

CHAPTER II

LITERATURE SURVEY

2.1 Quartz

Quartz is a simple, well-characterized, very common component of many ores and has been widely studied in the ore flotation literature. Quartz is primarily SiO_2 and is abundant in nature.

Gaudin and Fuerstenau (1955) studied quartz flotation with anionic collectors. In this study, the quartz particle size was the 48/65 mesh fraction obtained after crushing selected quartz crystals. Results of streaming potential experiments indicated that hydroxyl and hydrogen ions were potential-determining ions for quartz. The adsorption of hydrogen and hydroxyl ions gave changes in the electrical potential at the quartz interface. Upon crushing quartz, $-\text{Si}-\text{O}-\text{Si}-$ bonds are broken and a very polar surface is created as depicted in Figure 2.1. In aqueous media, H^+ ions react with the negative oxygen site and OH^- ions react with the positive silicon site. The surface charge originates from dissociation of H^+ ions from this *surface silicic acid*. The extent of this dissociation can be simply determined by the concentration of the H^+ ions in solution; thus, pH will be potential determining for quartz. When there is no dissociation of the surface silicic acid, the surface potential is zero; a zero zeta potential for quartz occurs in solution at pH 3.7 and at this pH there is no electrical double layer around quartz particles in water. Since the charge at the quartz surface is determined by the concentration of hydrogen and hydroxyl ions in solution, the pH of the solution will affect markedly the adsorption of electrolytes at the quartz-solution interface.

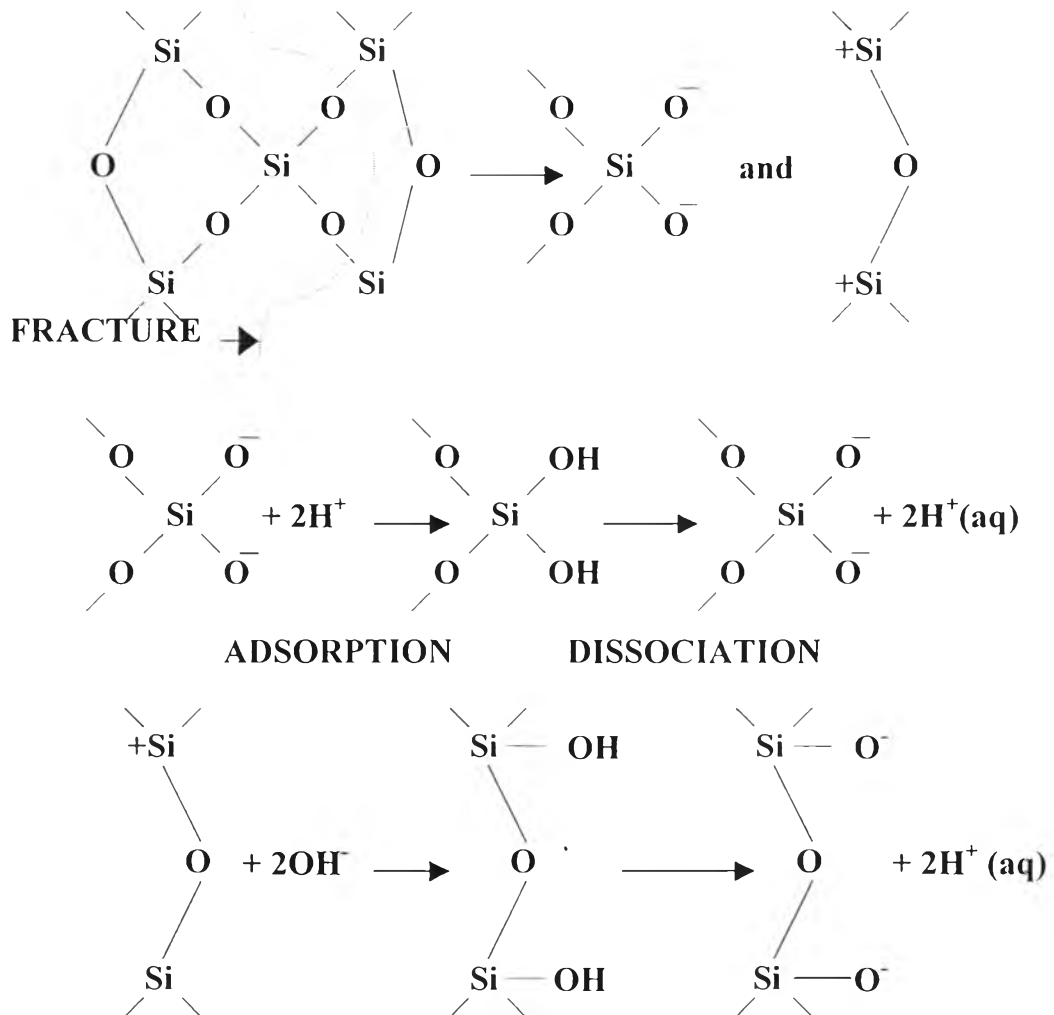


Figure 2.1 Mechanism for the origin of the electrical charge at the quartz surface in aqueous solution.

2.2 Nature of Surfactants

Surfactant, which is an abbreviation term of surface-active-agent, is a substance. When present at a low concentration in a system, it has the property of adsorbing onto the surface or interface of the system and altering to a marked degree the surface or interfacial free energies, as shown by the surface

tension. The term “surface” indicates a boundary between any two immiscible phases when one phase is a gas, usually air. Surfactants have a unique molecular structure consisting of a group that has very little attraction for the solvent, known as a lyophobic group, together with a group that has strong attraction for the solvent, called the lyophilic group. This is known as an amphiphathic structure. In aqueous solution the lyophobic and lyophilic groups are called hydrophobic and hydrophilic group, respectively. When a surfactant is dissolved in water, the hydrophobic group in the water causes distortion of the water structure, thereby increasing the free energy of the system. It means that less work is needed to bring a surfactant molecule to a surface than to bring a water molecule to the surface. This presence of the surfactant will therefore decrease the work needed to create a unit area of surface (the surface free energy per unit-area, or surface tension). On the other hand, the presence of the hydrophilic group prevents a separate phase, since that would require dehydration of the hydrophilic group (Adamson, 1990).

In a polar solvent such as water, ionic or highly polar groups of surfactant act as lyophilic (hydrophilic) groups whereas in a non-polar solvent such as heptane they may act as lyophobic (hydrophobic) groups. The hydrophobic group is usually a long-chain hydrocarbon residue, and less often a halogenated or oxygenated hydrocarbon or siloxane chain. The hydrophilic group is an ionic or highly polar group. Depending on the nature of the hydrophilic group, surfactants are classified into four main groups as:

1. *Anionic*. The surface-active portion of molecule bears a negative charge, for example RCOO^-Na^+ (soap).
2. *Cationic*. The surface-active portion bears a positive charge, for example $\text{RN}(\text{CH}_3)_3^+\text{Cl}^-$ (quaternary ammonium chloride).
3. *Zwitterionic*. Both positive and negative charge are present in the surface-active portion, for example, $\text{RN}^+\text{H}_2\text{CH}_2\text{COO}^-$ (long chain amino acid).

4. *Nonionic*. The surface-active portion bears no apparent ionic charge, for example $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$ (monoglyceride of long chain fatty acid).

Most natural solids including quartz have negatively charged surfaces. Therefore, if the surface is to be made hydrophobic (water-repellent) by use of a surfactant, then the best type of surfactant to use is a cationic. This type of surfactant will adsorb onto the surface with its positive charged hydrophilic head group oriented toward the negative charged surface (because of the electrostatic attraction) and its hydrophobic group oriented away from the surface, making the surface water-repellent. Anionic surfactant adsorption on negative surfaces like quartz generally requires addition of an activator containing a divalent cation, like Ca^{++} .

Cationic surfactants have many types. Quaternary ammonium salts are once type of cationic surfactants, for example $(\text{RNCH}_3)_3^+\text{Cl}^-$ or $\text{RN}(\text{CH}_3)_3^+\text{Br}^-$ (n-alkyltrimethylammonium chloride or bromide), and n-benzyl-n-alkyl-diammonium halides. This type of cationic surfactant is unaffected by pH changes, where the positive charge remains whether in acidic, natural, and alkaline media (Adamson, 1990). Thus, a quaternary ammonium salt was chosen for this study.

2.3 Critical Micelle Concentration

Micelle formation is one of the most important properties of surfactants. When the aqueous solution contains a large amount of surfactant, surfactant molecule will nucleate to form aggregates of colloidal size in the solution. The surfactant concentration at which this phenomenon occurs is called the critical micelle concentration (CMC). For aqueous system, micelles form with hydrophobic groups in the interior part and hydrophilic (polar or ionic groups)

exposed to water. These aggregates may be spherical, rod-like, cylindrical, disk-like or lamellar structures as shown in Figure 2.2. Aggregate formation always result in removal of the hydrophobic group from the contact with the water. Figure 2.3 shows physical properties of aqueous solution with respect to the CMC value.

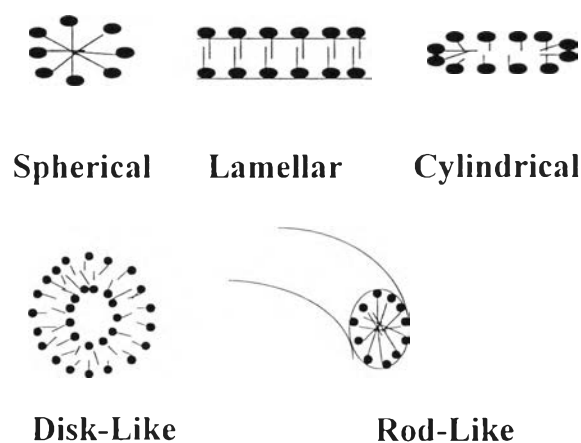


Figure 2.2 Structures of micelle formation.

A discontinuity in the slope of the curve of almost every measurable physical properties as a function of surfactant concentration is shown in Figure 2.3. Determination of the value of CMC can be carried out by use of any of these physical properties. Electrical conductivity, surface tension, and light scattering, (or refractive index concentration) are commonly employed in determining CMC values because of the simplicity of measurement of these physical properties. Figure 2.4 illustrates the plot between surfactant concentration and surface tension. Theoretically, the value of surface tension remains constant above the CMC value. For a surfactant concentration below but near the CMC the slope of the curve is relatively constant. The continuing reduction in the surface tension is due mainly to the increased activity of the surfactant in the bulk phase rather than at the interface (Van Voorst Vader, 1960a). It is important to note that surfactant readily adsorbs at the air/water surface at concentrations well below the CMC. It would be expected, therefore, that surfactant would also adsorb on hydrophobic surfaces below the CMC.

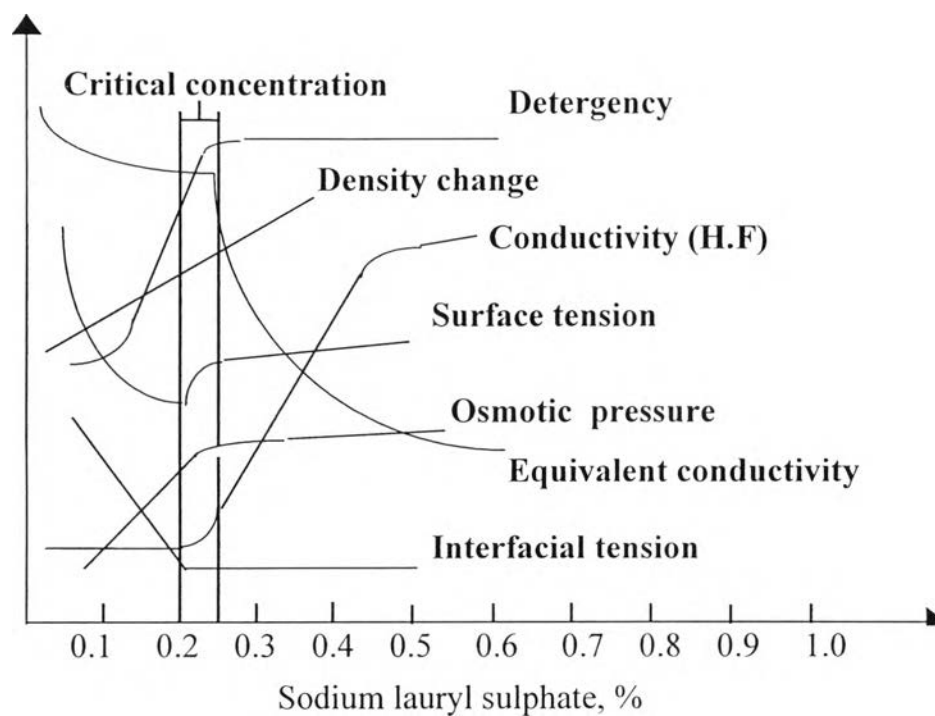


Figure 2.3 Physical properties of an aqueous solution in the neighborhood of the critical micelle concentration of sodium dodecylsulfonate (Rosen, 1989: p. 110).

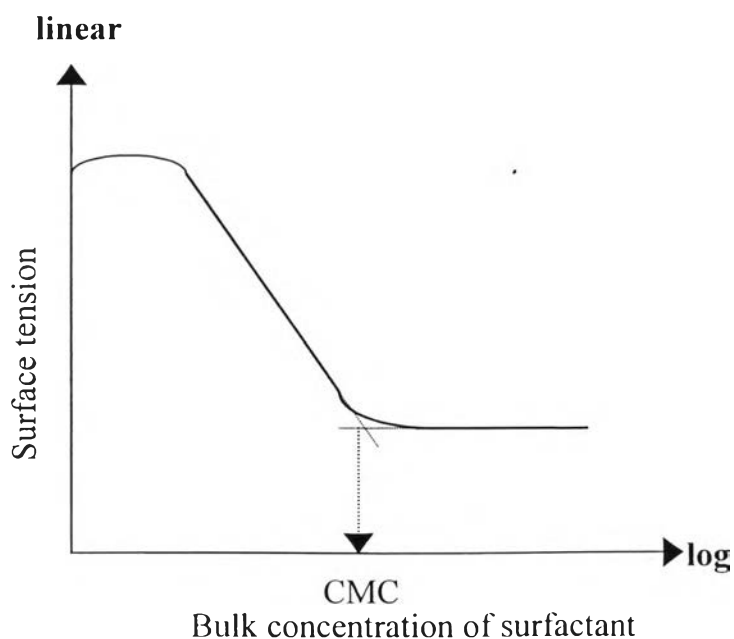


Figure 2.4 Relationship between surface tension and bulk phase concentration of surfactant.

2.4 Surfactant Adsorption Isotherm

Somasundaran and co-workers (1966) studied adsorption of anionic surfactant on alumina and proposed the reverse orientation model for surfactant adsorption which is shown in Figure 2.5. The adsorption isotherm is divided into three (or four) distinct regions as follows:

Region I. The surfactant molecules adsorb individual molecule. The driving force for the adsorption is electrostatic attraction between the positive charge on the alumina surface and the negative charge of the head group of the surfactant. There is little or no interaction between individual adsorbed surface ions. The adsorption isotherm sometime referred to as the Henry's Law model. Scemahorn, *et al.* showed that the hydrophobic tail/surface interaction also affected the adsorption.

Region II. This region corresponds to the onset of surfactant aggregate formation on the mineral oxide surface, as indicated by the sharp increase in the slope of the isotherm. There is very strong experimental and theoretical evidence to indicate that these aggregates form locally on the surface (i.e., by patchwise adsorption). The aggregates are referred to as hemimicelles or admicelles to emphasize the micelle-like aspects of its structure and behavior. For hemimicelles, the surfactant molecules are pictured as oriented with their charged head portion toward the solid surface, while the hydrocarbon chains of the tail portion protrude into the aqueous phase. This results in forming hydrophobic patches on the solid surface, thus facilitating particle flotation. For admicelles, the patches are surfactant bilayers on the solid surface which expand in Region II eventually to form a more or less complete bilayer. It is not obvious why bilayers in Region II would facilitate particle/bubble adhesion.

Region III. Region III is indicated by a decrease in the slope of the adsorption isotherm as to the plateau region (region IV) usually near the critical micelle concentration (CMC). This decrease is believed to arise from either the

electrostatic repulsion of ions from the interface because of a change in the sign of the surface charge, from the distribution of patch adsorption energies, or from a Langmuir-like competition for surface sites between aggregates.

Region IV. The region called the plateau region occurs above the CMC or upon completion of bilayer coverage of the surface. Most surfactant/mineral oxide systems exhibit either an adsorption plateau or an adsorption maximum above the CMC. Scamehorn (1982) accounts for the plateau adsorption by describing the micelles as a chemical potential sink for surfactant monomers. Thus, as the overall surfactant concentration increases above the CMC, the additional surfactant molecules will contribute only to the formation of micelles while the monomer concentration and the adsorption density remain constant. The boundary between the region III and the region IV is, generally very close to the CMC determined by surface tension measurements.

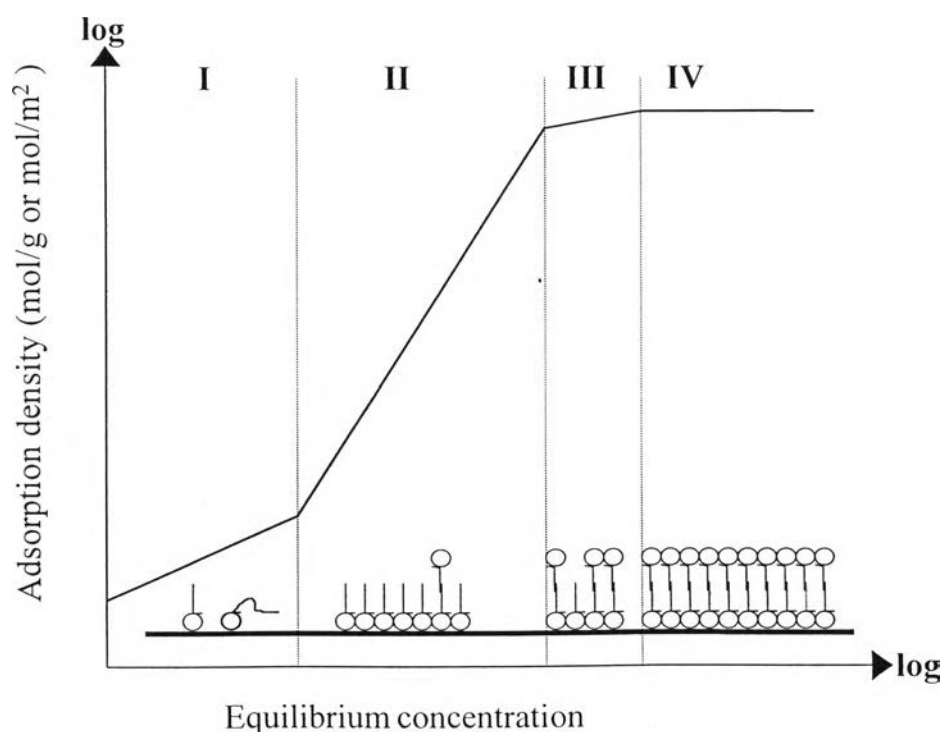


Figure 2.5 Schematic diagram of a typical adsorption isotherm for the reverse orientation model.

Harwell *et al.* (1985 and 1988) suggested the bilayer model to the orientation of the aggregate in Region II. The model is only slightly different from the reverse orientation model of Fuerstenau and Somasundaran. The bilayer model considers the adsorption isotherm having four main regions. In Region I, surfactant molecules adsorb on solid with electrostatic attractive for the surface. In Region II, local bilayer structures or admicelles form on patches of the solid surface at a critical solution concentration without hemimicelles forming at lower concentration. Region III occurs only when the surface because substantially covered with admicells below the CMC.

Gu *et al.* (1989-1991) suggested the small surface micelle model. The model is much different from the reverse orientation model. This model considers two steps on a linear scale adsorption isotherm. For the first step, the surfactant molecules adsorbed on the solid by electrostatic attraction which is the same as Region I of the reverse orientation model except aggregates adsorb rather than monomers. In the second step, surface micelles are adsorbed between the adsorbed surfactant micelles from first step. Then, the small *surface micelles* are formed. The small micelles are closely packed along the adsorption isotherm.

Fan *et al.* (1997) studied adsorption of alkyltrimethylammonium bromides on negatively charged alumina. In this study, the adsorption isotherm obtained was interpreted to agree very well with the reverse orientation model. The results suggest that the adsorption region III still exists but the difficulty in detecting it from the adsorption isotherm is probably the result of similar slope for regions II and III.

2.5 Wetting Phenomena and Contact Angle

According to Adamson (1990), the terms “wetting” and “non-wetting” as employed in various practical situations tend to be defined in terms of the effect desired. Usually, wetting means that the contact angle between a liquid and a solid is zero or close to zero and so the liquid spreads over the solid easily. In contrast non-wetting mean that the angle is greater than 90° so that the liquid tends to ball up and run off the surface easily.

Fuerstenau *et al.* (Chapter1 in Reagents in Mineral Technology edited by Somasundaran *et al.*, 1987) point out that ore beneficiation by froth flotation is based on differences in the affinity for water exhibited by mineral surfaces. Minerals having little affinity for water are called hydrophobic and easily attach to air bubbles. However, there are few minerals having naturally hydrophobic surfaces, examples being graphite, sulfur, talc, pyrophyllite, molybdenite, and stibnite. Coal, which has a carbonaceous skeleton, also exhibits natural flotability unless its surface is highly oxidized. These materials are hydrophobic because their surfaces are non-polar. Because most minerals are held together by ionic or covalent bonds, their surfaces are highly polar. Because of their polar nature, most mineral surfaces are hydrophilic and consequently, their surfaces easily becomes water wet. In applying flotation process to hydrophilic minerals, they must be transformed into non-wetted surface by adding suitable surface-active agents (collectors).

Contact-angle measurements have been traditionally used to assess the flotability of minerals. The contact angle, θ , of a bubble on a solid is defined as the angle measured across the liquid at the bubble point of solid contact (Figure 2.6).

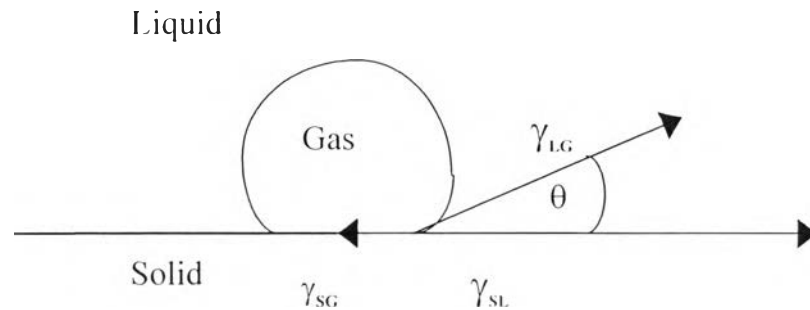


Figure 2.6 Schematic representation of the equilibrium contact between an air bubble and a solid immersed in a liquid.

Its magnitude is defined by the Young- Dupré equation,

$$\frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} = \cos\theta \quad (2.1)$$

where γ_{SG} , γ_{SL} , and γ_{LG} are the interfacial tensions (surface free energy per unit area) of the solid/gas, solid/liquid, and liquid/gas interfaces, respectively. If a mineral is hydrophilic, its contact angle is zero in water. Minerals such as molybdenite, graphite, and sulfur exhibit contact angles of about 80° , while that of paraffin wax is 110° . Excluding gravitational effects, the free-energy change (on a unit area basis) for the attachment of an air bubble to a mineral particle is given by

$$\Delta G_{\text{flot}} = \gamma_{SG} - \gamma_{SL} - \gamma_{LG} = (\cos\theta - 1)\gamma_{LG} \quad (2.2)$$

Thus, thermodynamically, flotation should take place whenever the contact angle is non-zero.

2.6 Foam

Foam is produced when air or some other gas is introduced beneath the surface of a liquid in the presence of a foam stabilizing agent such as a surfactant. Foam has a more or less stable honeycomb structure of gas cells

whose walls consist of thin liquid film with approximately plane parallel sides. These two-sided films are called the lamellae of the foam. Three or more gas bubbles commonly meet to form what is called the plateau border or Gibbs triangles (see Figure 2.7) (Rosen, 1988).

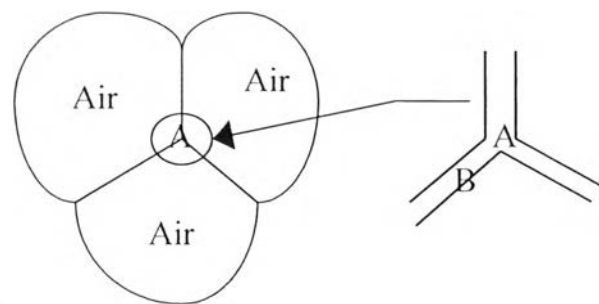


Figure 2.7 Plateau border at point of meeting of three bubble.

The pressure difference across a curved interface due to the surface or interfacial tension of the solution is given by the Laplace equation:

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2.3)$$

where R_1 and R_2 are the radii of curvature of the interface. Since the curvature in the lamellae is greatest at the plateau border, there is a greater pressure across the interface in these regions than elsewhere in the foam. Since the gas pressure inside an individual gas cell is everywhere the same, the liquid pressure inside the lamellae at the highly curved plateau border (A) must be lower than in the adjacent, less curved region (B) of the plateau area. This causes drainage of the liquid from the lamellae into the plateau borders (Rosen, 1988).

Absolute pure liquids do not foam. Foam formation is also not pronounced in mixtures of similar types of materials (e.g. aqueous solutions of hydrophilic substances). Bubbles of gas introduced beneath the surface of an

absolutely pure liquid rupture immediately on contacting each other or escape from the liquid as fast as the liquid can drain away from them. For true foaming to occur, the presence of a solute capable of being adsorbed at the L/G interface is required. The presence of this surface-active solute produces lamellae between the gas cells of the foam that have adsorbed monomolecular films of surfactant molecules on each side at the L/G interface. These adsorbed films provide the system with the property that distinguishes foaming from nonfoaming systems - the ability of the former to resist excessive localized thinning of the lamellae surrounding the bubbles, while general thinning of the lamellae proceeds.

Foam stability is important in the effective removal of a substance by foaming techniques. Many factors affect foam stability such as capillary effects, hydrostatic stability of foams, bubble size, temperature variation, bubble lifetimes, gas density, pH and concentration of electrolyte in solution (Clarke and Wilson, 1983).

2.7 Previous Works

De Bruyn (1955) studied the relationship between the floatability of quartz in vacuum flotation and the adsorption density of dodecylammonium acetate. In this study, ground quartz was used. The quartz particle size was less than 100 mesh fraction. It was found that the incipient flotation of quartz took place at a surface coverage of 5-6 % of complete monolayer of DAA at about neutral pH.

Gaudin and Fuerstenau (1955) studied quartz flotation with anionic collectors. In this study, the ground quartz particle size was the 48/65 mesh fraction and anionic collector were sodium chloride, sodium nitrate, sodium hydroxide, hydrochloric acid, sodium laurate, sodium oleate, barium nitrate and

aluminum nitrate. The result suggested that the factors causing ions to adsorb on quartz are pH, ionic strength, and the valency of the ions.

Ball and Fuerstenau (1971) studied thermodynamics in the adsorption behavior in the quartz/aqueous surfactant system. In this study, the ground quartz particle size was again the 48/65 mesh fraction. The study was to determine the effect of temperature on the surfactant adsorption. It was found that the measured effects must be due to changes occurring at, or associated with, both the stern plane and the shear plane.

Takeda and Usui (1986) studied adsorption of dodecylammonium ion on quartz in relation to its flotation. In this study, natural high grade quartz was ground to have an average size less than 10 μm . It was found that at pH 5, complete flotation of quartz required the adsorption density of DAA of only about 1 % surface monolayer coverage, while at pH 9.8 the complete flotation of quartz required the adsorption density of DAA to be more than the equivalent of monolayer adsorption.

Fan *et al.*(1996), studied adsorption of alkyltrimethylammonium bromides on negatively charged alumina. In this study, alkyltrimethyl ammonium bromides (dodecyltrimethyl-, tetradecyltrimethyl-, and cetyltrimethylammonium bromide) were cationic surfactant and solid negatively charge was alumina in aqueous phase. Cationic surfactant and alumina were used for studying adsorption and flotation at pH 10 and at a constant ionic strength of 0.03 M NaCl. In this case, only three distinct region were observed, regions I, II, and IV in the adsorption isotherm. These seemed to lack adsorption region III (but still exist). The existence of region III in the present system can hence be concluded in the basis of flotation experiment. The difficulty in detecting it from the adsorption isotherm is probably the result of similar slope for region II and III. According to the original four region model, region III should have a smaller slope than region II. In region II, adsorption is favored both by the strong electrostatic interaction between the

head group and the hydrophobic attraction between the tails. In region III, only the latter attraction exists with electrostatic repulsion building up as adsorption continues. For the transition between region II and III is not perceptible on a conventional isotherm, which implies the presence of similar force for adsorption in this region. To account for this, the hydrophobic attraction in region III is proposed to be much stronger than that in region II so as to offset the electrostatic attraction in region II. A penetrating architecture with head-in and head-out orientations in the adsorption layers, resulting in a strong hydrophobic interaction in region III, is proposed toward this purpose. This was attributed by the authors to the loose and interpenetrating solid structure in the case of the anionic amine/positively charge alumina system.