

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 2.1. 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).

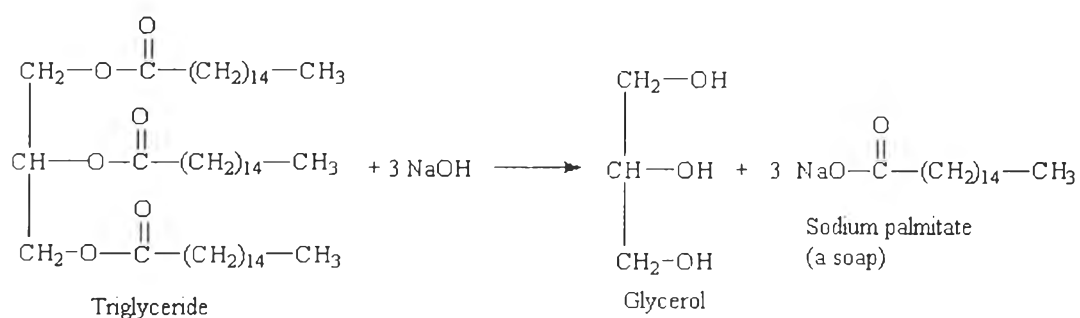


Figure 2.1 Saponification of a triglyceride.

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 2.1 (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 ₈ H 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	C16:1	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 2.2, 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).

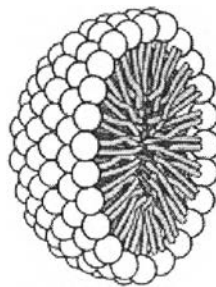


Figure 2.2 The structure of a micelle.

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 2.3 (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).

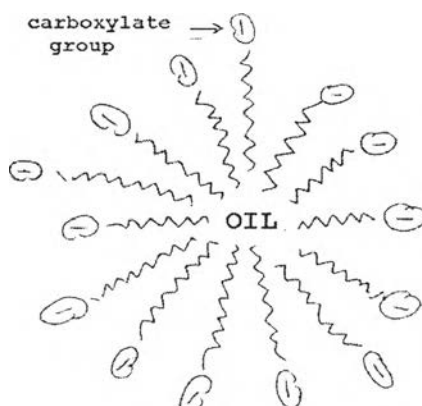


Figure 2.3 Oils dissolve inside micelle.

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 known as soap scum as shown in the following equation (Othmer, 2006):



Soap scum occurs from calcium or magnesium ions reacting strongly with negatively-charged carboxylate groups, which are located outside the micelle to form insoluble compounds. As a result, the effectiveness in the cleaning process of soap is reduced because soap scum will destroy the properties of soap and leave a film on the surface of shower bathtubs or all water fixtures. This film may prevent the removal of soil and bacteria from the surface (Soontravanich *et al.*, 2010).

2.5 Removal of Soap Scum

In every household, a cleansing agent has been used in order to remove a stain from sanitary wares. Most cleansing agents mainly contain hydrochloric acid, which is very corrosive and irritates skin. One way to solve this problem is using an appropriate surfactant with a chelating agent.

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 (C₈APG), and dimethyldodecylamine oxide (DDAO). They also studied the effect of a chelating agent; disodium ethylenediaminetetraacetate (Na₂EDTA) at various solution pH (4-11). From the results, using an amphoteric surfactant showed the highest equilibrium solubility of Ca(C₁₈)₂ at low solution pHs. However, in the presence of a chelating agent, the highest equilibrium solubility of Ca(C₁₈)₂ was found in an amphoteric surfactant solution at high solution pHs because, at a high solution pH, the chelating agent effectively binds calcium and leaves stearate anion forms mixed micelles with the amphoteric surfactant in zwitterionic form easily. For an anionic surfactant, SDS, gave the highest equilibrium solubility of

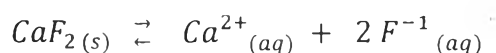
$\text{Ca}(\text{C}_{18})_2$ in a present of chelating agent at the lowest solution pH whereas nonionic surfactant, C_8APG , gave the highest equilibrium solubility of $\text{Ca}(\text{C}_{18})_2$ in the present of chelating agent at high solution pHs.

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_2EDTA) at various solutions pHs (4-11). The results showed that using amphoteric surfactant, DDAO, gave the highest equilibrium solubility of $\text{Ca}(\text{C}_{18})_2$ at a low solution pH while the highest equilibrium solubility of $\text{Ca}(\text{C}_{18})_2$ was found at high solution pH when chelating agent was present which was corresponding to Soontravanich's work.

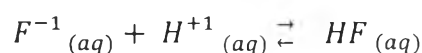
2.6 Effect of Solution pH

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.



Since the fluoride ion is the conjugate base of a weak acid (HF), so fluoride ion can react with any proton to form HF.



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).

2.7 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 2.4.

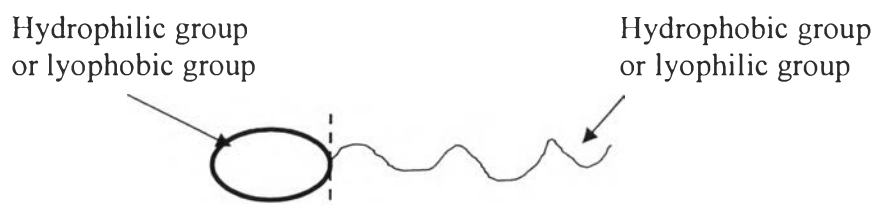


Figure 2.4 The surfactant molecule.

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 form 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, $C_{12}H_{25}SO_3-Na^+$ (sodium dodecyl sulfate), $RC_6H_4SO_3-Na^+$ (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 Chelating Agents

Chelation is the formation or presence of two or more separate bindings between a polydentate (multiple bonded) ligand and a single central atom. Table 2.2 gives a short overview of the different terms that are used in this respect to chelating agents.

Table 2.2 Definitions for chelating agent (Nowack *et al.*, 2005)

ligand	coordinating ligand
chelating agent	multidentate ligand
chelate	the metal-chelating agent complex
chelant	synonym for chelating agent
chelator	synonym for chelating agent
chelon	synonym for chelating agent
APC	abbreviation for aminopolycarboxylates
complexon	synonym for APCs

Usually these ligands (ligare Latin = to bind) are organic compounds, and are called chelants, chelators, chelating agents, or sequestering agents. The ligand forms a chelate complex with a substrate and the monodentate ligands can form only one bond with the central atom. Chelating agents, according to ASTM-A-380, are chemicals that form soluble, complex molecules with certain metal ions, inactivating the ions so that they cannot normally react with other elements or ions to produce precipitates or scale (<http://chelation-wikipedia, the free encyclopedia.html>). A chelating is sometimes added into cleaning products to prevent precipitation of active ingredients with divalent cations naturally found in hard water by forming a water soluble complex with the ions. The chelating agents belonging predominantly to two different groups i.e. aminopolycarboxylates (APCs) and polyphosphates are commonly used. APCs containing carboxylic groups connected to one or a few atoms of nitrogen are able to complex metal ions by formation around them one or a few stable heteroatom rings. Forming of stable complexes with metal ions is the base of their application for analytical and industrial purposes. The complexes formed due to chelation are dissolved in water and metal ions found in them do not exhibit such chemical activity as uncomplexed ions. Because of the importance of chelating agents they are produced and used in large quantities and their behavior as well as their effect in the environment has received considerable attention.

An application of APCs are used as component or process chemicals in a wide variety of applications, however, according to Figure 2.5 only pulp and paper, cleaning, chemical processing, agriculture and water treatment constitute 80% of their consumption (Kołodzyńska, 2011).

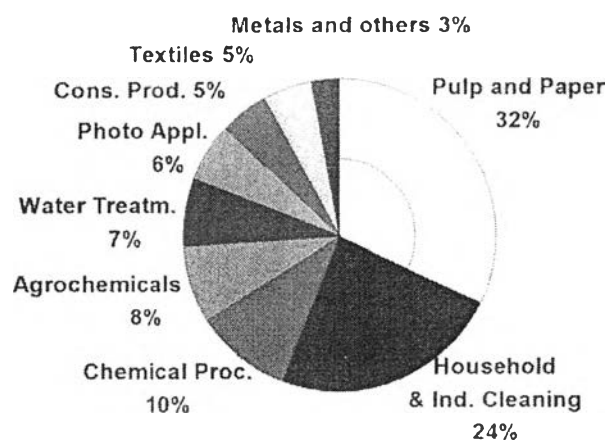


Figure 2.5 The percentage contribution of different applications of APCs.

One of APCs application is for household and industrial cleaning e.g. removal of hard water scale, soap film and inorganic scales, for example to improve the bottle cleaning in the beverage industry; detergents, soap processing to prevent from precipitation of calcium and magnesium salts (deliming action) and their deposition on clothes, prevention soaps from becoming rancid and etc.

The studied chelating agent will be introduced as an example of APCs; a conventional chelating agent (EDTA) and two biodegradable chelating agents (GLDA and EDDS).

1. Na₂EDTA ethylenediaminetetraacetate disodium salt or EDTA in this study has the chemical structure as shown in Figure 2.6. It is a common complexing agent, which has four main active sites that can form a water-soluble complex with cations. One molecule of EDTA can react with one molecule of calcium ion stoichiometrically (Martell and Motekaitis, 1992). The effectiveness in metal complex formation depends on the equilibrium constants effectiveness in metal complex formation depends on the equilibrium constants or stability constants of the ligand with cation. Moreover, there are five possible forms of EDTA in the absence of divalent cations, depending on solution pH (H₄Y, which has four ionizable

hydrogens, H_3Y^- , H_3Y^{2-} , HY^{3-} , and Y^{4-}) and only two forms (HY^{3-} and Y^{4-}) can form complexes with calcium ions (Martell and Motekaitis, 1992).

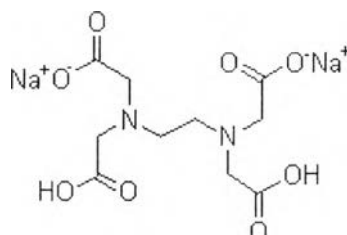


Figure 2.6 Chemical structure of EDTA.

At a high pH, the major species found is Y^{4-} , which is the most effective form of EDTA in chelating calcium ions. The molecule of EDTA in an acidic solution is less effective than that in a basic solution due to the protonation of active site on the EDTA. EDTA was patented in Germany in 1935 by F. Munz. The synthesis of EDTA consisted in the reaction of monochloroacetic acid with ethylenediamine in the presence of sodium hydroxide. Another way to obtain EDTA is the reaction of ethylenediamine with sodium cyanide and formaldehyde in the presence of sodium hydroxide. Since EDTA is a chelate ligand with a high affinity constant to form metal-EDTA complexes and highly stable molecule, it is offering a considerable versatility in industrial and household uses. Because it is applied predominantly in aqueous medium, it is released into the environment through wastewaters. Its presence in soil may be due to agrochemical application or to the disposal of products containing EDTA in garbage reservoir. It is highly unlikely to find the compound in the air because of the impossibility of volatilization from waters or soils. There is increasing concern about the direct or indirect potential effects of the presence of EDTA in the environment. Numerous field studies have shown that complexation of EDTA may mobilize contaminant metal ions. EDTA may avoid the precipitation of heavy metals in solution or, on the contrary, cause a dissolution effect to heavy metals absorbed in sediment (Oviedo *et al.*, 2003). Moreover, some undesired features such as their persistence or slow transformation in the environment, remobilization of toxic metal ions mainly from sediments and soils as well as radionuclides from radioactive waste and their application in eutrophication of

natural water systems are of great concern. Hence, EDTA, whose effluent emissions are already banned in some states and countries and is considered as non-readily biodegradable chelating agent (Jones *et al.*, 2001). Besides, their replacement and the use of chelating agents with improved biodegradability are necessary because of the renewed attention towards environmental protection issues i.e. BREF documents, EU EDTA risk reduction strategy documents or OSPAR documents (Kołodzyńska, 2011).

2. **EDDS** ethylenediamine-N,N'-disuccinic acid (H_4edds , EDDS) (CAS No. 144538-83-0) is a structural isomer of EDTA. On a commercial scale this complexing agent is produced, among others, by Innospec Inc., UK (formerly Octel) as Enviomet™. It forms four isomers: S,S- (25%), R,R- (25%), R,S- (50%), and S,R- (50%). The S,S-isomer of EDDS, based on the naturally occurring amino acid i.e. L-aspartic acid, is readily biodegradable. According to the OECD 83% of S,S- EDDS convert to CO_2 within 20 days (Jaworska *et al.*, 1999). Nonetheless, the others are partially or wholly non-biodegradable.

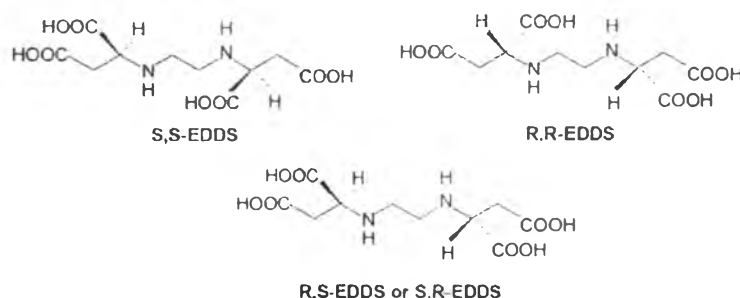


Figure 2.7 The structural isomers of EDDS.

The chemical structure of EDDS isomer is presented in Figure 2.7. The S,S-EDDS isomer is produced by the actinomycete strain *Amycolatopsis orientalis*. It can be obtained in the reaction between 1,2-dibromoethane and L-aspartic acid. At $pH > 10$, predominant form of H_4edds is $edds^{4-}$ presented in 62% while the $Hedds^{3-}$ form is present in 38% (Crouch *et al.*, 2001). The appropriate ligand protonation constant pK_s are very close to the data for EDTA. Metal ions in the formed complexes were

bound to two nitrogen atoms and one oxygen atom of each of the four carboxylate groups. Under some conditions of pH EDDS is more efficient than EDTA as far as chelation of metal ions is concerned. For example, in the case of Cs(I), Mg(II), Sr(II) they are not well complexed by EDDS at acidic and neutral pH and for them EDTA appears to be superior to EDDS. In 2002 EDDS production achieved 10,000 tons. Nowadays EDDS is a chelating reagent available in Europe on a large scale. The demand for ethylenediaminedisuccinic acid has been growing at the rate of 15 % per year. Also Innospec, the producer of EDDS was awarded by RoSPA (Royal Society for the Prevention of Accidents). Moreover, the EnviometTM was the winner of the UK Green Chemical Technology Award in 2003 as a chemical product and then awarded by CRYSTAL Faraday Partnership (Institute of Chemical Engineers, Royal Society of Chemistry, Chemical Industry Association) (Brochure of EnviometTM)

3. GLDA A novel readily biodegradable chelating agent, tetra sodium of N,N-bis(carboxymethyl) glutamic acid (also denoted as Dissolvine GL-38 or GLDA, CAS No. 51981-21-6) was also introduced on the commercial scale by Akzo Noble Functional Chemicals (The Netherlands). Its production process is based on the flavor enhancer monosodium glutamate (MSG) from the fermentation of readily available corn sugars and according to the following reaction in Figure 2.8. In contrast to the manufacture of EDTA whose carbon content is fossil based, the carbon source of GLDA is primarily biobased. Therefore, GLDA is the only chelating agent with 'green' carbon atoms. The biodegradation of GLDA is initiated by mono-oxygenases catalysing the removal of carboxymethyl groups. According to the Swedish Society for Nature Conservation GLDA is 86% based on natural, raw materials. It also possesses good solubility at both low and high pH. Greater than 60% of L-GLDA degrades within 28 days. Dissolvine GL-38 consists only of the L-form. This is significant, because the D-form is not biodegradable. The thermal stability of GLDA is surprisingly high. When tested at temperatures above 573 K it showed no significant decomposition. This property has been used to develop water treatment systems for operating boilers to reduce the effect of hard water. Tests have also shown up to 10 times higher solubility of GLDA in 25% NaOH sodium hydroxide solution compared to EDTA. It is also characterized by excellent solubility at low pH (Seetz *et al.*, 2008). Since, GLDA possesses complexing

properties comparable to EDTA therefore, it can be an alternative to EDTA. The benefit of GLDA in such formulations is its broad effective pH range for the chelation of calcium and magnesium ions equal to 4-12. GLDA is directly used in all ordinary industrial cleaning applications. It has further potential uses in the production of micronutrient fertilizers. In Table 2.3 showed the physicochemical properties of EDDS and GLDA.

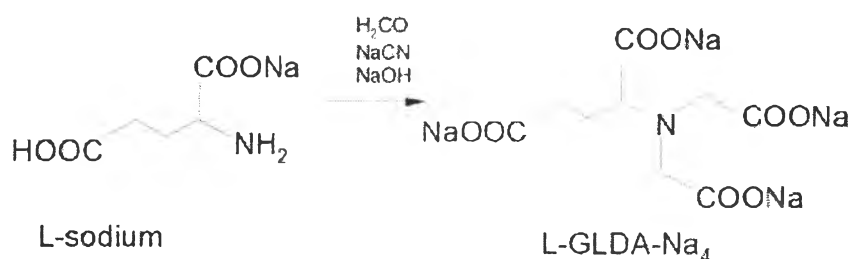


Figure 2.8 Scheme of GLDA production.

Table 2.3 Physicochemical properties of EDDS and GLDA

Name	Physicochemical characteristics
EDDS (ethylenediaminedisuccinic acid)	Molecular weight: 358.2 Appearance: colorless to yellowish pH: 9.2 Density: 1.26 g/ml Solubility in H ₂ O: in any ratio Biodegradability: > 60%
GLDA N,N-bis(carboxymethyl)-L-glutamic acid	Molecular weight: 351.1 Appearance: colorless to yellowish pH: 13.5 Density: 1.38 g/ml Solubility in H ₂ O: in any ratio Biodegradability: > 83%