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A Comparison of Conventional and Biodegradable Chelating Agent in Different Type of Surfactant Solutions for Soap Scum Removal

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Abstract**—**One of the most challenges for hard surface cleaning product is to get rid of soap scum, a filmy sticky layer in the bathroom. The deposits of soap scum can be removed by using a proper surfactant solution with chelating agent. Unfortunately, the conventional chelating agent, ethylenediamine tetraacetic acid (EDTA), has low biodegradability, which can be tolerance in water resources and harmful to aquatic animal and microorganism. In this study, two biodegradable chelating agents, ethylenediamine disuccinic acid (EDDS) and glutamic acid diacetic acid (GLDA) were introduced as a replacement of EDTA. The result shows that using GLDA with amphoteric surfactant gave the highest equilibrium solubility of soap scum.

Keywords**—**Biodegradable chelating agent, EDDS, GLDA, Soap scum.

I. INTRODUCTION

THE sticky stain on sanitary wares (e.g. ring around bathtub) is also known as soap scum which is resulted from our daily routine. Because when personal care product that contains soap is exposed to hard water which consists of earth alkaline divalent cations especially Ca(II) and Mg(II), soap scum is generated [1]. In addition, covering for a long period of time will make it more difficult to remove and lead to the formation of mold and mildew. The bottom line is an unpleasant odor and appearance for example the color of sticky stain is change from white to yellow precipitate by bacteria. Calcium distearate or calcium stearate($Ca(C_{18})_2$, was used as a soap scum model in this work because its solubility is very insignificant (about 0.04 g/l of water at 15 °C).Thus, soap scum removal can be achieved by using appropriate aqueous solution of a chelating agent for calcium or magnesium complexation with a micelle-forming surfactant [2].

Chelating agents of ethylenediamine based are used in many applications especially in washing and cleaning agents. EDTA (ethylene diamine tetraacetic acid), the most widely used chelating agent, which can be toxic to aquatic life and can also persevere in the environment resulting from its low biodegradability [3]. Furthermore, at high concentrations, it istoxic to bacteria and mammals seeing that chelation of metals in an outer membrane or ingestion changes excretion of metals that can affect cell membrane permeability as well [4]. Since in many developed countries, especially in Western Europe, application of the substances including chelating agents was restricted [5]. This caused necessity of the use of substitutes, among which biodegradable complexing agents characterized by good eco-profile plays a major role.

One of the most promising biodegradable chelating agents is EDDS, ethylene diamine dissuccinate. It is structural isomer of EDTA. As a biodegradable replacement, only the (S,S) isomer is of interest and should not be confused with the other stero-isomers of EDDS (RR-, RS-, SR-) where they are unable to biodegradable or partly biodegradable [6]. In addition, tetrasodium salt of N,N-bis(carboxymethyl) glutamic acid (GLDA), marketed as Dissolvine GL-38, is a direct alternative to EDTA as well [7]. According to the Swedish Society for Nature Conservation GLDA is 86% based on renewable resources because it is produced from flavor enhancer monosodium glutamate (MSG) [8]. Hence, GLDA is classified as readily biodegradable according to the internationally recognized OECD 301D test and is the only chelating agent that contains green carbon atoms contrary to the production of EDTA whose carbon content is based on fossil. However, only GLDA in L-form is concerned with Dissolvine GL-38 because the D-form is unable to biodegrade.

The purpose of this research is to compare an ability to dissolve soap scum by using different surfactants with conventional and biodegradable chelating agents.

II. EXPERIMENT

A. Materials

Stearic acid (98.5+% purity), calcium hydroxide (99.995% purity), dimethyldodecylamine oxide (DDAO) (99+% purity) and ethylenediamine disuccinic acid (EDDS) were purchased from Sigma-Aldrich (St. Louis, MO). Methyl ester sulfonate (MES) (88.6% purity) was provided by PTT-Chemical. Alcohol ethoxylate (EO9) (99.95% purity) was supplied from

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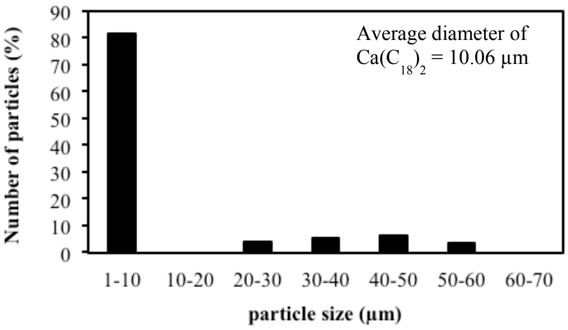

Fig. 1 Particle size distribution and average diameter of soap scum model (calcium stearate)

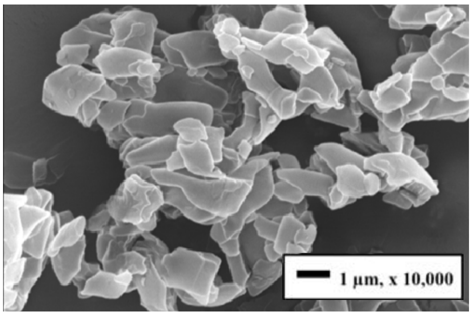

Fig. 2 SEM images of calcium stearate

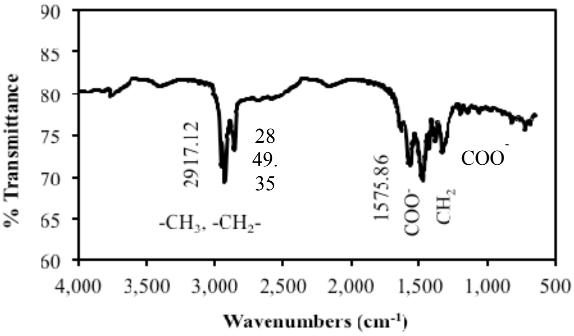

Fig. 3 FT-IR spectra of calcium stearate

purchased from Italmar. Acetone (A.C.S. grade) was obtained from J.T. Baker (Pathumwan, BKK). Sodium hydroxide was obtained from J.T. Baker (Phillipsburg, NJ) and hydrochloric acid was obtained from Lab Scan (Phillipsburg, NJ). Both were used as received to adjust the solution pH. The chemicals were used without further purification. All solutions were made with deionized water.

B. Soap Scum Preparation

Calcium stearate isthe models of soap scum used in the experiments. For the calcium stearate, it was synthesized from the reaction between calcium hydroxide and stearic acid as a ratio of 1:1. The calcium hydroxide was dissolved in deionized water while the stearic acid was dissolved in ethanol. Then, the stearic acid solution was mixed with the calcium hydroxide solution. After that, soap scum was formed as white solid particles. The solution was left for a day to reach equilibrium. Then, the solution was filtered by using a 0.2 micron nylon membrane and follows by rinsing with water, ethanol and acetone in order to remove the excess calcium ions and unreacted stearic acid. Finally, the precipitate was dried in a vacuum oven at 30°c for 3 h.

C. Solubility Experiments

For the equilibrium solubility of calcium soap scum, the experiments were done by using various types of surfactants; anionic surfactant (MES), nonionic surfactant (EO9) and amphoteric surfactant (DDAO) with different biodegradable chelating agents; GLDA and EDDS. An excess amount of each synthesized soap scum was added in a solution containing 0.1 M of surfactant and 0. 1 M of chelating agent. Then, the mixtures were equilibrated for one night. After that, the filtrate samples were taken for analysis of calcium or magnesium using atomic spectrophotometry.

D. Soap Scum Dissolution Experiments

An excess amount of synthesized calcium soap scum was added to a solution containing different surfactant and chelating agent at different equilibrium solution pH values. After that the solution was heated to around 70°C in a water bath for 3 h. Next, all samples were equilibrated at 25°C in the temperature-controlled water bath at least 1 week with routine shaking. After that, the solutions were filtered using a 0.2 micron nylon filter membrane to separate the remaining undissolved soap scum. Finally, the clear solutions were analyzed by the atomic absorption spectrometer (AAS)(SpectrAA-300, Varian)for the concentration of dissolved calcium or magnesium. The average data were obtained from at least 3 times with less than 1% error.

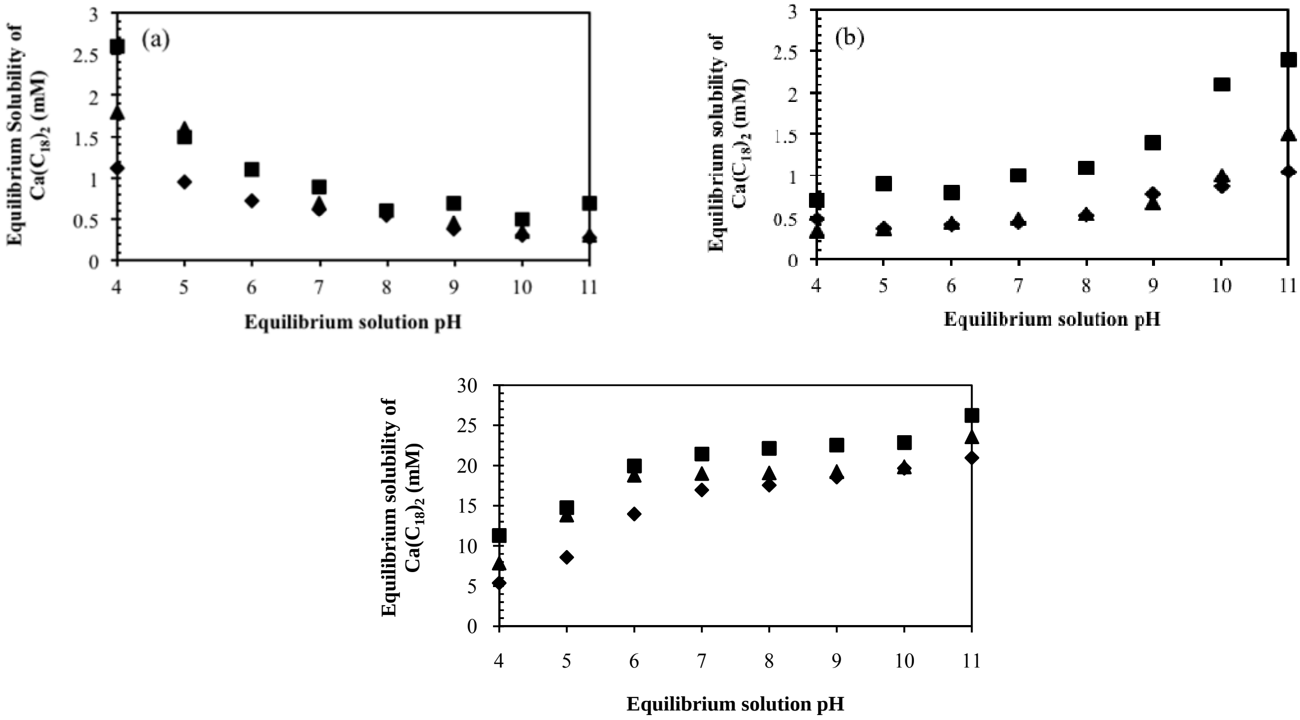

Fig. 4 Equilibrium solubility of calcium stearate in (a) MES (b) EO9 and (c) DDAO system
■GLDA ◆EDTA ▲EDDS

III. RESULTS AND DISCUSSION

A. Characteristics of Synthesized Soap Scum

Particle size distribution and average diameter of calcium soap scum is shown in Fig. 1. The average particle size of calcium stearate was 10.06 µm and it had almost uniform particle size in the range of 1 to 10 µm. Fig. 2 shows the SEM images of calcium soap scum which showed smooth and non-porous surface. Fig. 3 shows the FT-IR spectra of calcium stearate that showed no peak of –OH of carboxylic acid group [9], suggesting the stearic acid completely reacted with calcium ions. For calcium stearate, the peak at 1575 cm^{-1} indicated COO^{-} in carboxylic acid salts stretching that wavenumbers present at 1610-1560 cm^{-1}. These can confirm that calcium ions can react with stearic acid and produce absolutely calcium stearate. For another peak, $-CH_3$ and $-CH_2-$ in aliphatic compounds (CH-antisym and CH-sym stretching) presented at 2990-2850 cm^{-1} [9].

B. Effect of Surfactant with Chelating Agent

The results in terms of the equilibrium solubility of soap scum model (calcium stearate) at various equilibrium solution pHs are presented in Fig.4. Ranging from the top to the bottom are the 0.1 M of chelant systems with (a) 0.1% wt/v of MES, (b) 0.1% wt/v of EO9, and (c) 0.1 M of DDAO, respectively. These soap scums are added at a concentration about 10 times higher than their solubility in water.

With every chelating agent system, the equilibrium solubility of EO9 and DDAO system increase with increasing solution pH due to a better complexation between calcium ions and chelating agent which in contrast to those in MES systems. The system with DDAO showed the highest solubility of soap scum at a solution pH of 11. At solution pH of 4, it was found to be the lowest solubility due to the less effectiveness of complexation. However, in MES system, at the solution pH of 4 gave the highest solubility. At low pH, soap scum is in non-ionic stearic acid that forms mixed micelles with the added surfactant. These mixed micelles are expected to be effective in either cationic (DDAO at low pH) or anionic surfactant since cationic/non- ionic or anionic/nonionic surfactant synergism exists. For an intermediate pH, stearic acid and stearate anion form mixed micelles with added surfactant. An amphoteric surfactant, DDAO, is composed of both cationic and zwitterionic micelles due to the mixed cationic (DDAO) and anionic (stearate) surfactants. But at low pH, calcium stearate solubility is lower and led the solubility of stearate is low in equilibrium with calcium stearate when no calcium is complexed. Besides, less protonated stearic acid is formed than at low pH.At high pH, most of soap scum remains as an undissolved solid precipitate because its low solubility. Though there is any stearate anion, there is still an electrostatic repulsion between stearate and MES in micelles, which caused the low solubility of calcium stearate. In DDAO system, zwitterionic is form completely and form micelles synergistically with stearate, but stearate solubility is still low in equilibrium with calcium stearate without chelation [6].

C. Chelating Agent Comparison

EDTA, GLDA and EDDS have the same metal-ligand ratio, which is 1:1 (M(II):EDTA or GLDA or EDDS). For EDTA, there are five forms of chelating that depend on solution pH (H_4Y, H_3Y^-, H_2Y^{2-}, HY^{3-} and Y^{4-}) but Y^4 is the most effective form to bind with calcium ions, which presents at high solution pH and leaves behind a stearate anion. But among of all, GLDA showed the highest solubility in every surfactant system and has more environmental friendly profile compare with EDTA. Furthermore, GLDA has broad effective pH range for calcium chelation, ranging from 4 to 12 [10].In EDTA system,as the solution pH decreases, the co-micellization of the anionic MES with the nonionic stearic acid tends to be stronger than that with the anionic stearate and higher than the descending complexation effectiveness of the Na_2EDTA chelating. The solubility of the calcium stearate in the nonionic EO9 system slightly decreases with increasing solution pH in the pH range of 4 to 6 (as a result from increasing in protonation of stearate to stearic acid) and significantly increases afterward.The highest solubility was found in the DDAO system, particularly at higher solution pHs of 7 and above. Solubility was exceedingly higher in magnitude than in the MES and EO9 systems due to lesser degrees in synergism in the mixed micelles of the anionic/anionic MES and the anionic/nonionic EO9 than the anionic/zwitterionic DDAO.

For biodegradable chelating agent, both GLDA and EDDS follow the same trend as EDTA system only EDDS in DDAO system that slightly increases the solubility at below solution pH of 8 then, dramatically increases afterward.

IV. CONCLUSION

In the present work, studies of biodegradable chelating agents (GLDA and EDDS) were carried out in compared with EDTA for calcium soap scum dissolution. The obtained results can be summarized as follows:

(1) An amphoteric surfactant seems to be the most promising surfactant at a high pH for calcium soap scum removal.
(2) Focus on chelating agent replacement, the results showed that GLDA gave the highest solubility of soap scum and the highest soap scum dissolution.

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