CHAPTER II
LITERATURE REVIEWS

2.1 Soap

Soap is a salt of a fatty acid which is produced from the saponification or hydrolysis reaction of a triglyceride that comes from animal fat or vegetable oil as shown in Figure 2. From the reaction, fats are broken down by strong base especially sodium or potassium hydroxide to yield crude soap and transformed into salts of fatty acids known as soap (Zoller, 2009).
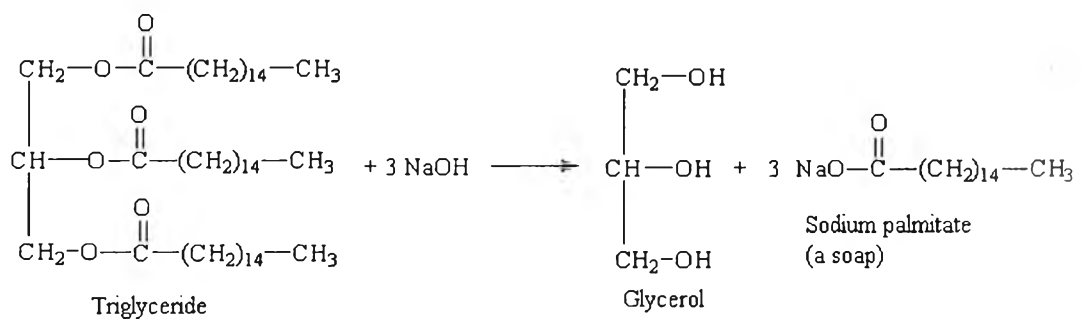

Figure 2.1 Saponification of a triglyceride.

Fatty acids are rarely found as free molecules in nature but are most often a part of a larger molecule called a triglyceride. There are straight-chain monocarboxylic acids. The most common fatty acids range in size from 10 to 20 carbons and most often have an even number of carbon atoms including the carboxyl group carbon (Spurlock, 2011).

These fatty acids are weak acids composed of two parts which are a carboxylic acid group and hydrocarbon chain that bond with the carboxylic acid group. The carboxylate end of the soap molecule is attracted to water or hydrophilic end (water–loving) while the hydrocarbon chain or hydrophobic end is attracted to oil or grease and repelled by water (water–hating) (Othmer, 2006).

Soaps can be made by using a variety of fatty acids which will give off various properties of soap especially the cleaning (Sukhija et al. 1990). The

compositions of fatty acids of various natural oils and fats are shown in Table 1 (Hill *et al.*, 2004). From this table, tallow and animal fats contain mainly stearic acid and palmitic acid. As a result stearic acid is one of the most popular fatty acid to produce soap and other industrial products. For the fatty acids which have carbon less than or equal to 10 are not used in soap manufacture because of bad odors and irritate to the skin. Furthermore, sodium stearate is used extensively in cleansing for personal care in bar soaps (Rosen, 2004).

Table 2.1 Typical Composition of Natural Oils and Fats (Bartolo *et al.*, 1997)

Common name	Chemical name	Chemical formula	Symbol	Tallow	Lard	Coconut	Palm kernel	Soybean
Saturated fatty acids								
Caprylic	Octanoic	$C_8H_{16}O_2$	C8			7	3	
Capric	Decanoic	$C_{10}H_{20}O_2$	C10			6	3	
Lauric	Dodecanoic	$C_{12}H_{24}O_2$	C12			50	50	0.5
Myristic	Tetradecanoic	$C_{14}H_{28}O_2$	C14	3	1.5	18	18	0.5
Palmitic	Hexadecanoic	$C_{16}H_{32}O_2$	C16	24	27	8.5	8	12
Margaric	Heptadecanoic	$C_{17}H_{34}O_2$	C17	1.5	0.5			
Stearic	Octadecanoic	$C_{18}H_{36}O_2$	C18	20	13.5	3	2	4
Unsaturated fatty acids								
Myristoleic	Tetradecenoic	$C_{18}H_{26}O_2$	C14:1	1				
Palmitoleic	Hexadecenoic	$C_{18}H_{30}O_2$	C161	2.5	3			
Oleic	Octadecenoic	$C_{18}H_{34}O_2$	C18:1	43	43.5	6	14	25
Linoleic	Octadecadienic	$C_{18}H_{32}O_2$	C18:2	4	4	1	2	52
Linolenic	Octadecatrienic	$C_{18}H_{30}O_2$	C18:3	0.5	0.5	0.5		6

2.2 Cleansing Process

Soap has a good biodegradability and is an excellent cleansing agents because soap molecules have both polar and non–polar part, so soap molecules work as a bridge between polar water molecules and non–polar oil molecules by forming micelles, as shown in Figure 3, which is an aggregation of soap subunits by having a hydrophilic as exterior to attract with water while having a hydrophobic as interior to dissolves oil (Mul *et al.*, 2000).
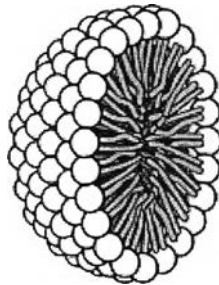

Figure 2.2 The structure of a micelle.

In cleansing process, soap micelles come into contact with the dirt which is insoluble in water such as oils, grease and fats and these micelles will coat on the dirt. So the dirt will dissolve inside micelle because of "like dissolve like" as shown in Figure 4 (Spurlock, 2011). For the hydrophilic part, the carboxylic acid or carboxylate groups will form hydrogen bond with water so now this dirt can dissolve in water and can wash away by water as well. Moreover, from the carboxylate groups, these negative charges on the outside of the micelle will not allow the micelles come closer and combine to form a large drop of oil (Shandilya, 2010)
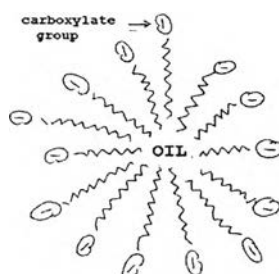
Figure 2.3 Oils dissolve inside micelle.

2.3 Water Hardness

Pure water, which is tasteless, colorless and odorless, is a good solvent and picks up impurities easily. When water moves through soil and rock, it dissolves very little amounts of minerals and holds them in solution. Multivalent ions such as calcium (Ca^{2+}), magnesium (Mg^{2+}), bicarbonates, and sulfates (Shankar, 2009) dissolved in water but the most common minerals are calcium and magnesium that make water "hard" (Rosen, 2004) but their effects are usually insignificant and difficult to measure. The degree of hardness becomes greater as the calcium and magnesium content increases and is related to the concentration of multivalent cations dissolved in water.

Hard water is generally not harmful to one's health but it has impact on almost every cleaning task from laundering and dishwashing to bathing and personal grooming. Moreover, hard water may causes a film on glass shower doors, shower walls, bathtubs, sinks, faucets and etc. (Doran *et al.*, 2009).

2.4 Soap Scum

The degree of hardness minerals in water affects the amount of soap and detergent necessary for cleaning process. Bathing with soap in hard water causes a white precipitate knows as soap scum as shown in the following equation (Othmer, 2006):

$$2C_{18}H_{37}COONa + Ca^{2+} \rightarrow (C_{18}H_{37}COO)_2Ca\ (s)\ + 2Na^+$$
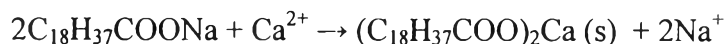
Soap scum occurs from calcium or magnesium ions react strongly with negatively–charged of carboxylate group which located outside the micelle to form insoluble compounds. As a result, the effectiveness in cleaning process of soap were reduced because soap scum will destroy the properties of soap and leaves a film on the surface of shower bathtubs or all water fixtures. This film may prevent removal of soil and bacteria from the surface (Soontravanich *et al.*, 2010).

2.5 Removal of Soap Scum

In every household, cleansing agent has been used to get rid of a stain from the sanitary wares. Most of cleansing agents mainly contain hydrochloric acid which is very corrosive and irritate skin. One of the ways to solve this problem is using surfactant.

Soontravanich et al. (2010) studied the dissolution of the salts of long chain fatty acids (soap scums) by using three different surfactants; sodium dodecyl sulfate (SDS), octyl polyglycoside (C_8APG), and dimethyldodecylamine oxide (DDAO). They also studied the effect of chelating agent; disodium ethylenediaminetetraacetate (Na_2EDTA) at various solution pH (4-11). From the results, using amphoteric surfactant showed the highest equilibrium solubility of $Ca(C_{18})_2$ at low solution pHs. However, in a presence of chelating agent, the highest equilibrium solubility of $Ca(C_{18})_2$ was found in amphoteric surfactant solution at high solution pHs because, at a high solution pH, the chelant effectively binds calcium and leaves stearate anion forms mixed micelles with the amphoteric surfactant in zwitterionic form easily. For anionic surfactant, SDS, gave the highest equilibrium solubility of $Ca(C_{18})_2$ in a present of chelant at the lowest solution pH whereas nonionic surfactant, C_8APG, gave the highest equilibrium solubility of $Ca(C_{18})_2$ in the present of chelant at high solution pHs.

Itsadanont et al. (2011) studied the dissolution of calcium and magnesium soap scums by using three different types of surfactant; methyl ester sulfonate (MES), alcohol ethoxylate with 9 ethylene oxide groups (EO9),

dimethyldodecylamine oxide (DDAO) in the presence of chelant; disodium ethylenediaminetetraacetate (Na$_2$EDTA) at various solutions pHs (4-11). The results showed that using amphoteric surfactant, DDAO, gave the highest equilibrium solubility of Mg(C$_{18}$)$_2$ at a low solution pH while the highest equilibrium solubility of Mg(C$_{18}$)$_2$ was found at high solution pH when chelating agent was present which was corresponding to Soontravanich's work.

2.6 Kinetic Analysis

A first order reaction rate is used to model the dissolution rate of soap scum:

$$-r = \frac{dM}{dt} = -kM \qquad (1)$$

Integrating equation (1) to get

$$ln\left(\frac{M}{M_0}\right) = -kt \qquad (2)$$

Where r is the rate of Ca(C$_{18}$)$_2$ dissolution; k is the apparent rate constant of soap scum dissolution (min^{-1}); and M$_0$ and M are the initial mass and the remaining undissolved of soap scum at time t, respectively. The value of k can be obtained from a slope of a plot of $ln\left(\frac{M}{M_0}\right)$ versus t.

Soontravanich et al. (2010) studied the kinetic dissolution of calcium soap scum by using three different types of surfactant; sodium dodecyl sulfate (SDS), octyl polyglycoside (C$_8$APG), and dimethyldodecylamine oxide (DDAO) in the presence of chelant; disodium ethylenediaminetetraacetate (Na$_2$EDTA). The results showed that increasing solution pH caused the increasing dissolution at all time for both DDAO and C$_8$APG but showed the opposite trend for SDS. Moreover, the highest rate of soap scum dissolution was found in DDAO or C$_8$APG at high solution pH.

2.7 Surfactant

Surfactants are wetting agents that lower the surface tension of a liquid, allowing easier spreading, and lower the interfacial tension between two liquids. The general structure of a surfactant includes a structural group that has strong attraction with a solvent, known as a lyophilic group (solvent-loving), and another group that has little attraction with the solvent, called the lyophobic group (solvent-hating). This is known as an amphipathic structure, as shown in Figure 2.2.
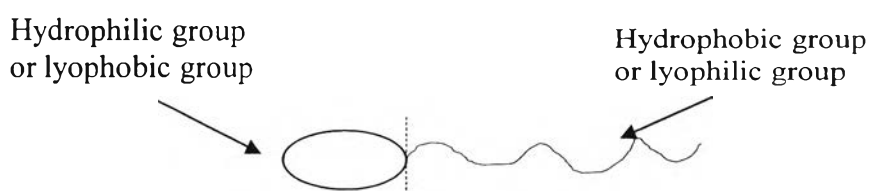
Hydrophilic group   Hydrophobic group
or lyophobic group   or lyophilic group

Figure 2.4 The surfactant molecule.

When water is used as the solvent, one end usually calls a hydrophilic or head group and another end calls a hydrophobic or tail group. In an aqueous solution, a significant amount of surfactant can adsorb at the air/water interface with the hydrophobic tail moving out from water, resulting in the reduction of Gibbs free energy of the system (Holmberg et al., 2002). Another important property of surfactant is to form aggregates, known as micelles. The lowest surfactant concentration to from a first micelle is called the critical micelle concentration (CMC) (Porter, 1994).

The lyophilic or hydrophobic group of surfactant is usually a long chain hydrocarbon residue or nonpolar group, and less often a halogenated or oxygenated hydrocarbon or siloxane chain while the lyophobic or hydrophilic group is an ionic or highly polar group. This dual functionality, hydrophobic and hydrophilic, provides the basis for characteristics useful in cleaning and detergent formulation, including surface tension modification, foam, and separation (Scamehorn, and Harwell, 1989).

Surfactants are characterized by the nature of the hydrophilic group as the following categories:

1. Anionic surfactants: The surface-active portion of the molecule is a negative charge, for example, C12H25SO3-Na+ (sodium dodecyl sulfate), RC6H4SO3-Na+ (alkylbenzene sulfonate).

2. Cationic surfactants: The surface-active portion of the molecule is a positive charge, for example, $RN(CH_3)_3^+Br^-$ (tetradecyltrimethyl ammonium bromide (TTAB)), RNH_3^+Cl (salt of a long-chain amine).

3. Nonionic surfactants: The surface-active portion of the molecule bears no apparent ionic charge. These are a class of synthetic surfactants that are prepared by attaching ethylene oxide molecules to a water-insoluble molecule, such as $RCOOCH_2CHOHCCH_2OH$ (monoglyceride of long-chain fatty acid), alcohol ethoxylate.

4. Zwitterionic surfactants: They have both positive and negative charges present in the surface-active portion, for example, dimethyldodecylamine oxide (DDAO), $RN^+H_2CH_2COO^-$ (long-chain amino acid).

2.8 Effect of Solution pH

Changing in the solution pH may affect the molecule which containing carboxylate groups (Pandit, 1989). Since changing in the solution pH may convert ionic group which has strong adsorption because oppositely charged sites to a neutral molecule which has an adsorption via hydrogen bonding or dispersion forces (Rosen, 2004).

Solid calcium fluoride is used as an example of the effect of solution pH on the solubility of salt.

$$CaF_{2\,(s)} \;\rightleftarrows\; Ca^{2+}_{(aq)} + 2F^{-1}_{(aq)}$$
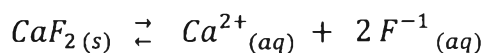
Since the fluoride ion is the conjugate base of a weak acid (HF), so fluoride ion can react with any proton to from HF.

$$F^{-1}_{(aq)} + H^{+1}_{(aq)} \rightleftarrows HF_{(aq)}$$
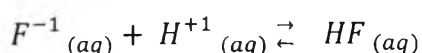
According to LeChatelier's Principle, as F^{-1} ions have been removed by react with H^{+1} ion, so the reaction have to move to the right hand side to balance the equilibrium between solid calcium fluoride and its ions in aqueous solution. It means that calcium fluoride will be dissolved more. Therefore, calcium fluoride is expected to be more soluble in acidic solution than in pure water. Moreover, in general, salts of weak acids should be expected to be more soluble in acidic solutions. (Cook, 2011)

2.9 Effect of Salinity

In aqueous solution the presence of electrolyte such as NaCl or KBr causes a changing in the critical micelle concentration (CMC) which has the effect to ionic surfactant more than zwitterionic and nonionic surfactant. In the presence of the electrolyte, the electrical repulsion between ionic head groups has been decreased. (Aswal, 2003). Moreover, the addition of the electrolyte appears to increase the extent of solubilization of hydrocarbon (Rosen, 2004).

Abe (1988) studied the effects of inorganic electrolytes and solution pH on micelle formation of amphoteric-anionic mixed surfactant systems. The results showed that the critical micelle concentration (CMC) decreased with increasing the NaCl concentration due of the decreasing in the molecular interaction between amphoteric-anionic molecules.