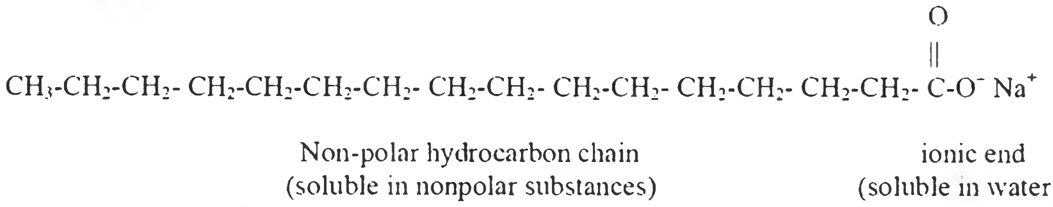
CHAPTER II
LITERATURE REVIEW

2.1 Soap

2.1.1 Characteristic of Soap

Soap is mainly used as surfactant for cleaning washing and bathing. A soap molecule consists of a long hydrophobic (water-fearing) hydrocarbon "tail" and a carboxylic group hydrophilic (water-loving) anionic "head". The length of the hydrocarbon depends on the type of fat or oil, however, most of which are quite long. On the other side, a carboxylic acid group ionic end is usually balanced by either positively charged sodium (Na^+) or potassium (K^+) cation. The structure of a soap molecule is represented in Figure 2.1 (Zoller, 2009).



$$CH_3\text{-}CH_2\text{-}CH_2\text{-}\ CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\ CH_2\text{-}CH_2\text{-}\ CH_2\text{-}CH_2\text{-}\ CH_2\text{-}CH_2\text{-}\ CH_2\text{-}CH_2\text{-}\ \overset{O}{\overset{\|}{C}}\text{-}O^-\ Na^+$$

Figure 2.1 The structure of soap molecule (http://www.chemistryexplained.com/Ru-Sp/Soap.html).

In chemistry, soap is a salt of fatty acid which is produced by strong alkaline hydrolysis of a triglyceride such as sodium hydroxide. The three molecules of soap are produced for every molecule of triglyceride in this reaction and by product is glycerol which is useful as in food industrial. This process is called saponification and is illustrated in Figure 2.2 (Katz, 2000).

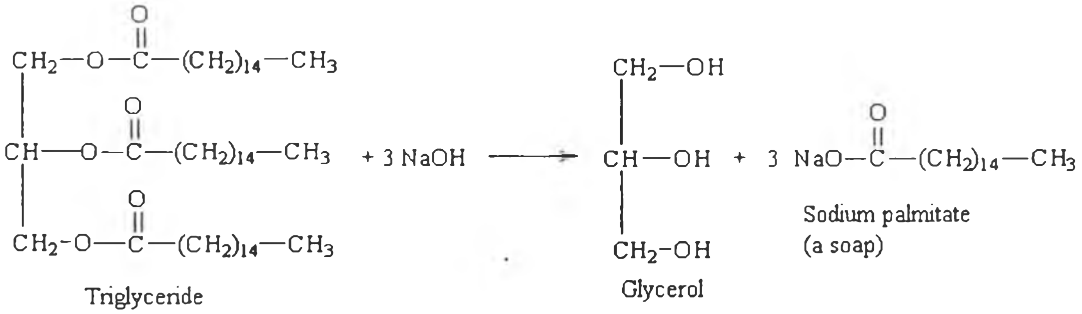


Figure 2.2 Saponification of triglyceride (http://www.chemistryexplained.com/Ru-Sp/Soap.html).

2.1.2 Fatty Acid

Fatty acid is an important component of lipids in plants, animal and microorganism. It consists of a carboxylic acid group (COOH) and long hydrocarbon chain which usually derived from triglycerides. When they are not attached to other molecules, they are called "free fatty acids". In nature, they range mostly in size from 10 carbon atoms to 20 carbon atoms and they are usually found even number of carbon atoms and no branch. If hydrocarbon chain consist of alkane, they are known as saturated and they are called unsaturated, when hydrocarbon chain consist of double bond or alkene (Spurlock, 2011).

The fatty acids are weak acids which bond between carboxylic acid group and hydrocarbon chain. The carboxylic acid group is attracted to water or hydrophilic (water-loving), while the hydrocarbon chain is attracted to oil or hydrophobic (water-hating)(Othmer, 2006).When soaps are added in water, the soap molecules work as a bridge between polar water molecules and non-polar oil molecules. Since soap molecules have both properties of non-polar and polar molecules.

In cleaning process, soaps are produced by various fatty acids so 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 (Hill *et al.*, 2004). 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. Especially, popular sodium stearate is 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 because of bad odors and irritate to the skin (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 Cleaning Process

The stains or dirt cannot be cleaned out completely by water. The soap is added into the water to get rid of dirt, however, because of its dual nature. The soap molecule has a polar, water-soluble head (carboxylate salt) and a long, oil-soluble tail (the hydrocarbon chain). In polar solvent, the soap has the molecules from clusters, known as micelles, in which the polar ends of the molecules are on the outside of the cluster and the non-polar ends are in the middle as shown in Figure 2.3 (Spurlock, 2011).

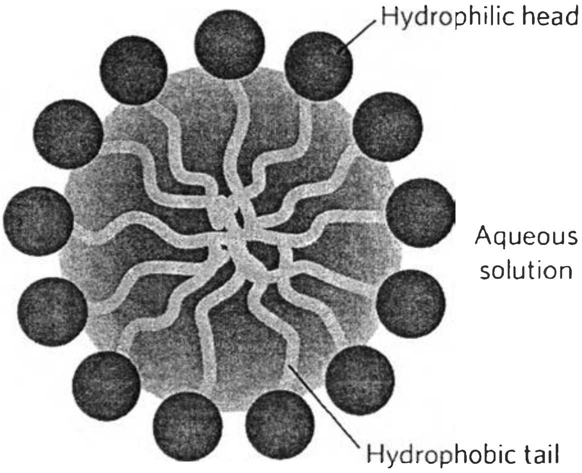


Figure 2.3 The structure of a micelle (http://www.nature.com/nmat/journal/v9/n5/images/nmat2761-f1.html).

In cleaning 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).

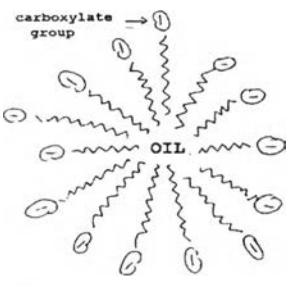


Figure 2.4 Oils dissolve inside micelle (http://homepages.ius.edu/Dspurloc/c122/soap.htm).

2.3 Water Hardness

The hardness of water is determined that the content of divalent ions such as iron, manganese, calcium and magnesium ions. The most common hardness water ions are calcium and magnesium (Park *et al.*, 2007). In natural water, the average level of Ca to Mg concentration is 4 to 1 ratio (Dissanayake *et al.*, 2009). The water hardness is caused by carbon dioxide gas dissolved in the rain water which causes carbonic acid. The rain water seeps into the ground through the decomposition of soil organic substance. Carbonic acid will have more features. When the water permeates into soil or contact with the rock, especially limestone, which is the main component is calcium carbonate and magnesium carbonate. Water can dissolve these elements made of calcium ions and magnesium ions increase. Therefore, in general, surface water such as rivers, lakes are less strong than underground water. Hard water is generally not harmful to one's health and it can be consumed, especially with hard water ions such as carbonate ions have good taste and fresh. However, the hardness of the water will make the water inconvenient to clean with soap. Because hardness ions will make the performance of cleaning soap reduced by react chemically with the soap (stearate anion) causes calcium stearate or magnesium stearate or also known as soap scum. It is responsible for two harmful effects; formation of deposits and destruction of soap which the deposits of hardness ion generally occur due to the reaction with soap anions (Slowinski *et al.*, 2011). 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 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):

$$2C_{18}H_{37}COONa + Ca^{2+} \rightarrow (C_{18}H_{37}COO)_2Ca\ (s) + 2Na^{+}$$

and

$$2C_{18}H_{37}COONa + Mg^{2+} \rightarrow (C_{18}H_{37}COO)_2Mg\ (s) + 2Na^{+}$$

The soap scum formation occurs from divalent cation especially calcium and magnesium ions in hard water 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 decreased because soap scum will destroy the soap properties and leave a strain on the surface of shower bathtubs or all water fixtures (Soontravanich *et al.*, 2010).

2.5 Removal of Soap Scum

In every household, cleansing agent has been used in order to remove 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 an appropriate surfactant with chelating agent.

2.5.1 Equilibrium Solubility

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 chelating agent 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 chelating agent at the lowest solution pH whereas nonionic surfactant, C_8APG, provided the highest equilibrium solubility of $Ca(C_{18})_2$ in the present of chelating agent at high solution pHs.

Itsadanont et al. (2013) 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 indicated that using amphoteric surfactant, DDAO, provided the highest equilibrium solubility of $Ca(C_{18})_2$ at a low solution pH while the highest equilibrium solubility of $Ca(C_{18})_2$ was found at high solution pH when chelating agent was presented which was corresponding to Soontravanich's work.

Although the additional of EDTA can increase the solubility equilibrium both calcium and magnesium soap scum, it can be harmful to the environment resulting from its low biodegradability. Itsadanont et al. (2013) (Paper3) 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 biodegradable chelating agent; tetrasodium glutamatediacetate (Na_4GLDA), Trisodium ethylenediaminedisuccinic acid (Na_3EDDS) at various solutions pHs (4-11). The results showed that the highest equilibrium solubility of $Ca(C_{18})_2$ and $Mg(C_{18})_2$ were found at high solution pH when DDAO amphoteric surfactant, and Na_4GLDA chelating agent was presented.

2.5.2 Dissolution Rate

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

$$-r = \frac{dM}{dt} = -kM \tag{1}$$

Integrating equation (1) to get:

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

where r is the rate of soap scum dissolution; k is the apparent rate constant of soap scum dissolution ($\min^{-1}$); and M_0 and M are the initial and the final weight of dissolved soap scum at time zero and t, respectively. The k-value can be obtained from a slope of a plot between $\ln\left(\frac{M}{M_0}\right)$ and time.

Soontravanich et al. (2010) studied the kinetic dissolution of calcium soap scum by using the different types of surfactant; sodium dodecyl sulfate (SDS), octyl polyglycoside (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 time 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.

Itsadanont et al. (2013) studied the dissolution rate of calcium soap scum by using DDAO amphoteric surfactant with different chelaing agents as Na_2EDTA and Na_4GLDA. The results showed that DDAO/ Na_2EDTA system provided the highest dissolution rate at pH 11.

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.

$$CaF_{2\,(s)} \rightleftarrows Ca^{2+}{}_{(aq)} + 2\,F^{-1}{}_{(aq)}$$

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.

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.

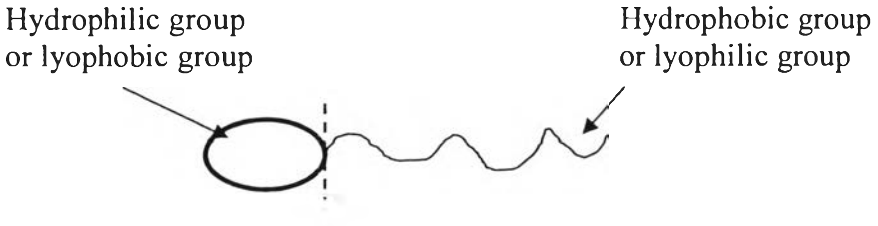


Figure 2.5 The surfactant molecule.

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 hydrophile is a negatively charged group, for example, $C_{12}H_{25}SO_3$-Na+ (sodium dodecyl sulfate), $RC_6H_4SO_3$-Na+ (alkylbenzene sulfonate).

2. Cationic surfactants: The hydrophile bears 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).

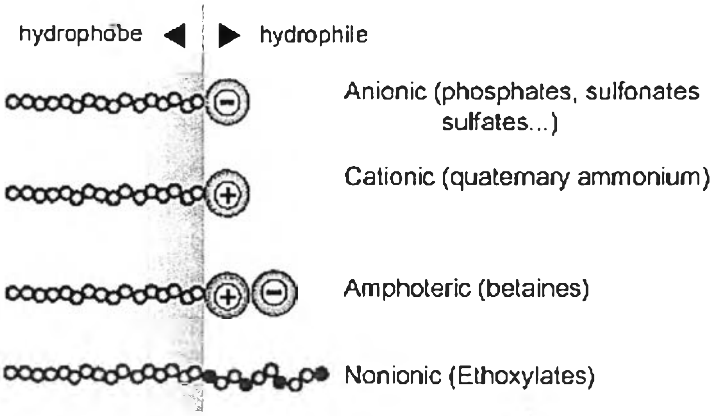


Figure 2.6 Type of surfactant (www.themafrosisters.blogspot.com/2013_08_01_archive.html).

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 diferent 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 behaviors as well as their effect in the environment have received considerable attention.

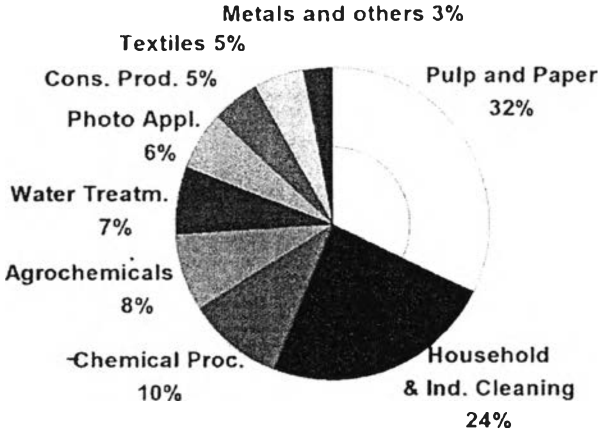


Figure 2.7 The percentage contribution of different applications of APCs.

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.

2.8.1 Disodiumethylene Diaminetetraacetate (Na_2ETDA)

In this study has the chemical structure as shown in Figure 2.7. 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 (H_4Y, 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).

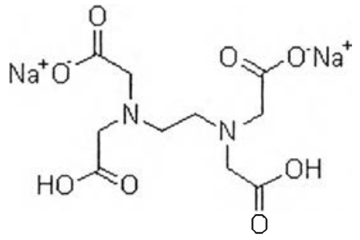


Figure 2.8 Chemical structure of Na_2EDTA.

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 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 concerned. Hence, EDTA, which its 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 award attention towards environmental protection issues i.e. BREF documents, EU EDTA risk reduction strategy documents or OSPAR documents (Kołodyńska, 2011).

2.8.2 Tetrasodium Glutamatediacetate (Na_4GLDA)

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

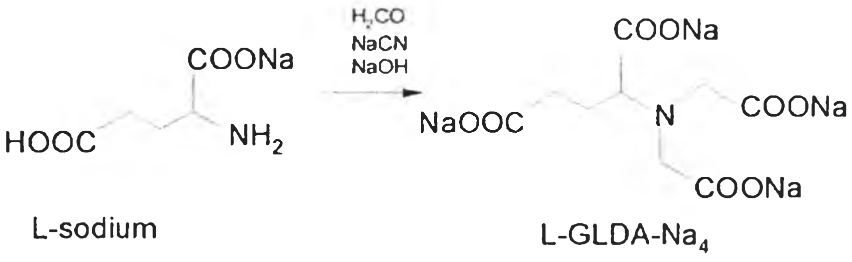


Figure 2.9 Scheme of GLDA production.

Table 2.3 Physicochemical properties of GLDA

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_2O: in any ratio Stability constant: Ca(II) 6.1, Mg(II) 5.2 Biodegradability: > 83%