CHAPTER IV
RESULTS AND DISCUSSION

By following the procedure and all chemicals used in the experiments from the previous work, only chelating agent that has to be replaced by biodegradable chelating agent in order to compares the equilibrium solubility of soap scum with EDTA. The equilibrium solubility of two soap scum (calcium stearate; $Ca(C_{18})_2$ and magnesium stearate; $Mg(C_{18})_2$) were investigated at constant temperature at 25°C and various solution pHs (ranging from 4 to 11) under the presence of different types of surfactants: anionic surfactant (MES), nonionic surfactant (EO9) and amphoteric surfactant (DDAO) with biodegradable chelating agent (GLDA or EDDS).

4.1 Characteristics of synthesized soap scum

The particle size distribution and average diameter of each soap scum are shown in Figure 4.1. The average particle size of the calcium stearate was almost 3 times lower than that of the magnesium stearate. Remarkably, the calcium soap scum had a more uniform particle size in the range of 1 to 10 µm whereas the magnesium soap scum had a wider range from 10 to 80 µm.

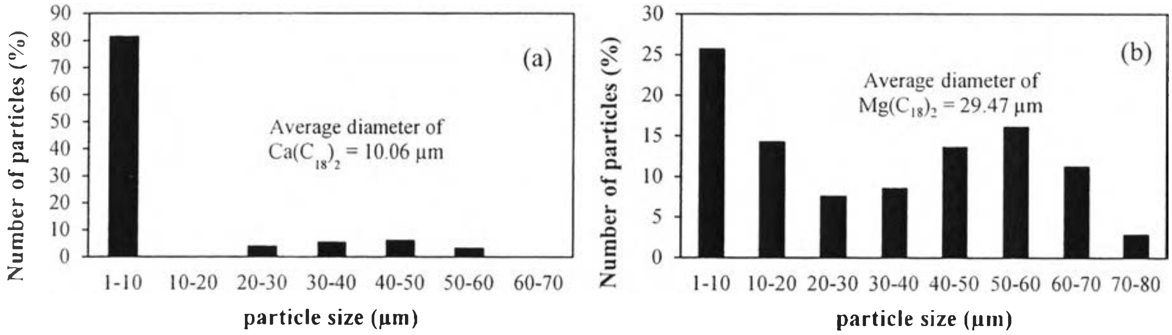


Figure 4.1 Particle size distribution and average diameter of two soap scum: (a) calcium stearate; and (b) magnesium stearate.

In Figure 4.2 shows the SEM images of both soap scum with smooth and non-porous surfaces but the calcium stearate exhibits smaller sizes and a higher particle size distribution than the magnesium stearate. Figure 4.3 shows the FT-IR spectra of the calcium stearate and magnesium stearate. Both of them showed no peak of –OH of carboxylic acid group, suggesting the stearic acid completely reacted with calcium or magnesium ions. For the calcium stearate, the peak at 1575 cm^{-1} indicated COO^- in carboxylic acid salts (Lambert). For the magnesium stearate, the peak at 1702 cm^{-1} indicated C=O in carboxylic acid ester stretching that wavenumbers present at 1710-1690 cm^{-1} (Lambert, Silverstein). These can confirm that calcium or magnesium ions can react with stearic acid and produce calcium or magnesium stearate stoichiometrically. For other peaks, $–CH_3$ and $–CH_2$- in aliphatic compounds (CH-antisym and CH-sym stretching) presented at 2990-2850 cm^{-1} (Lambert).

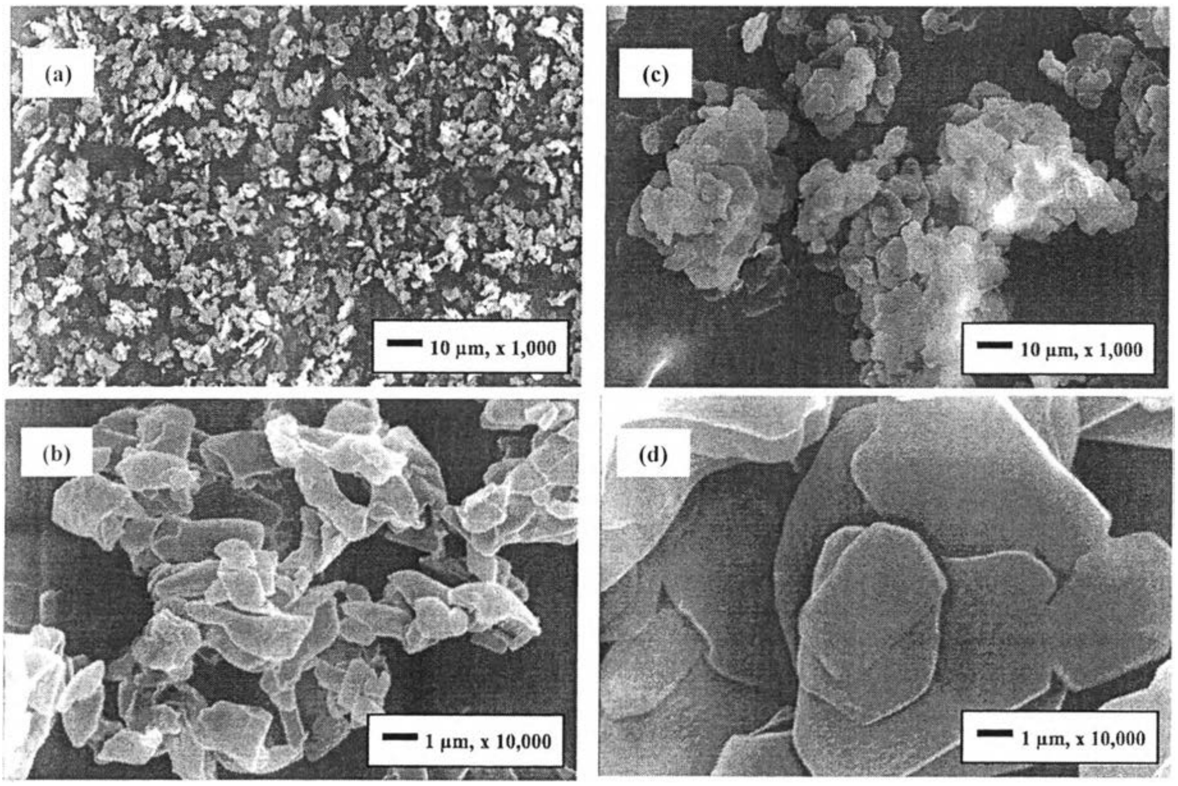
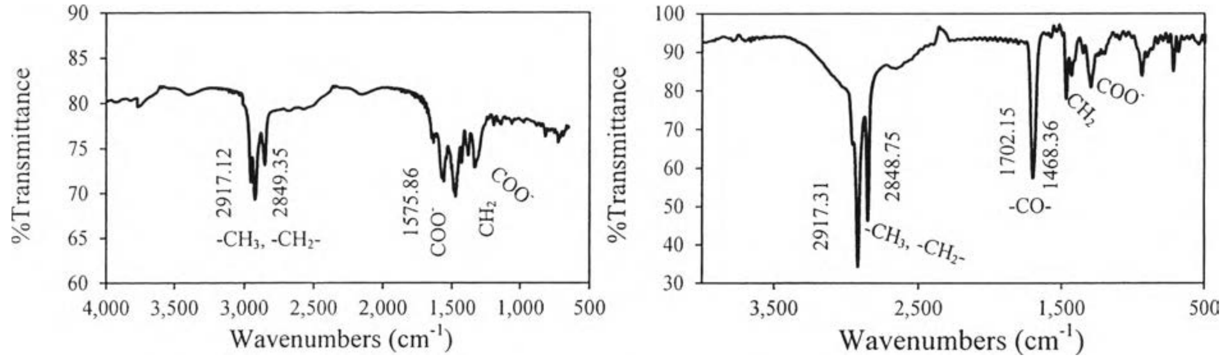


Figure 4.2 SEM images of: (a), (b) calcium stearate; and (c), (d) magnesium stearate.



(a) (b)

Figure 4.3 FT-IR spectra of (a) calcium stearate and (b) magnesium stearate.

4.2 Chelating agent-only systems

Figure 4.4 and 4.5 show the equilibrium solubility of both calcium and magnesium soap scum in 0.1 M chelating agent solution, respectively. Either GLDA or EDDS alone showed an insignificant effect on the equilibrium solubility of both soap scum at any given solution pH. Due to the protonation at low solution pH, soap scum will be protonated to the nonionic stearic acid, which has very low solubility (K_{sp}). However, chelating agent has the most effective at high solution pHs, which the complexation between chelating agent and soap scum took place when GLDA or EDDS chelated with divalent cation (Ca^{2+} or Mg^{2+}) and left the stearate anion behind. At high solution pH, soap scum will be dissociated to the stearate anion. Since stearate anion has poor solubility (K_{sp}) and there was no micelle formed in the system to improve the solubilizing, the equilibrium solubility of both soap scum was still very low. In a comparison of two soaps scum models according to Figure 4.1, it is explainable why calcium soap scum has slightly higher equilibrium solubility than the magnesium soap scum. Because the average particle size of calcium soap scum is smaller than that of magnesium soap scum. The smaller particle size makes the system a better solubilizing.

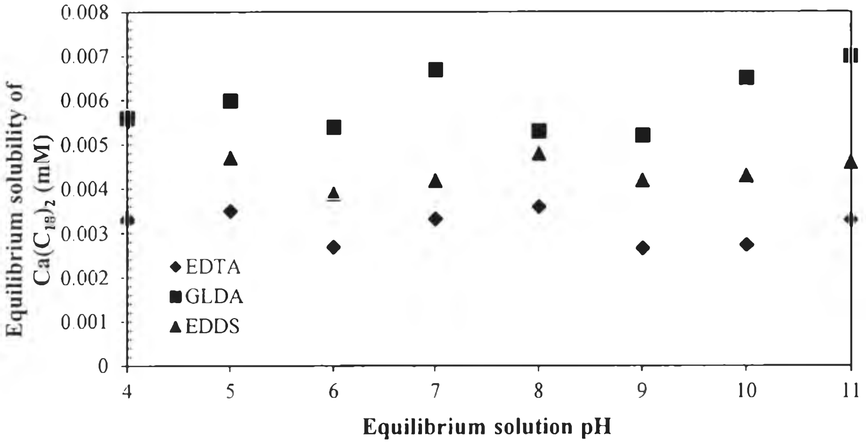


Figure 4.4 Equilibrium solubility of calcium soap scum in chelating agent-free system at various solution pH.

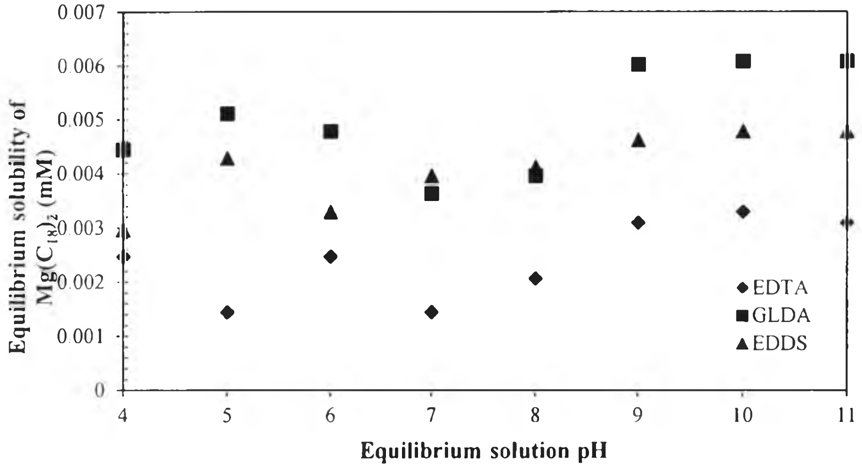


Figure 4.5 Equilibrium solubility of magnesium soap scum in chelating agent-free system at various solution pH.

4.3 Surfactant-Chelating agent systems

This study emphasizes on the effect of surfactant in the presence of chelating agent. The results in terms of the equilibrium solubility of two soap scum models (calcium and magnesium stearate) at various solution pH are presented ranging from Figure 4.6 to 4.11 are the 0.1 M of chelating agent (GLDA or EDDS) systems with (1) 0.1% wt/v of MES, (2) 0.1% wt/v of EO9, and (3) 0.1 M of DDAO, respectively. The mechanism of soap scum dissolution in the system of surfactant mixed with chelating agent can be explained as when chelating agent binds with divalent cation (Ca^{2+} or Mg^{2+}), the remaining stearate will co-micellize with surfactant that can improve the equilibrium solubility of soap scum.

For the MES system, the equilibrium solubility of either calcium or magnesium soap scum decreases with increasing solution pH. Due to the effect of solution pH on soap scum structure, at low pH, there was a co-micellization between anionic MES and the nonionic stearic acid, which improves the equilibrium solubility of both soap scum. When solution pH increases, soap scum will be dissociated to the poor solubility stearate anion and the equilibrium solubility will descend as a consequence of electrostatic repulsive force between anionic MES and stearate anion co-micelles. From both Figure 4.6 and 4.7, GLDA has the highest equilibrium solubility of either calcium or magnesium soap scum. It can form complex with two calcium or magnesium ions because of the substitution of four vacancies whereas, EDDS and EDTA can form the lesser bond with those ions. In a comparison of EDDS and EDTA, EDDS has three vacancies that can form only one bond as in EDTA but it might have the complexation with more stable form. Thus, in a comparison among the studied chelating agents, the effectiveness of chelating agents for soap scum dissolution is in the following order: GLDA > EDDS > EDTA. According to stability constant of divalent cation complexes with chelating agent, calcium has higher stability constant, which can be explained the higher equilibrium solubility than magnesium soap scum.

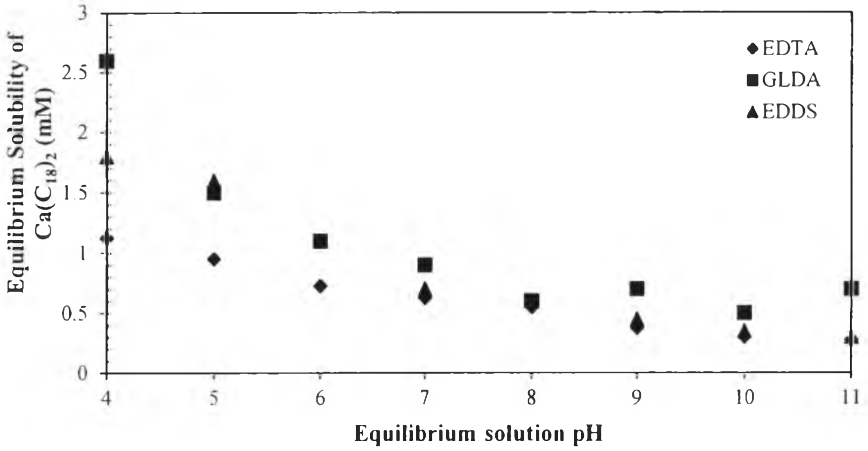


Figure 4.6 The Equilibrium solubility of calcium soap scum in MES with chelating agent system at various solution pH.

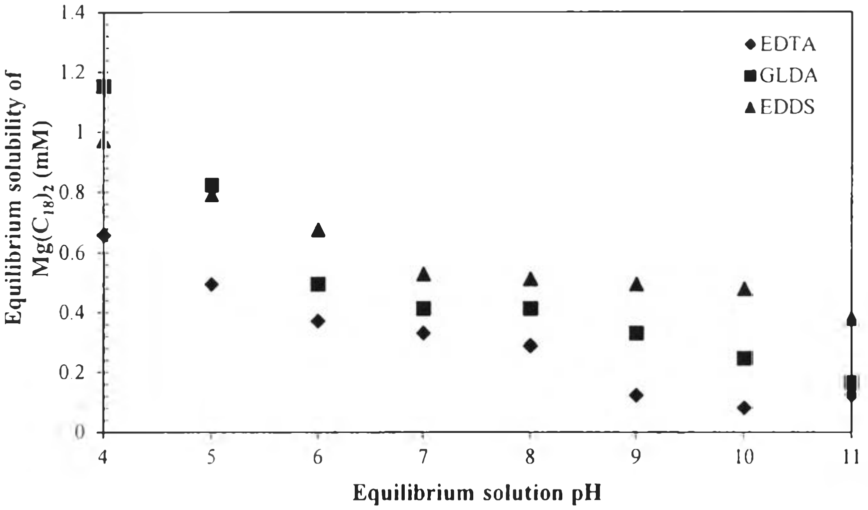


Figure 4.7 The Equilibrium solubility of magnesium soap scum in MES with chelating agent system at various solution pH.

From Figure 4.8 and 4.9, the equilibrium solubility of both calcium and magnesium in the EO9 system shows increasing equilibrium solubility with increasing solution pH in contrast to MES. Since nonionic stearic acid/nonionic EO9 is not well co-micellizing at low pH. nonionic/nonionic mixed micelles cannot improve the equilibrium solubility of soap scum due to the lack of synergy to form micelle. While at high solution pH, stearate anion/nonionic EO9 mixed micelles have increased equilibrium solubility owing to the co-micellize synergism. The performance in the dissolution of calcium soap scum in Figure 4.8 was found that GLDA showed the highest soap scum dissolution follow by EDDS and EDTA, which showed similar equilibrium solubility. At solution pH 11, the equilibrium solubility of calcium soap scum has improved in EDDS compared to EDTA because the ratio of stearate anion to nonionic stearic acid was increased. Thus, the synergism of stearate anion/nonionic EO9 mixed micelles improved the dissolution of calcium soap scum at the highest solution pH. In Figure 4.9, GLDA also showed the highest equilibrium solubility in magnesium soap scum followed by EDDS and EDTA as same order as in Figure 4.8 but the calcium has the higher equilibrium solubility.

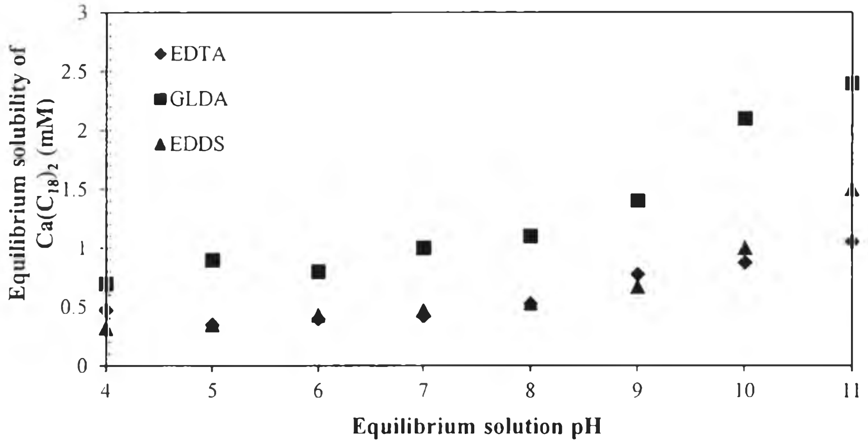


Figure 4.8 The Equilibrium solubility of calcium soap scum in EO9 with chelating agent system at various solution pH.

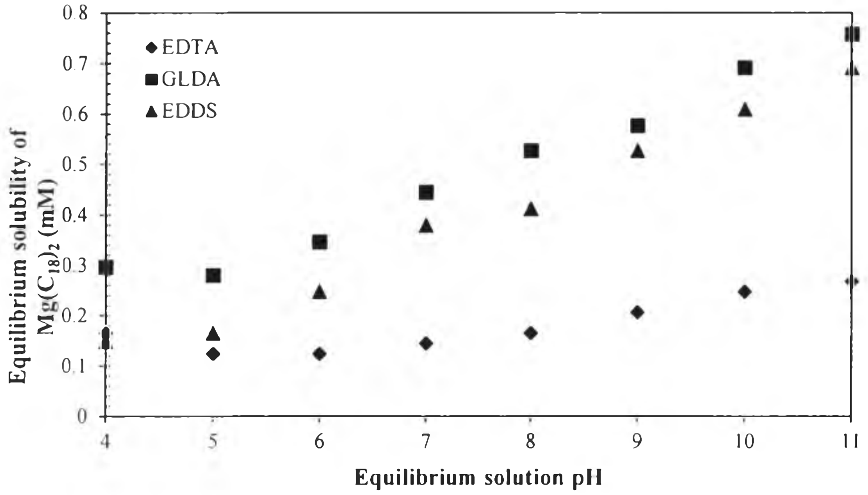


Figure 4.9 The Equilibrium solubility of magnesium soap scum in EO9 with chelating agent system at various solution pH.

The highest equilibrium solubility of both soap scum was found in the DDAO system according to Figure 4.10 and 4.11. Solubility was exceedingly higher in magnitude than the MES and EO9 systems due to the greater mixed micelle synergism of nonionic stearic acid/cationic DDAO at low solution pH and stearate anion/zwitterionic DDAO at high solution pH. For chelating agent comparison, it was found that the effectiveness in chelation for the dissolution of both soap scum is in the same order as those in MES and EO9 systems (GLDA > EDDS > EDTA). By comparing calcium and magnesium soap scum, the equilibrium solubility of calcium soap scum is significantly higher than that of magnesium soap scum. Since the Ksp of calcium soap scum is greater than that of magnesium soap scum about two times (Itsadanont, 2011) Moreover, calcium soap scum had much smaller particle size and higher particle dispersion than magnesium soap scum, which is easier to dissolve in surfactant solution.

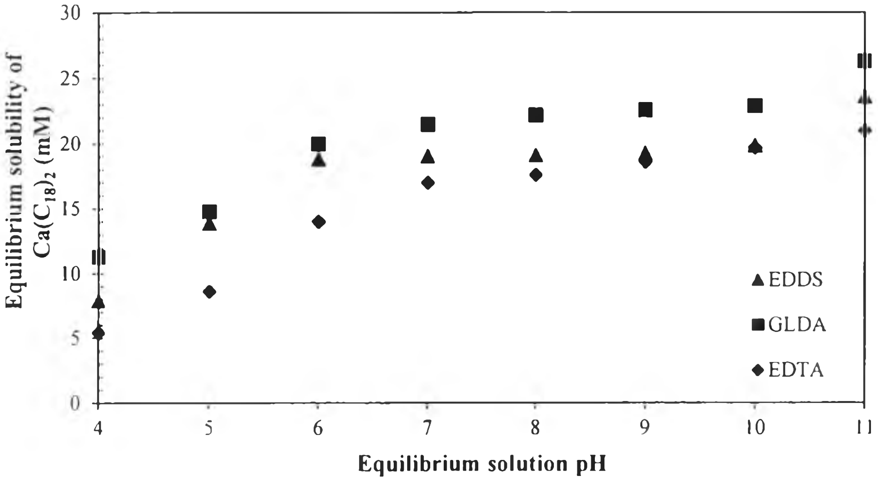


Figure 4.10 The Equilibrium solubility of calcium soap scum in DDAO with chelating agent system at various solution pH.

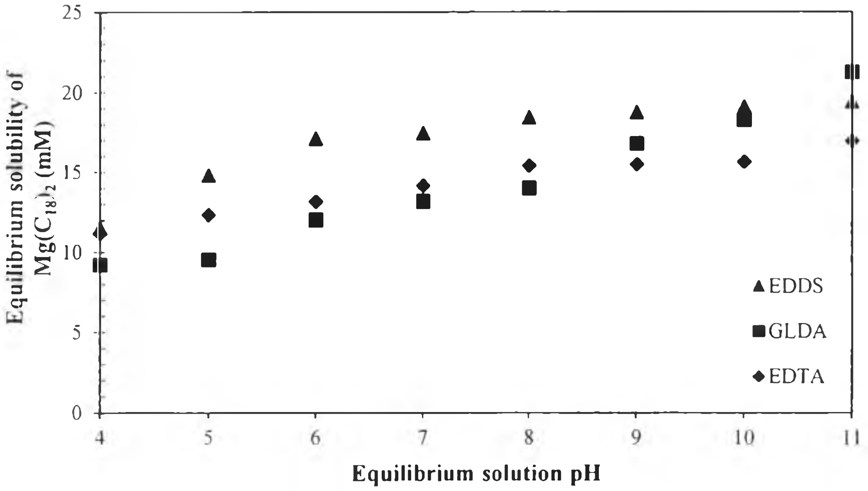


Figure 4.11 The Equilibrium solubility of magnesium soap scum in DDAO with chelating agent system at various solution pH.