

CHAPTER II

LITERATURE SURVEY

2.1 General Definition of Classification of Contact Angle

Contact angle has been studied for almost 200 years since the publication by Young (Marmur, 1996). Contact angle is the angle obtained between a surface substrate and a liquid droplet. The well known Young equation (Serre *et al.*, 1998; Paterson *et al.*, 1998) was developed for an ideal solid surface, namely a perfectly smooth, chemically homogeneous rigid, insoluble and non-reactive surface. The contact angle on such a solid surface is called the "intrinsic contact angle". Most real solid surfaces are rough and chemically heterogeneous. For such surfaces, the contact angle may change from one point to another along the contact line. The angle between the direction of the tangent to the solid surface at a given point and the direction of the tangent to the liquid-fluid interface at the point is called "the actual contact angle". The angle between the direction of the tangent to the "smooth" solid surface, as seen by using relatively low magnifications, and the direction of the tangent to the liquid-fluid interface is called "the apparent contact angle" (Marmur, 1996).

2.2 Contact Angle Measurement

Measuring contact angle by the sessile drop technique is widely used in many researches by depositing a droplet of liquid or solution on the surface and measuring contact angle by a goniometer or simply placing a tangent to the drop by a computer program (Janczuk *et al.*, 1997; Rosen, 1989). This method is convenient and fast but the error can be made by an operator. The

contact angle can be analyzed by the method suggested by Wilhelmy. The method consists of measuring the force exerted by a fluid/fluid interface on a solid surface as the latter moves across the interface, and the contact angle is calculated by equation, $F = \text{weight} + P_{\text{buoyancy}} + 2(l + e)\gamma\cos\theta$, where F is the measured force that has three components; the weight of the slide, the buoyancy, and the vertical component of the interfacial tension (γ); θ is the contact angle and l and e are the width and thickness of the slide respectively (Paterson *et al.*, 1998). This method is independent of personal error and the results are highly reproducible (Berg, 1993).

Contact angles on finely divided solids are more difficult to measure, but are often more desired and more important than those on large solid surfaces. The contact angle is obtained by packing the powder into a glass tube and measuring the rate of penetration of the liquid into it. The distance of penetration (l) in time (t) of a liquid of surface tension (γ_{LA}) and viscosity (η) is given by the modified Washburn equation.

$$l^2 = \frac{(kr)t\gamma_{LA}\cos\theta}{2\eta} \quad (2.1)$$

Where r is the mean equivalent radius of a capillary and k is a constant to allow for the tortuous path through them (Rosen, 1989, Subrahmanyam *et al.*, 1996).

2.3 Wetting and Its Modification by Aqueous Solution

Wetting can occur when the surface tension of liquid less than critical surface tension of solid. When a droplet of a high surface tension liquid is placed on a solid of low surface energy, the liquid surface tension will cause the droplet to form a spherical shape (lowest energy shape). A common

illustration of this phenomenon is the behavior of water droplets on a freshly waxed surface such as an automobile fender. Conversely, when the solid surface energy exceeds the liquid surface tension, the droplet is a flatter, lower profile shape. This is easily seen in the case of a red wine glass as the wine wets or "sheets" the surface (Hudson, 1997). Nearly all liquids other than liquid metals, that have surface energy less than 75 ergs/cm^2 , can spread over high melting solids (eg. silica) having surface energy from several thousand to hundred ergs/cm^2 (Rosen, 1989).

There are several investigations of wetting modifications by surfactant. Shiao *et al.* (1998) reported the effect of chain length compatibility of sodium alkyl sulfate/alkanol mixtures on contact angle. The spreading coefficient is maximum, the contact angle is minimum and the surface tension is minimum when the chain length of the surfactant is equal to that of the alkanol. This can be explained by the closer packing of the monolayer expected for matched surfactant/alkanol pairs. Chesters *et al.* (1998) reported that a key element in the wetting behavior appears to be the boundary condition arising from a surfactant balance at the contact line, which gives rise to surfactant accumulation and hence to surface immobilization. Immobilization tends to be self-maintaining (hysteresis) and surfactant concentration many orders of magnitude greater than the equilibrium level can be maintained near the contact line, disproportionally reducing static contact angle. Alexandrova and Grigorov (1998) reported that the surfactant changes the three-phase contact angle (wetting properties) of copper minerals, pyrite and molybdenite, and in this way leads to a significant reduction in deleterious froths. Janczuk *et al.* (1997) reported that CTAB adsorption at the teflon/water interface is the same as at the water/air interface. However, at a low CTAB concentration in aqueous solution the adsorption of CTAB at the teflon/water interface is several times higher than at the water/air interface. It may result from the presence of a weak acid-base interaction across the

teflon/water interface, which can play an important role in the mechanism of adsorption at low CTAB concentration.

Bahr *et al.* (1999) suggested the existence of two spreading regimes exhibiting different spreading characteristics. Firstly, non diffusive regime, the spreading is very rapid and controlled to different extents by inertia, gravity and capillarity depending on the drop size, impact energy and interfacial tension balance. Secondly, diffusive controlled regime, is characterized by slower concentration dependent spreading rates that are mainly controlled by the diffusive transport of surfactant to the expanding liquid-vapor interface. Bigelow and Brockway (1956) reported that the most important factor in determining the oleophobic properties of fatty acids film and similar polar organic compounds adsorbed on solid surfaces is the density of the adsorbed molecules on the surfaces. Decreases in the densities of the films are accompanied by decreases in their oleophobic properties. The length of the adsorbed polar molecules is not a major factor in determining the oleophobic properties of the films. However, the roughness of the substrate surface may be large compared with the dimensions of the polar molecules, and increasing the length of the molecules may improve their ability to form film having the required surface characteristics.

Christenson and Yaminsky (1997) has explained the correlation between contact angle hysteresis and the range of the hydrophobic attraction. Surfaces which show a small difference between advancing and receding contact angles of a sessile water droplet exhibit no long-range force. These surfaces are stable and no rearrangement, mobility or desorption of hydrophobic groups can occur. Vogler (1998) reported that hydrophobic surface ($\tau^{\circ} < 30$ dyn/cm) supports adsorption of various surfactants and proteins from water because expulsion of solute from solution into the interphase between bulk solid and solution phase is energetically favorable. Adsorption to hydrophobic surfaces is driven by the reduction of interfacial

energetic concomitant with replacement of water molecules on the surface by adsorbed solute. Pitt *et al.* (1996) found that increasing the number of tails lowers the limiting value of the surface tension. Branching the tails also tends to lead to lower limiting values of the surface tension due to the increase in methyl groups.

2.4 Factors Affecting Contact Angle

Contact angle can be affected by a number of reasons, for examples, surface roughness, surface heterogeneity, and temperature.

Kwok *et al.* (1997, 1998) reported that many of the liquids yield slip/stick behavior. Such slip/stick behavior could be due to non-inertness of the surface. An energy barrier for the drop front exists, resulting in sticking, which causes contact angle to increase at constant radius. However, as more liquid is supplied into the sessile drop, the drop front possesses enough energy to overcome the energy barrier and results in slipping, which causes contact angle to decrease suddenly. For these reasons, the contact angle measured when these phenomena occur cannot be used for interpretation in terms of surface energetic. Nakae *et al.* (1998) showed that contact angles are not constant for two rough surfaces. For a hemispherical close-packed model, the effect of height roughness on wetting can be explained by a change in curvature radius of liquid in trapped air pocket at a solid/liquid interface. Rosen (1989) reported that roughness reduces contact angle when a value on a smooth surface is less than 90° and increases the contact angle when the value greater than 90° . Drelich *et al.* (1996, 1994), and Lin *et al.* (1995) reported that contact angle can be modified by surface heterogeneities depending on a position where the three phase contact lines are located.

The temperature dependence of contact angle is not well understood or documented, although it has been reported to decrease with increasing

temperature. Adamson (1990) reported that the temperature derivatives of contact angle is negative with $|d\theta/dT| \approx 0.1 \text{ deg K}^{-1}$ for many systems at low temperature (5-100 °C). Ruijter *et al.* (1998) reported that the relaxation of the contact angle depends on the temperature. Molecular kinetic, hydrodynamic, and combined approaches were used to model the data. It was shown that parameters from the molecular kinetic model seem to be more physical in the experiments, indicating that the dissipation near the wetting line is more important compared to the dissipation due to the flow in the wedge. Chandra *et al.* (1996) reported the effect of varying the liquid-solid contact angle on droplet evaporation. Spreading of the droplet increases heat transfer area between the droplet and surface reducing droplet evaporation.

Basu *et al.* (1998) reported that the bitumen dynamic and static contact angle decrease above a certain NaCl concentration for a particular pH when compared with the results for no-salt case. The dynamic and static contact angles of bitumen decrease significantly with increasing NaCl concentration at high pH and decrease with increasing pH.

2.5 Applications and Related Works

Davies and Rideal (1963) reported that the contact angles measured when the solid surface is advancing into the liquid (advancing contact angle measured by using Wilhelmy plate method) may be greater than when the plate is being withdrawn (receding contact angle). Large advancing contact angle may be due to a film of some material which prevents the liquid adhering to the solid. The film may be wholly or partially removed after contacting with the liquid, so that the contact between the liquid and the solid becomes more complete, and thus gives the smaller receding angle. Zettlemoyer (1968) reported that the adsorption of the sodium ions and dodecyl sulfate anions at Graphon/solution interface exhibited double

plateaus. First plateau, below the CMC, the amount of sodium ions taken up was less than the dodecyl sulfate anions. The second one, above the CMC, the surface had a lower packing of dodecyl sulfate anions than sodium ions and the adsorbed dodecyl sulfate film took up sodium ion preferentially leaving the micelles deficient. Valignat *et al.* (1998) reported that the complete wetting was observed when increasing the relative atmosphere humidity (RH) up to 80 %, but when humidity was more than 85 %, the liquid became macroscopically nonwetting because of a progressive autophobic effect due to the change of conformation of molecules lying on the solid surface in the first layer. Chen *et al.* (1997) found that line tension can be calculated by using a method based on the lens size dependence of contact angle. To compute the line tension with this scheme, three derivatives are needed in addition to two contact angles and three surface tensions. This approach provides a potentially important approximation in term of a single surface tension and a lens-size dependent contact angle.

2.6 Phase Boundary and Precipitation

Phase boundary represents the minimum or maximum concentration of an additive required to form an infinitesimal amount of precipitate in the aqueous surfactant solution at constant temperature at various surfactant concentrations. The boundary separates concentration regimes in which precipitation occurs at equilibrium from regimes where no precipitate is present. Phase boundary can represent the hardness tolerance or minimum concentration of multivalent cation required to precipitate anionic surfactant.

At equilibrium, surfactant precipitation will occur if the product of the surfactant activity and the counterion activity equals the solubility product of the surfactant salt. Below the CMC, when no micelles are present, surfactant precipitation can be described by activity based solubility product written

between the surfactant and counterion. Above the CMC, where micelles exist, the solubility product must be written between the unbound (unassociated) counterion and the monomeric (unassociated) surfactant activity.

Scamehorn and Harwell (1989) reported that at low surfactant concentration below the CMC, the minimum Ca^{2+} concentration required to cause precipitation decreases as the surfactant concentration increases to satisfy the solubility product relationship since all the surfactant and calcium are unassociated. Above the CMC, the hardness tolerance increases with increasing SDS concentration. This is due to the micelles formed above the CMC binding with calcium, making it unavailable for precipitation. Another reason is when more SDS is added to the system, a higher concentration of unbound sodium is present in solution, lowering the CMC, increasing the fraction of surfactant which is present in micelles instead of monomeric form.