor type II is a water-in-oil microemulsion, the surfactant is mainly dissolved in oil phase and has remain the excess water phase. That mean the surfactant-rich oil phase coexists with the surfactant-poor aqueous phase.

- Winsor type III, is three-phase system, oil and water phase is separated by lamellar layer with ultra-low IFT. The middle phase microemulsioon has surfactant molecules, which orientate with solubilized oil and water in a bicontinuous form.

Transformation of microemulsion phase behavior from Winsor type I to Winsor type III to Winsor type II is depend on many parameters, such as salinity, temperature, oil phase, cosurfactants, types and concentration of surfactants, etc. In usually, the salinity is mainly effect for ionic surfactants and temperature is mainly effect for non-ionic surfactants phases transition.

2.3.1 Solubilization parameter

Volume of water and oil that dissolved within the micellar solutions is well-known for determine the surfactant solubility, which is call "solubilization parameter". Wu et al. (1997) defined oil solubilization parameter in the term of solubilized oil volume per mass of surfactant that dissolves the oil.

$$SP_o = \frac{V_o}{M_s}$$

Where SP_o, V_o and M_s are represented as oil solubilization parameter, oil solubilized volume and total mass of surfactant(s) respectively. M_s value is addition of all surfactants that are presented in the dissolve phase, but excluding the mass of alcohol (if used).

The optimum solubilization parameter (SP*) of microemulsion systems occurs when oil solubilization parameter equal with water solubilization parameter (SP$_w$). It can be defined as

$$SP* = SP_o = SP_w$$

A symmetry distribution of the middle phase that mean volume of solubilized oil/water in the middle phase are equal. Surfactant mass is also the same, so the optimum solubilization parameter (SP*) is occurs at this condition. Solubilization parameter transition by salinity effect is shown in Figure 2.7
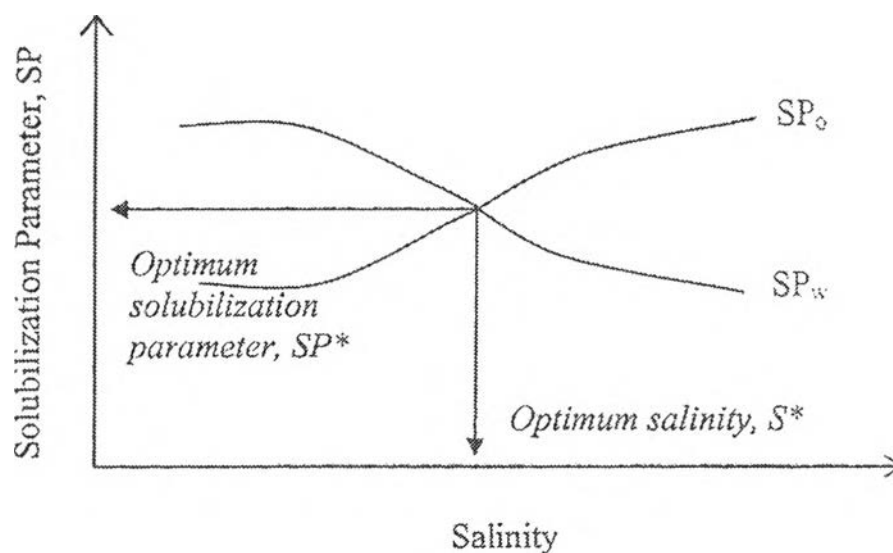

Figure 2.7 Solubilization parameter as a function of salinity (Lohateeraparp, 2001).

At Winsor type I region, SP$_w$ value is greater than SP$_o$ since all water phase is dissolved by the surfactant and remain the excess oil. SP$_o$ is become to increase at Winsor type III region, because some volume of oil is more dissolved than Winsor type I. SP$_w$ is become to decrease, because some of water is expelled from the surfactant and surfactant layer is occur at the middle only. At the intersection point of SP$_o$ and SP$_w$ lines is determined as the optimum solubilization

parameter (SP*). If continue to increase the salinity after this point, the water will expelled from the microemulsion phase since Winsor type II is occurred.

2.4 Spontaneous imbibition

Spontaneous imbibition is well-known process that uses one fluid to displace another fluid from a porous medium as a result of capillary forces and/or gravity. The porous medium that saturated with one fluid will submerge into the brine solution.

Figure 2.8 shows an experimental set up for spontaneous imbibition. The oil-saturated core is submersed in the brine solution. Oil is dissolved out from the core will accumulate at the top of brine solution due to it lighter than brine solution. The spontaneous imbibition can also be classified as co-current and countercurrent imbibition. Co-current imbibition occurs when both the inlet and outlet are open to an invading fluid, or in other words both displacing and displaced fluid moves in the same direction. Countercurrent imbibition occurs when only one of the ends (inlet) is open, or displaced fluid moves in opposite direction.

In naturally fractured systems with high degree of interconnection, imbibition forces must be strong enough for surfactant-enhanced water flood to be effective.
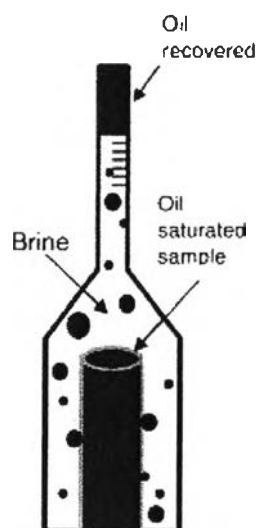

Figure 2.8 Experimental set up for spontaneous imbibition.

2.5 Rock Surface Charge

Rock surface charge is effects to surfactant type selection for EOR process. Carbonate rock, which surface is considered as positive charge, will repulse to cationic surfactant due to the same kind of charge. Limestone and sandstone rock, which surface is considered as negative charge, will repulse to anionic surfactant due to the same kind of charge too. This mechanism is useful for EOR process, the repulsion between surface and surfactant will cause the losses of surfactant by surface adsorption is reduced as shown in Figure 2.9.
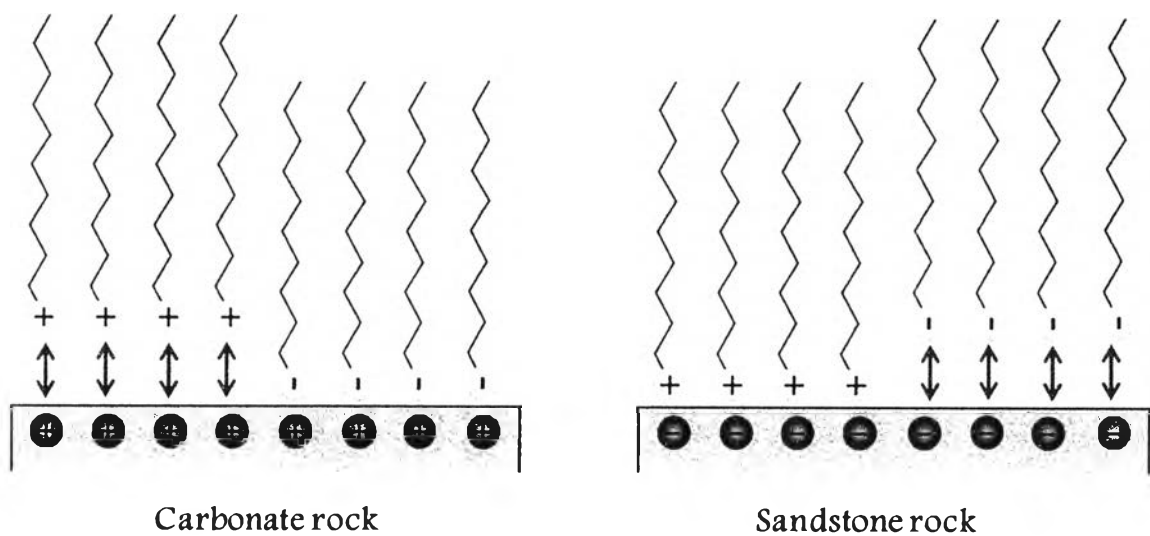

Carbonate rock   Sandstone rock

Figure 2.9 Effect between charge from surfactant and rock surface.