# CHAPTER II

# THEORETICAL BACKGROUND AND LITERATURE REVIEW

Study of wetting was started two hundred years ago, to one of the many achievements of the eminent British scholar Thomas Young. He suggested a simple equation relating the contact angle between a liquid surface and a solid substrate to the interfacial tensions involved.

## 2.1 Contact Angle

### 2.1.1 Measurement

Contact angle ($\Theta$) is a quantitative measure of wetting a solid by a liquid. It is geometrically illustrated in Figure 1.1, the angle on the liquid side of the tangential line drawn through the three phase boundary where a liquid, gas and solid intersect, or a second immiscible liquid and solid intersect. Low contact angle corresponds to higher wettability whereas high contact angle means poor wettability. Mittal (1999) stated that contact angle exists when a liquid does not completely spread on a substrate (usually a solid). The shape of the drop and the magnitude of the contact angle are controlled by three interaction forces of interfacial tensions ($\gamma_{SV}$, $\gamma_{LV}$, and $\gamma_{SL}$) of each participating phase. Marmur (1996) stated that common techniques to measure contact angle are Whilmey plate, inclined plate, and sessile drop (captive bubble in liquid). The most complex, but also the theoretically most precise method for calculating the contact angle is the sessile drop. Taking considerations of this technique, the theory is based on the equilibrium of an axisymmetric sessile drop on a flat, horizontal, smooth, homogeneous, isotropic, and rigid solid. In general, contact angles are accessible experimentally. Moreover, Young's equation is often used to measure the contact angle. Many other theoretical approaches based on the Young's equation have therefore been developed to account for non-ideal contributions. In ideal situation, equation (2) is applicable. This analysis involves the interfacial free energies between the three phases.

In the case of non-ideal conditions due to environmental conditions, roughness, and chemical heterogeneity, deviations from ideal relationship will occur. The non-ideal contact angles are referred to as apparent contact angles. However, the common fact about interfacial tension between solid-vapor and solid-liquid are not directly accessible whereas liquid-vapor can only be obtained directly.

### 2.1.2 Contact Angle Hysteresis

Hysteresis, which is the difference between the maximum (advanced/advancing) and minimum (receded/receding) contact angle value. Mittal (1999) reported that the measured contact angle value depends on the surface pretreatment and how liquid drop is deposited on the surface and chemical heterogeneity and surface roughness were considered to be responsible of contact angle hysteresis. It has been used to help characterize surface heterogeneity, roughness and mobility. For such case, which surfaces are not homogeneous, there will be an existence of domains on the surface which present barriers to the motion of the contact line. For the case of chemical heterogeneity these domains represent areas with different contact angles than the surrounding surface for which when wetting with water, hydrophobic domains will pin the motion of the contact line as the liquid advances thus increasing the contact angles. When the water recedes the hydrophilic domains will hold back the draining motion of the contact line thus decreasing the contact angle.

## 2.2 Wettability

Adamson (1990) stated that wettability or wetting is the actual process when a liquid spreads on a solid substrate and it can be measured by determining the contact angle or calculating the spreading coefficient. It can be qualitatively estimated with the contact angle as shown in Figure 2.1
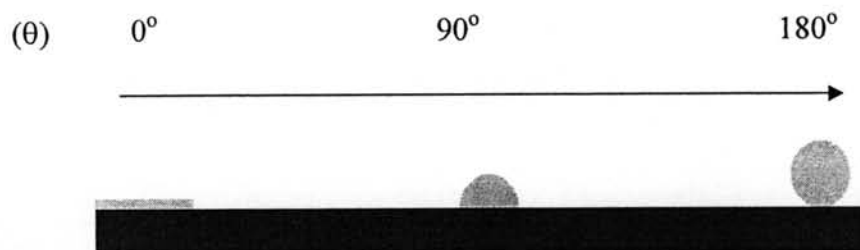
($\theta$)  0°  90°  180°

**Figure 2.1** Degree of Wetting

The degree of wetting is quantified by the spreading coefficient given by equation (1) or by the contact angle values according to the degree of wetting such 180° exhibits as non wetting, $180°<\theta^0 <0$ as partial wetting, and 0 as complete wetting.

## 2.3 Factors affecting Contact Angle and Wettability

Contact angles on surfaces are merely not only influenced by the interfacial tensions, thus other factors that may affect will cause Young's equation to be invalid. The common problems are surface roughness, chemical heterogeneity, sorption layers, molecular orientation, swelling, and partial solution of the surfactants or low-molecular constituents in the surfactant material. These effects have to be considered when contact angle measurements are used to calculate the solid surface tension. (Kwok, et al., 1999). Other common reasons of variation of contact angle and wettability are the effects of surface preparation and the presence of contaminants, the vapor environment, pressure and temperature, drop size, and precision of measurement.

Saguy et al. (2004) reported that it is important to notice that the calculated ideal contact angles on the various rough surfaces turn out to be practically identical. Nakae et al. (1998) examined the different contact angle of two rough surfaces. The effect of height of roughness can be known by a change in curvature radius of liquid trapped air pocket at a solid/liquid interface for a hemispherical close-packed model. Rosen (1989) reported that the surface roughness reduced contact angle at a smooth surface.

Drelich et al. ( 1994) and Lin (1995) reported that the fluctuations of contact angle were due to surface heterogeneity as well as McHale et al. (2001) evaluated the

same effects of drop flattening and surface heterogeneity on the cross sectional and planar shapes of the droplets of liquids resting on the solid surface through the use of simultaneous planar and side view microscopy of sessile drop.

Ruijter et al. (1998) reported that the relaxation of the contact angle depends on the temperature.

Sefiane et al. (2003) found out that concentration of high volatile component affect highly the dynamic contact angle of a binary mixture system of water and ethanol.

Rao and Vijapurapu (2004) found out some inaccuracy to contact angle due to the insensitivity of the Wilhelmy technique at low oil–water interfacial tensions, this technique was found to be unsuitable for measuring dynamic contact angles in crude oil–brine–rock systems containing surfactants.

If the surface tensions of the system and the volume of the droplet remain constant, the contact angle does not make any change. In practice, the changes in the surface tension or droplet volume cause contact angles to changes. When the surface tension changes, a new equilibrium of three forces acting on a droplet sets a different contact angle. When the droplet volume changes, commonly due to evaporation, it results in a decrease of the contact angle in a constant contact line mode (Erbil et al., 2002).

Kruss (www.kruss.info) emphasized proper procedure of using instrument, which stated that during the measurement of the advancing angle the syringe needle remains in the drop throughout the whole measurement. A drop with a diameter of about 3-5 μL (with the needle of 0.5 mm diameter which is used in KRÜSS measurement systems) is formed on the solid surface and then slowly increased in volume. At the beginning, the contact angle measured is not independent of the drop size because of the adhesion to the needle. At a certain drop size the contact angle stays constant; in this area the advancing angle can be measured properly.

## 2.4 Surfactant

### 2.4.1 Structure of Surfactants and Application

Surface-active-agent is abbreviated as surfactant, which are amphiphilic molecules consist of a hydrophilic, polar head group and a hydrophobic, and non-polar tail as shown in Figure 2.2. Due to their amphiphilic nature, surfactant molecules have a high affinity towards surfaces and interfaces. Surfactants may be classified into four different groups, depending on the nature of the polar head group: anionic surfactants, cationic surfactants, zwitterionic surfactants and non-ionic surfactants. Surfactants are commonly organic compounds.
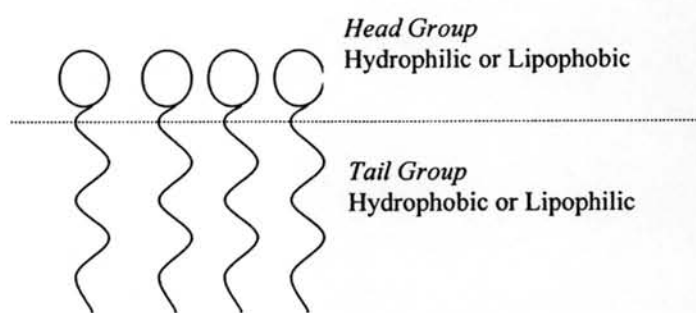


**Figure 2.2** Structure of surfactant

All surfactants possess the common property of lowering surface tension when added to water in small amounts. They are typically soluble in both organic solvents and water. Surfactants reduce the surface tension of water by adsorbing at the air-water interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. Surfactants play an important role in many practical applications and products including detergents, emulsifiers, paints, adhesives, inks, foaming, defoaming, and wetting.

### 2.4.2 Micelle Formation

Rosen (2004) defined micelle as a cluster of surfactant molecules. Such molecules display distinct behavior when interacting with water. The polar part of the molecule seeks to interact with water while the non-polar part shuns interaction with water. Micelles only form when the concentration of surfactant is greater than

the critical micelle concentration (CMC) the core of a micelle consists of the hydrophobic portion of the molecules, while the hydrophilic groups remain on the surface of the molecule so that they can maintain favorable contact with water.

There are two ways in which such a molecule achieves both these states. An amphiphilic molecule can arrange itself at the surface of the water such that the polar part interacts with the water and the non-polar part is held above the surface (either in the air or in a non-polar liquid) as shown in Figure 2.3. The presence of these molecules on the surface disrupts the cohesive energy at the surface and thus lowers the surface tension. Such molecules are called 'surface active' molecules or surfactants.

Another arrangement of these molecules can allow each component to interact with its favored environment. Molecules can form aggregates in solution, such micelles and vesicles. Focusing micelles, it can be classified as normal ( tail groups forming the core and head groups coating this oil-like interior ) in aqueous solution; or reverse where the tail groups are on the micelle exterior exposed to an organic solvent. Normal micelles are much easier to form than of reverse micelles.
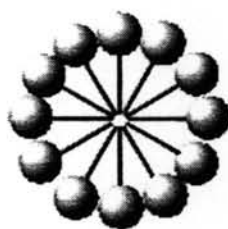


**Figure 2.3** Example of normal micelle

Furthermore, the proportion of molecules present at the surface or as micelles in the bulk of the liquid depends on the concentration of the amphiphile. At low concentrations surfactants will favor arrangement on the surface. As the surface becomes crowded with surfactant more molecules will arrange into micelles. At some concentration the surface becomes completely loaded with surfactant and any further additions must arrange as micelles. This concentration is called the Critical Micelle Concentration (CMC). It follows that measurement of surface tension and

contact angles may be used to find CMC value of a solution (Dechabumphen et al., 2001).

Figure 2.4 shows the graph of surface tension versus log of concentration of surfactant added identifying the CMC point and appearance of micelles.
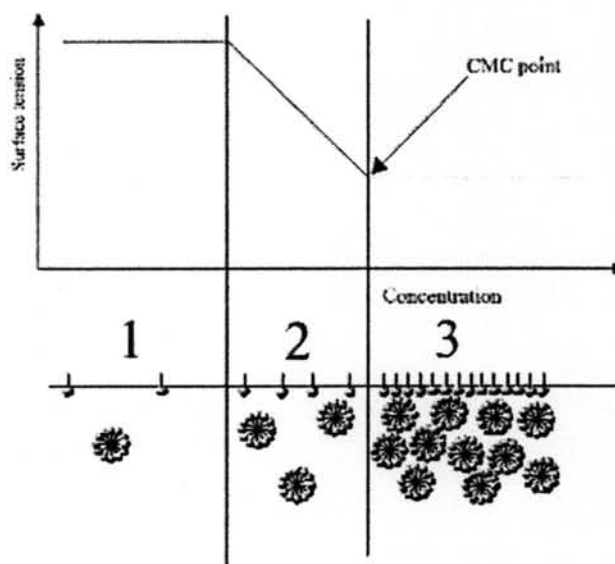


**Figure 2.4** Surface tension vs. log of concentration (Rosen, 2004)

In case of <u>nonpolar</u> solvent, the hydrophilic groups form the core of the micelle, and the hydrophobic groups remain on the surface of the micelle. When surfactants are present above the CMC, they can act as emulsifiers (Mittal, 1999)

### 2.4.2 Precipitation of Surfactants

Scamehorn et al. (2004) stated that above the CMC, many surfactants form solutions in which the micelles are no longer randomly distributed but are organized into structures called liquid crystals. Surfactants form into four main types of liquid crystals, such as hexagonal, lamellar, discontinuous cubic, and biscontinuous cubic. As surfactant concentration increases, structures transform into spherical micelles, cylindrical micelles, or any of the four liquid crystals. In case of cloudy appearance of solution at the cloud point, emulsion of coacervate phase exists in the dilute phase. This case happens due to the increase of the temperature of an

aqueous solution of nonionic surfactants eventually will cause transitions from one phase to a two-phase system. Moreover precipitation occurs when the solubility product of a charged surfactant monomer with ion on opposite charge is exceeded.

## 2.5 Zisman's Plot

Zisman method is used widely as the most precise technique in obtaining the critical boundary tension (γc) through Zisman's plot (Figure 2.5) which summarizes wetting behavior allowing predictions of an interpolative nature using a homologous series of liquids; the Solid-Liquid-Liquid Surface Energy Tool which evaluates the surface energy of a solid using contact angles. It summarizes wetting behavior allowing predictions of an interpolative nature using a homologous series of liquids. The method according to ZISMAN uses this relationship by plotting cos Θ against the surface tension for various liquids and extrapolating the compensation curve to cos Θ = 1. The corresponding value for the surface tension is known as the critical surface tension ($\gamma^c$) (Rosen, 1989).
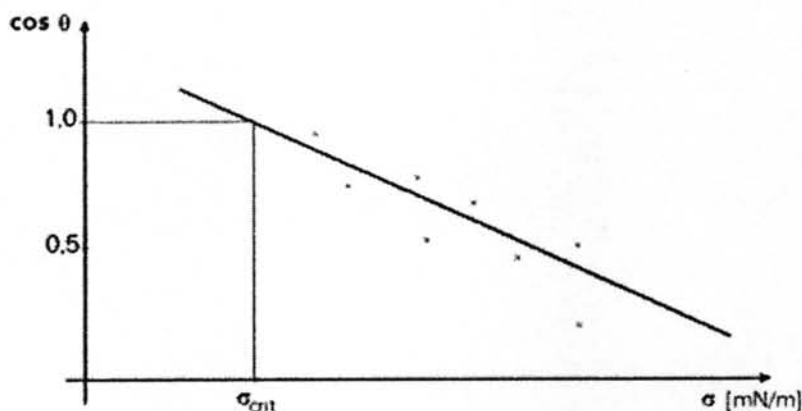


**Figure 2.5** Determining $\gamma^c$ according to ZISMAN  (Kruss, 2006)

## 2.6 Application of Related Work

Knowledge in wetting mechanism helps to understand deeper related chemical processes as it affects coating flows, flotation, printing, lubrication, drying, oil recovery from porous rocks, and detergency.

Garret (1993) stated that film rapture as particles become dewetted by the aqueous surfactants due to hydrophobic particles bridged the lamella surfaces.

Guy et al. (1996) applied the contact angle for characterization of solid surface of five different coal types ranking from brown to low volatile bituminous in the presence of water and other several organic liquids.

Alexandrova and Grigorov (1998) reported that the surfactant changes the three-phase contact angle of copper minerals, pyrite and molybdenite which led to reduction in deleterious froth.

Chandra et al. (1996) reported the effect of varying liquid-solid contact angle on droplet evaporation. Increase of heat transfer area between the droplet and surface reducing droplet evaporation as the droplet spreads.

Rao and Vijapurapu (2004) reported two simple techniques of surfactant addition and brine dilution to beneficially alter wettability and minimize capillary trapping of crude oil in reservoir rocks.