

CHAPTER II

LITERATURE REVIEW

2.1 Soap

2.1.1 Characteristic of Soap

Soap is chemically defined as the alkali salt of fatty acids. It is manufactured by the saponification or hydrolysis reaction, by which triglycerides that come from animal fats or vegetable oils are saponified with strong base especially sodium or potassium hydroxide to yield crude soap and transformed into alkali salts of fatty acids known as soap shown in Figure 2.1 (Bartoloet *al.*, 1997).

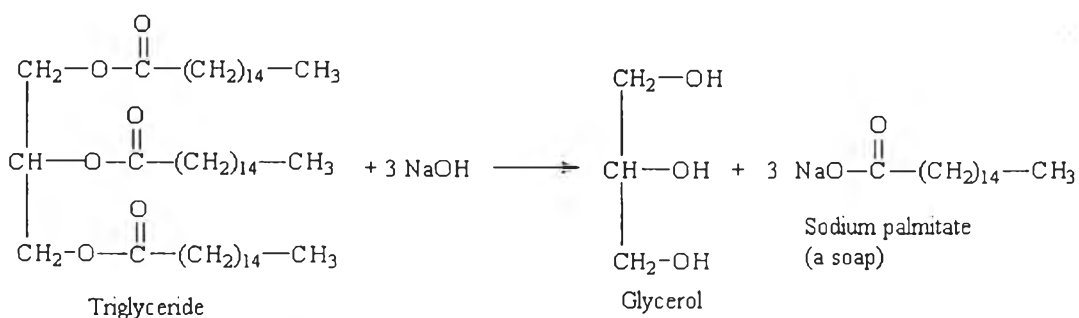


Figure 2.1 Saponification of triglyceride.

Soap is a class of surface active materials and has been widely used as surfactant for washing, bathing, and cleaning. The basic structure of all soaps is essentially the same consisting of a long hydrophobic (water-fearing) hydrocarbon "tail" and a hydrophilic (water-loving) anionic "head". The length of the hydrocarbon chain depends on the type of fat or oil which is usually quite long. The anionic charge on the carboxylate head is usually balanced by either positively charged sodium (Na^+) or potassium (K^+) cation. The structure of a soap molecule is shown in Figure 2.2 (Zoller, 2009).

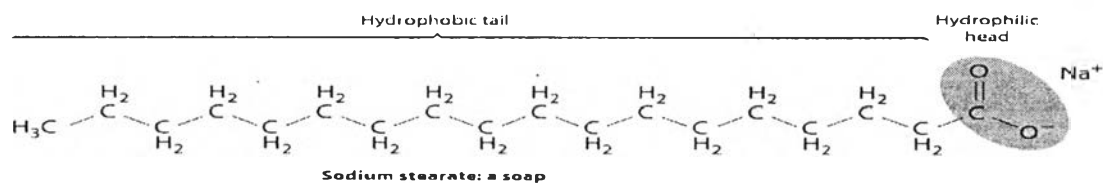


Figure 2.2 The structure of soap molecule.

2.1.2 Fatty Acid

Vegetable oils composed of 90 to 98% triglyceride molecules in which an ester derived from glycerol and three fatty acids and rarely found small amount of free fatty acids (generally 1 to 5%) in nature. 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, 2014). The difference of fatty acid backbone with glycerol leads to make different characteristic of vegetable oil. The common fatty acids found in vegetable oil are stearic acid, palmitic acid, oleic acid, linoleic.

In cleaning process, soaps are manufactured by various types of fatty acids therefore the properties of soap will be different (Sukhija *et al.*, 1990). The compositions of fatty acids of various natural oils and fats are shown in Table 2.1 (Bartolo *et al.*, 1997). From the table, stearic acid and palmitic acid is the main component of tallow and animal fats. The results showed that stearic acid is widely used in the manufacture of soap and other industrial products (Soontravanich *et al.*, 2010). Sodium stearate is popular used in cleansing for personal care in bar soaps. But for carbon fatty acid with a length less than or equal to ten is not popular due to bad odors and irritate to the skin.

These fatty acids are weak acids composed of two parts, which are a carboxylic acid group and hydrocarbon chain bonding 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) (Lange, 1999). When grease or oil (non-polar hydrocarbons) are mixed with a soap-water solution, the soap molecules work as a bridge between polar water molecules and non-polar oil molecules. So, the

soap can act as an emulsifier because soap molecules have both properties of non-polar and polar molecules.

Table 2.1 Typical Composition of Natural Oils and Fats.(Bartoloet *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	$C_{18}H_{30}O_2$	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 Cleaning Process

Soap is an excellent cleaning agent because of its ability to act as an emulsifying agent which can disperse one liquid into another immiscible liquid. Because oil doesn't naturally mix with water, so added soap can suspend oil/dirt and it can be removed. The organic part of a natural soap is a negatively-charged which is polar molecule. The hydrophilic (carboxylate group) as exterior interacts with water molecules via ion-dipole interactions and hydrogen bonding. The hydrophobic (long hydrocarbon chain) does not interact with water molecules. The hydrocarbon chains are attracted as interior to each other by dispersion forces and cluster together, forming structures called micelles as shown in Figure 2.3 (Helmenstine, 2014).

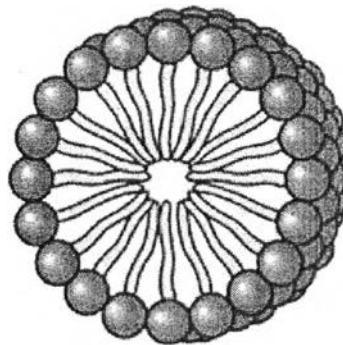


Figure 2.3 The structure of a micelle.

In cleansing process, Grease and oil are nonpolar and insoluble in water. When soap and soiling oils are mixed, the nonpolar hydrocarbon portion of the micelles breaks up the nonpolar oil molecules into molecule called micelle and then forms different type of micelle with nonpolar soiling molecules in the center because of "like dissolved like" as shown in figure 2.4. Thus, grease, oil and dirt inside the micelle can be lift off the surface, disperse into water and wash away by water as well. Moreover, the carboxylate groups form a negatively-charged spherical surface will not allow the micelles come closer and combined to form a large drop of oil (Shadilya, 2010).

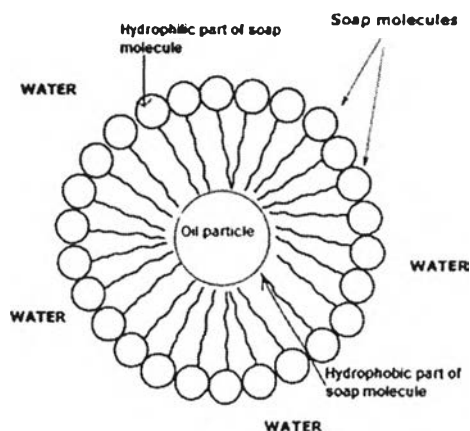


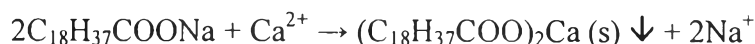
Figure 2.4 Oils dissolve inside micelle.

2.3 Water Hardness

Hard water contains a high concentration of calcium and/or magnesium (Stellner and Scamehorn, 1989). The hardness of water is determined by the contents of divalent ions such as iron, manganese, calcium and magnesium. Among the hardness ions, the dominant species in tap water are known as calcium and magnesium. The degree of hardness becomes greater as the calcium and magnesium content increased. In natural water, the average level of calcium to magnesium concentration is 4 to 1 ratio (Dissanake and Chandrajith, 2009). The dissolved of calcium ions and magnesium ions caused by getting into the water when water comes into contact with limestone and other rocks that contain calcium compounds for example, when rainwater flows over these rocks on its way to a reservoir. Hard water is generally not harmful to human health but hardness ions are responsible for two harmful effects (Park *et al.*, 2007). It can generate formation of precipitating soap scum on bathroom floor due to the reaction with soap anions. For another effect, hard water will destruct soap leading to decrease the detergent performance. In addition, hard water also has an 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 hardness of water affects the performance of soap and detergent which is necessary for cleaning process. Bathing with soap in hard water causes a white precipitate known as soap scum. The soap scum formation are shown in the following equation (Itsadanont *et al.*, 2013).



The soap scum generated from calcium or magnesium ions in hard water react strongly with negatively-charged of carboxylate group which located outside the micelle to form insoluble compounds. Therefore, the effectiveness in cleaning process of soap were reduced because soap scum will destroy the properties of soap and leaves a unpleasant stain on the surface of shower bathtubs or sanitary wares (Soontravanich *et al.*, 2010).

2.5 Removal of Soap Scum

Cleansing agent has been used to get rid of a stain and dirt from the sanitary wares in every household. Most of cleansing agents mainly contain hydrochloric acid which is very corrosive and irritate skin. To solve this problem, using suitable surfactant with the chelating agent are interested in this study.

2.5.1 Equilibrium Solubility

Soontravanich (et al.) (2010) investigated equilibrium dissolution of the salts of long chain fatty acids (soap scum) by using different types of surfactants; sodium dodecyl sulfate (SDS) as an anionic, octylpolyglycoside (C₈APG) as a nonionic, and dimethyldodecylamine oxide (DDAO) as an amphoteric with and without chelating agent (disodium ethylenediaminetetraacetate, Na₂EDTA) in the pH solution range from 4-11. From the results, using amphoteric surfactant only showed the highest equilibrium solubility of Ca(C₁₈)₂ at low solution pHs. But in a presence of chelating agent, the highest equilibrium solubility of Ca(C₁₈)₂ was found in

amphoteric surfactant solution at high solution pHs because at a high solution pH, the chelant effectively binds calcium ion and leaves stearate anion to form co-micellized with the amphoteric surfactant in zwitterionic form easily. The anionic surfactant (SDS), showed the highest equilibrium solubility of $\text{Ca}(\text{C}_{18})_2$ in a present of chelant at the lowest solution pH whereas the nonionic surfactant (C_8APG), showed the highest equilibrium solubility of $\text{Ca}(\text{C}_{18})_2$ in the present of chelant at high solution pHs.

Itsadanont (et al.) (2013) studied the dissolution of two models of soap scum which are calcium and magnesium soap scums by using three different types of surfactant; methyl ester sulfonate (MES) as an anionic, alcohol (EO9) as a nontonic, and dimethyldodecylamine oxide (DDAO) as an amphoteric in the presence of chelant (Na_2EDTA) at various solutions pHs (4-11). The results showed that the solubility of calcium soap scum was higher than that of magnesium soap scum except some DDAO system. Using amphoteric surfactant (DDAO) in the present of chelating agent at high pH gave the highest equilibrium solubility of $\text{Ca}(\text{C}_{18})_2$ and $\text{Mg}(\text{C}_{18})_2$. The DDAO showed the most effective surfactant under all conditions. When compared at a low solution pH in the present of chelating agent, the MES is more effective than the EO9 which is opposite trend at high solution pH which was corresponding to Soontravanich's work.

2.5.2 Dissolution Rate

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

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

Integration equation (1) to get

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

Where r is the rate of $\text{Ca}(\text{C}_{18})_2$ dissolution

k is the apparent rate constant of soap scum dissolution (min^{-1})

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 the different types of surfactant; sodium dodecyl sulfate (SDS), octylpolyglycoside (C_8APG), and dimethyldodecylamine oxide (DDAO) in the presence of chelant; disodium ethylenediaminetetraacetate (Na_2EDTA). The results showed that increasing solution pH caused the increasing dissolution at all times for both DDAO and C_8APG but showed the opposite trend for SDS. Moreover, the highest rate of soap scum dissolution was found in DDAO or C_8APG at high solution pH consistently with the trend of equilibrium solubility from previous work.

Itsadanont (et al.) (2014) studied the dissolution rate of calcium soap scum by using DDAO amphoteric surfactant with chelating agents as Na_2EDTA . The result showed that DDAO/ Na_2EDTA system provide the highest dissolution rate of soap scum as pH increased which relate to equilibrium solubility. Because the most effective form of chelant to bind with calcium ion presented at high pH solution. They also studied the effect of added NaCl. The added NaCl to to system showed the negative effect because it decreased equilibrium solubility and dissolutionrate. The reason is that Na_2EDTA has to bind with calcium ion and sodium ion.

2.6 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 2.5 (Farn, 2008).

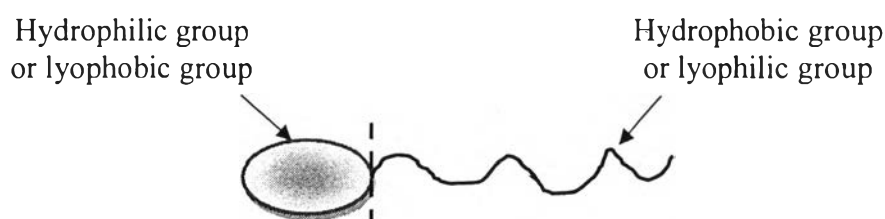


Figure 2.5 Simplified surfactant structure(Farn, 2008).

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.*, 2003). 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, $C_{12}H_{25}SO^3Na^+$ (sodium dodecyl sulfate), $RC_6H_4SO^3Na^+$ (alkylbenzenesulfonate). Anionic surfactants are the most common and inexpensive surfactant and mainly used in detergency and personal care products.

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). They are generally used as fabric softeners, hair conditioners and antibacterial agents.

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. Nonionic surfactants are commonly used in the formulation of emulsifier, dispersant and low temperature detergents

4. Zwitterionic surfactants: They have both positive and negative charges present in the surface-active portion charges depending on pH, for example, dimethyldodecylamine oxide (DDAO), $RN^+H_2CH_2COO^-$ (long-chain amino acid). They are widely used in toiletries, baby shampoos, and daily cleaners.

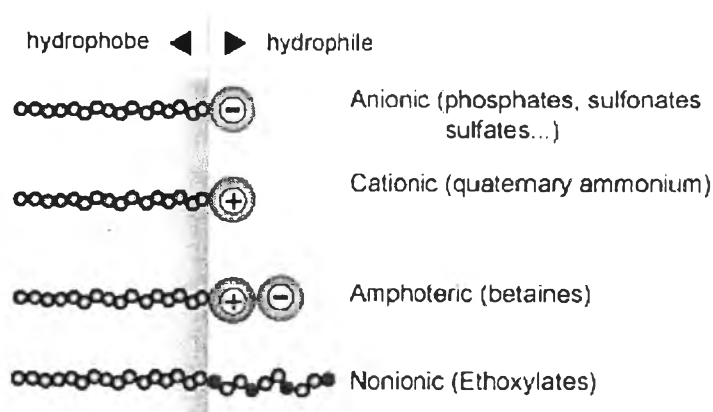
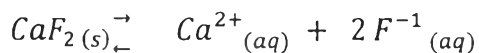


Figure 2.6 Surfactant classification.

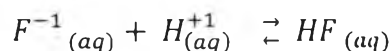
2.7 Effect of Solution pH

Changing in the solution pH may affect the molecule which containing carboxylate groups. 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.

2.8 Chelating Agent

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. showed a short overview of the different terms that are used in this respect to chelating agents.

Table 2.2 Definitions for chelating agent (Nowacket *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. In addition their effects in the environment have received considerable attention.

An application of APCs are used as component or process chemicals in a wide variety of applications, however, according to Figure 2.7 only pulp and paper, cleaning, chemical processing, agriculture and water treatment constitute 80% of their consumption (Kołodzyńska, 2011).

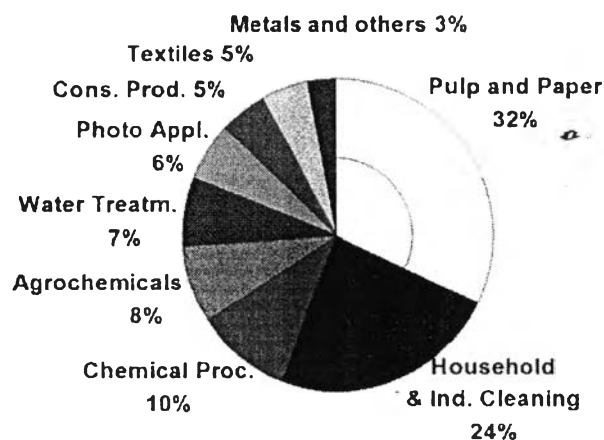


Figure 2.7 The percentage contribution of different applications of APCs.

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 (Na_2EDTA) and a biodegradable chelating agent (Na_4GLDA).

2.8.1. Ethylene Diamine Tetraacetate Disodium Salt (Na_2EDTA)

Ethylene diamine tetraacetate disodium salt or Na_2EDTA in this study has the chemical structure as shown in Figure 2.8. It is a common complexing agent, which has four main active sites that can form a water-soluble complex with cations. One molecule of Na_2EDTA 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 Na_2EDTA in the absence of divalent cations, depending on solution pH (H_4Y , which has four ionizable hydrogens, H_3Y^- , H_2Y^{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)

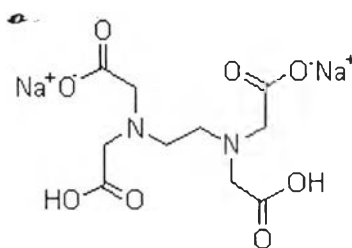


Figure 2.8 Chemical structure of Na_2EDTA .

At a high pH, the major species found is Y^{4-} , which is the most effective form of Na_2EDTA in chelating calcium ions. The molecule of Na_2EDTA in an acidic solution is less effective than that in a basic solution due to the protonation of active site on the Na_2EDTA . Na_2EDTA was patented in Germany in 1935 by F. Munz. The synthesis of Na_2EDTA consisted in the reaction of monochloroacetic acid with ethylenediamine in the presence of sodium hydroxide. Another way to

obtain Na_2EDTA is the reaction of ethylenediamine with sodium cyanide and formaldehyde in the presence of sodium hydroxide. Since Na_2EDTA 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 Na_2EDTA 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 Na_2EDTA in the environment. Numerous field studies have shown that complexation of Na_2EDTA may mobilize contaminant metal ions. Na_2EDTA 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 radionuclide from radioactive waste and their application in eutrophication of natural water systems are of great concern. Hence, Na_2EDTA , whose effluent emissions are already banned in some states and countries and is considered as a 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).

2.8.2. Tetrasodiumglutamatediacetate (Na_4GLDA)

A novel readily biodegradable chelating agent, tetra sodium of N,N-bis(carboxymethyl) glutamic acid (also denoted as Dissolvin GL-38 or Na_4GLDA , 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 2.9.

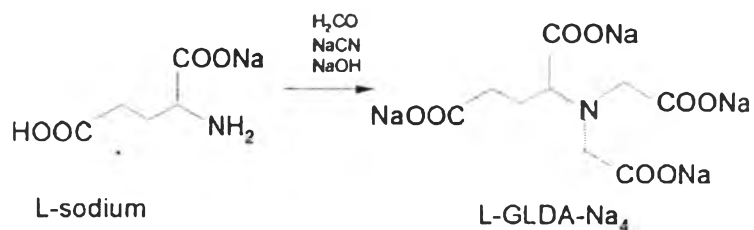


Figure 2.9 Scheme of Na₄GLDA production.

In contrast to the manufacture of Na₂EDTA whose carbon content is fossil based, the carbon source of Na₄GLDA is primarily biobased. Therefore, Na₄GLDA is the only chelating agent with 'green' carbon atoms. The biodegradation of Na₄GLDA is initiated by mono-oxygenases catalysing the removal of carboxymethyl groups. According to the Swedish Society for Nature Conservation Na₄GLDA 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 Na₄GLDA 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 Na₄GLDA in 25% NaOH sodium hydroxide solution compared to Na₂EDTA. It is also characterized by excellent solubility at low pH (Seetzel *et al.*, 2008).

Since, Na₄GLDA possesses complexing properties comparable to Na₂EDTA. Therefore, it can be an alternative to Na₂EDTA. The benefit of Na₄GLDA in such formulations is its broad effective pH range for the chelation of calcium and magnesium ions equal to 4-12. Na₄GLDA 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 Na₄GLDA.

Table 2.3 The properties of Na₄GLDA

Name	Physicochemical characteristics
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 Stability constant: Ca(II) 5.9, Mg(II) 5.2 Biodegradability: > 83%