CHAPTER IV
RESULTS AND DISCUSSION

By following the procedure and all chemicals used in the experiments from previous work, the models of soap scum are changed in order to study the synthesized soap scum from steric acid (S) or Lux commercial soap (CS) and water containing with pure Ca, pure Mg, mixed Ca and Mg at a molar ratio of Ca:Mg=4:1 or natural hard water (NHW) with a high hardness in different solution systems: pure water, tetrasodium glutamate diacetate /dimethyldodecylamine oxide (Na_4GLDA /DDAO), and disodium ethylene diaminetetraacetate/dimethyldodecylamine oxide (Na_2EDTA /DDAO) at a constant temperature of 25°Cand solution pH 11which is the optimum condition for the highest equilibrium solubility and dissolution rate of soap scums (Itsadanont*et al.*, 2013). So this condition would be used for all experiments.

4.1 Characteristics of Natural Hard Water

Table 4.1 shows the results of characteristics in natural hard water. It was found that the pH was 7.7 and the concentration ratio of the calcium to magnesium was 3.38 to 1 by weight and 2.05 to 1 by molar ratio.The total hardness was 530 mg/l as $CaCO_3$.

Table 4.1 Characteristics of natural hard water

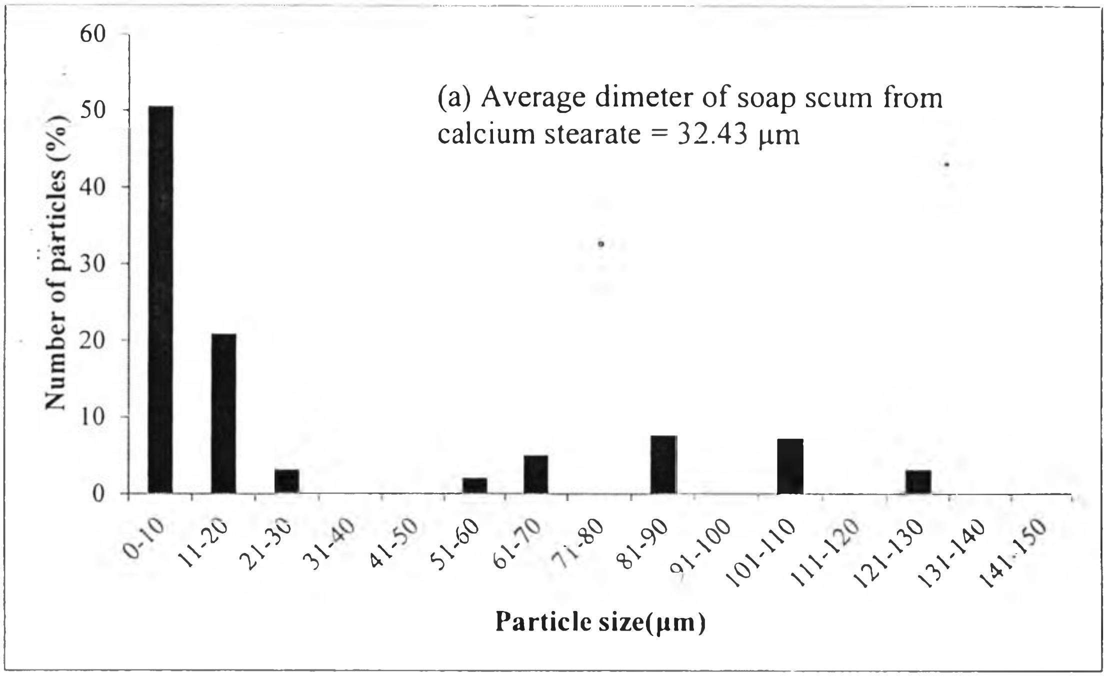
Parameter	Unit	Value
Calcium	ppm	142
Magnesium	ppm	42
Sodium	ppm	8.6
Potassium	ppm	138.5
Iron	ppm	0.26
Aluminium	ppm	0.3

Table 4.1 Characteristics of natural hard water (con't)

Parameter	Unit	Value
Zinc	ppm	0.001
Manganese	ppm	0.002
Strontium	ppm	0.65
Nitrate	ppm	2.1
Sulfate	ppm	26.3
Chloride	ppm	30
Conductivity	µs	579.9
Total hardness	ppm as $CaCo_3$	530
Total dissolved solid	ppm	433.9

4.2 Characteristics of Synthesized Soap Scum

The soap scum synthesized from stearic acid in natural hard water (NHW-S) has ratio calcium to magnesium = 4.60:1 by weight and 2.79:1 by molar ratio closed to the ratio of calcium to magnesium in natural hard water whereas commercial soap (NHW-CS) shown the different ratio is 1.57:1by weight and 1:1 by molar ratio which is not consistent with the theory ratio analyzed by AAS. According to the characteristic of natural hard water, it showed that the effects fromother ions in natural hard water and the commercial soap ingredient also affect to the formation of calcium and magnesium soap scum.However, the calcium soap scum formation was dominated form because amount of calcium ion higher than magnesium ion in natural hard waterresulting on more opportunities for precipitation.The particle sized distribution and average diameter of each soap scum are shown in figure 4.1 and 4.4. The particle sized distribution of soap scum from stearic acid in natural hard water showedthe homogeneous small sized trend while other soap scums are separated into two groups including small group and large group. The average diameter of stearic acid in natural hard water is 23.15 µmwhich is smaller sized than from commercial soap (78.87µm)obviously referringtosoap scum will be agglomerate. For pure calcium soap scum compared to pure magnesium soap scum generated from commercial soap, the average calcium and magnesium soap scum sized werenearly the same sized 47.27 and 52.28 μm. For 4:1 Ca/Mg ratio, the soap scum synthesized from stearic acid (42.32 μm) has smaller sized than soap scum synthesized from commercial soap (73.51μm). Therefore, Soap scum synthesized from various fatty acids in commercial soap which is more soluble in water than pure fatty acid formsbigger soap scum precipitation.



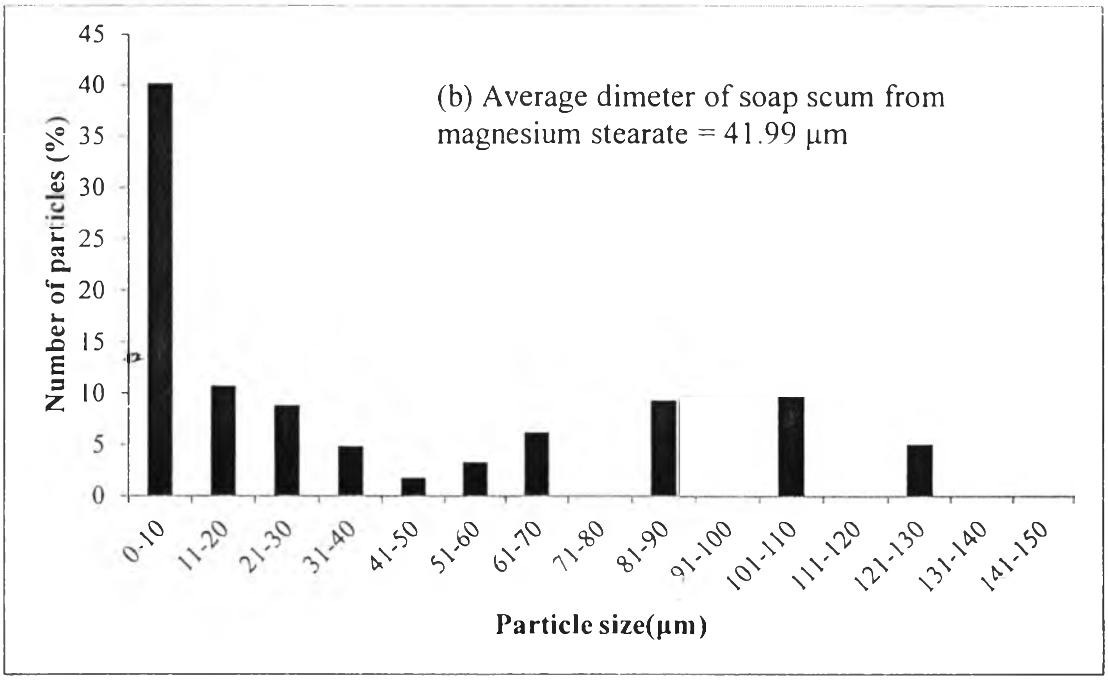
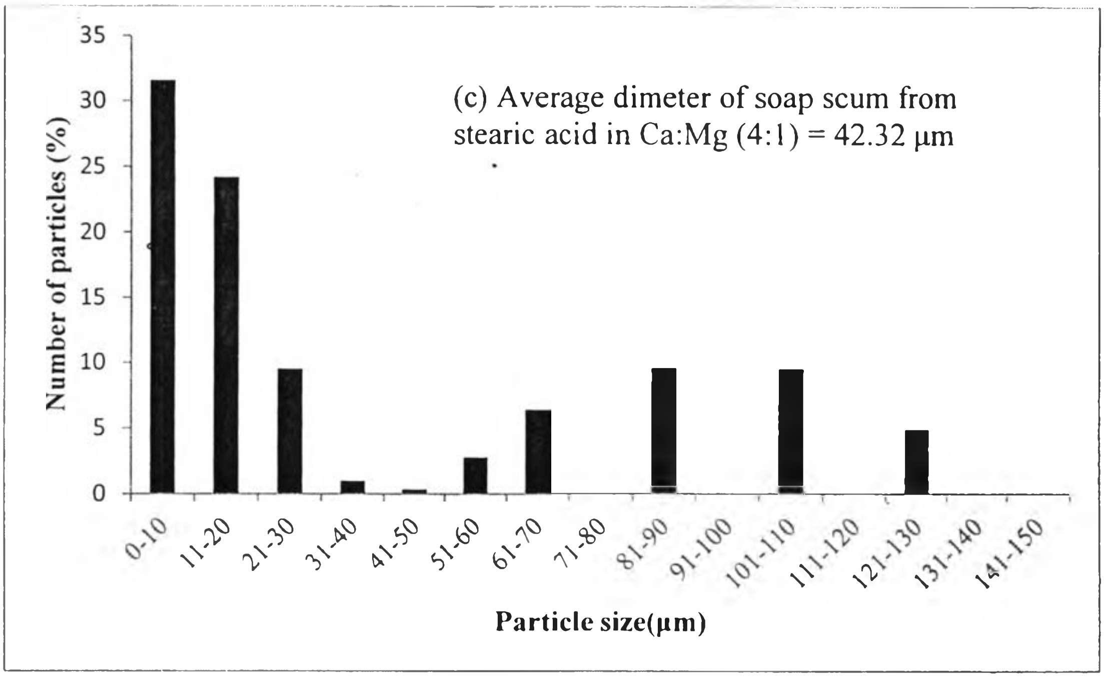


Figure 4.1 Particle sized distribution and average diameter of calcium stearate (a) and magnesium stearate (b).



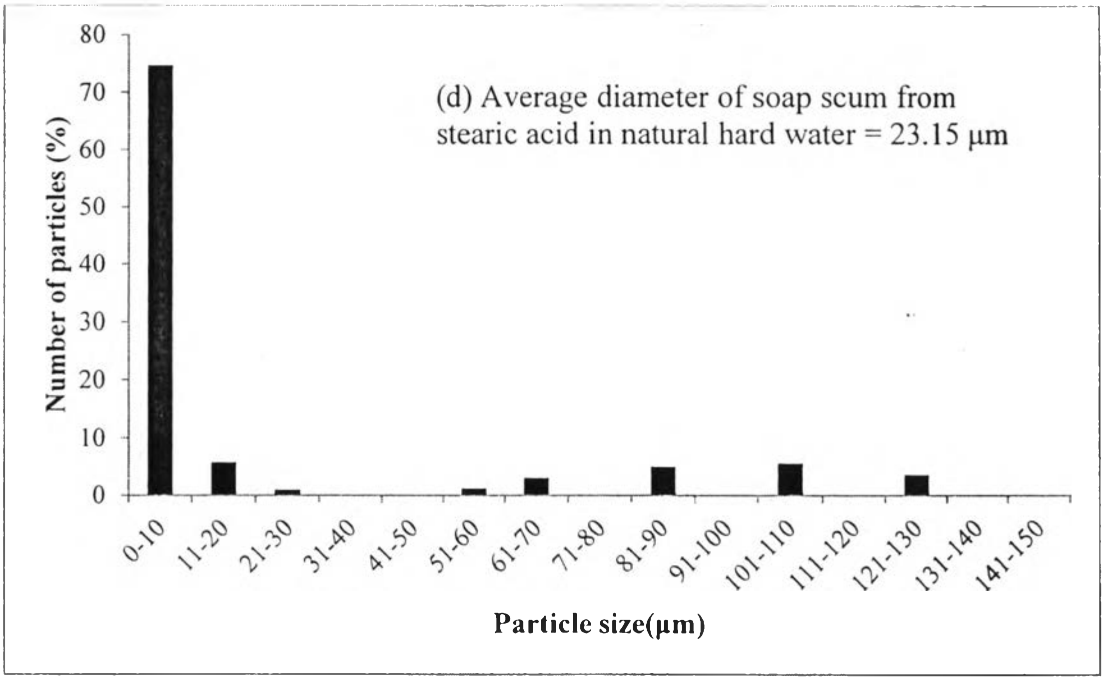
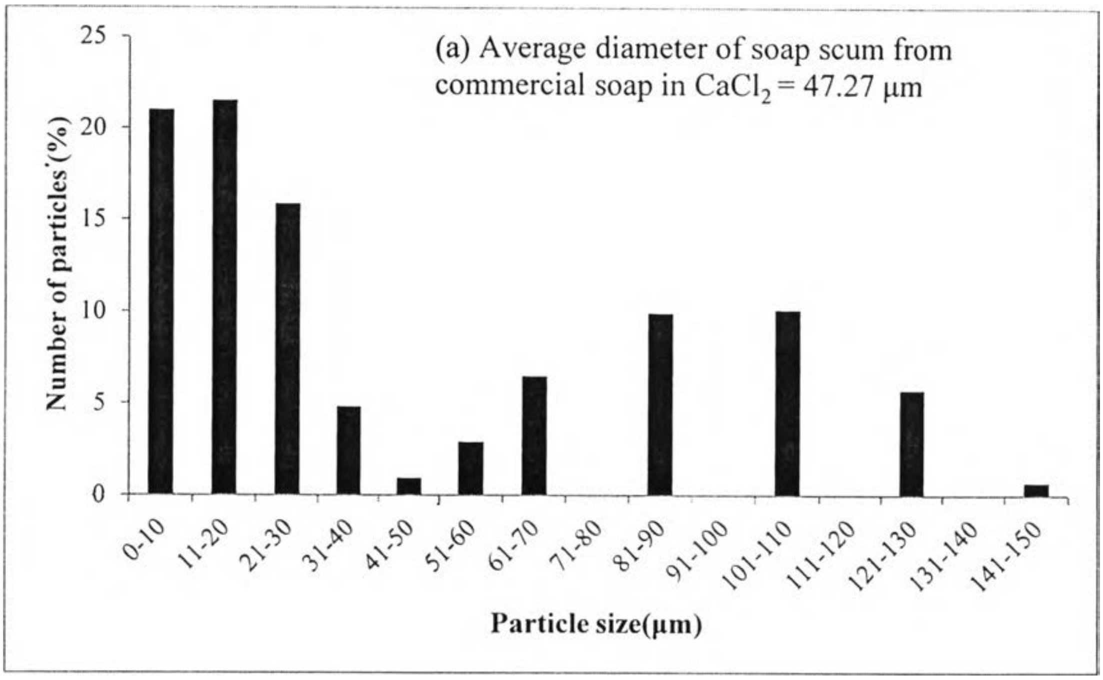


Figure 4.2 Particle sized distribution and average diameter of stearic acid in 4:1 Ca/Mg (c) and natural hard water (d).



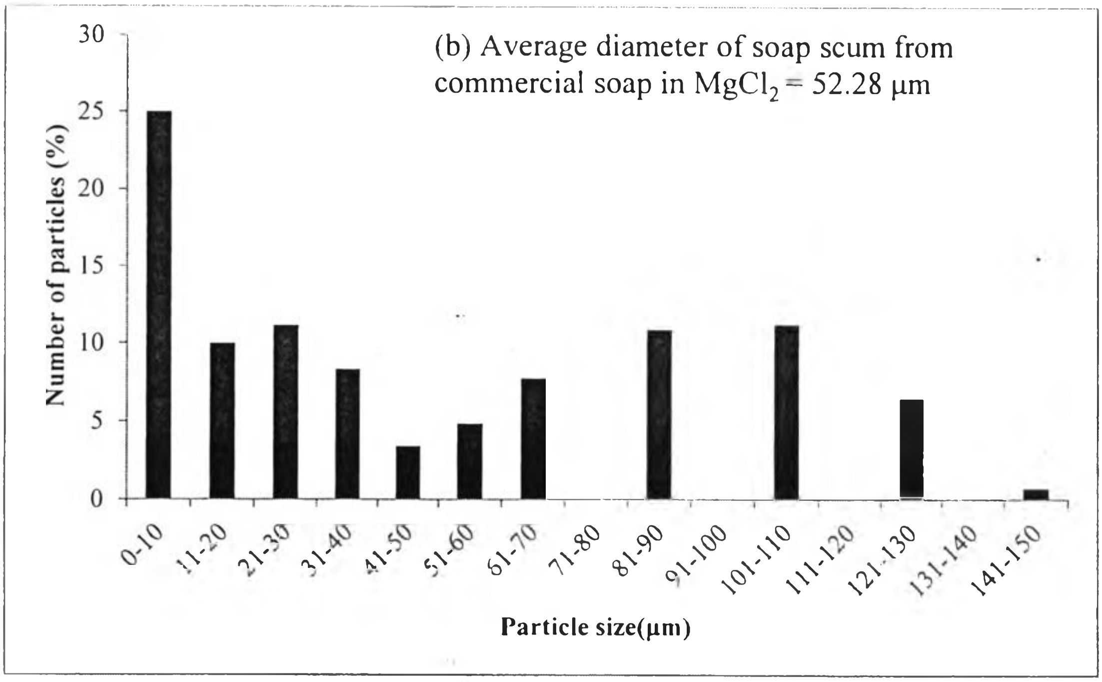
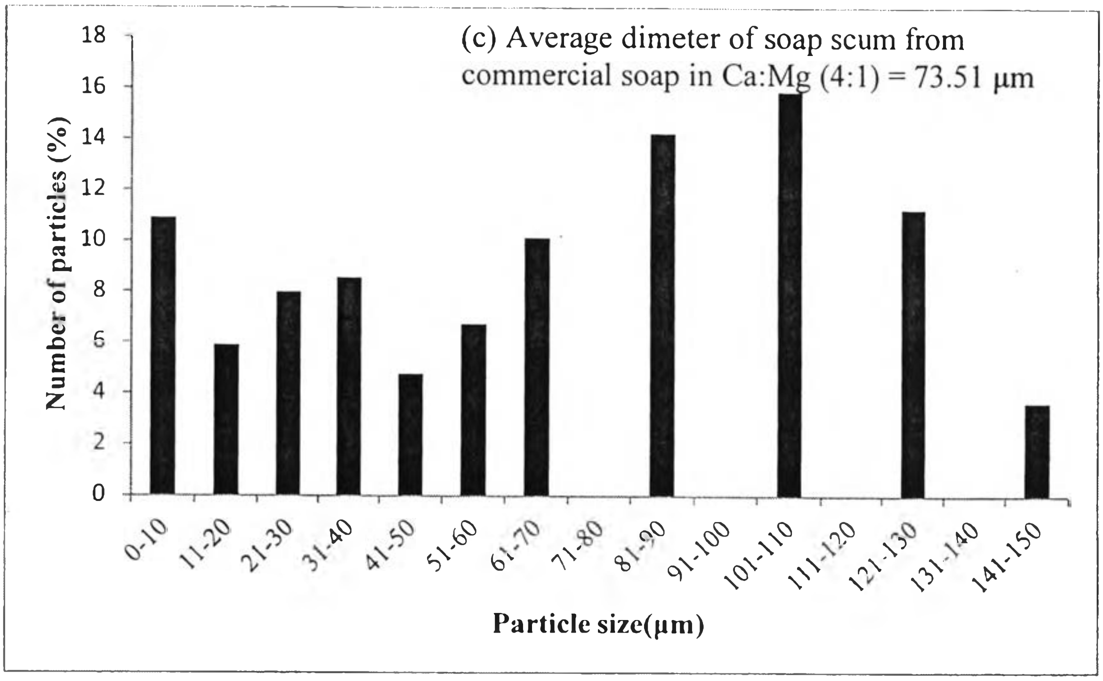


Figure 4.3 Particle sized distribution and average diameter of commercial soap in pure calcium (a) and pure magnesium (b).



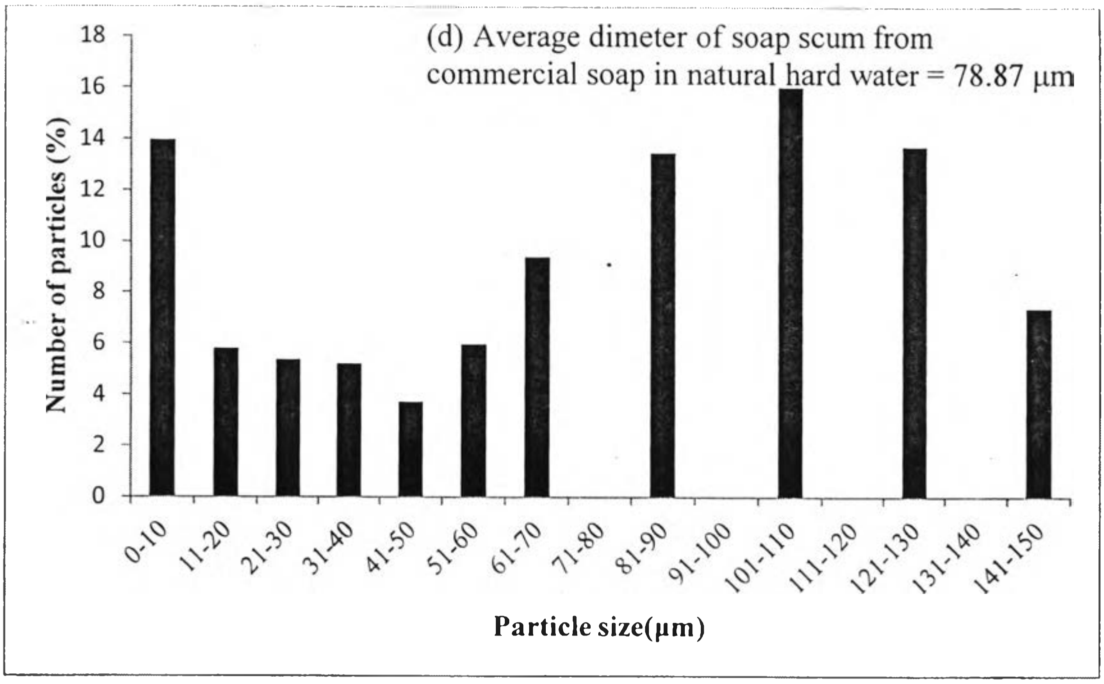


Figure 4.4 Particle sized distribution and average diameter of commercial soap in 4:1 Ca/Mg (c) and natural hard water (d).

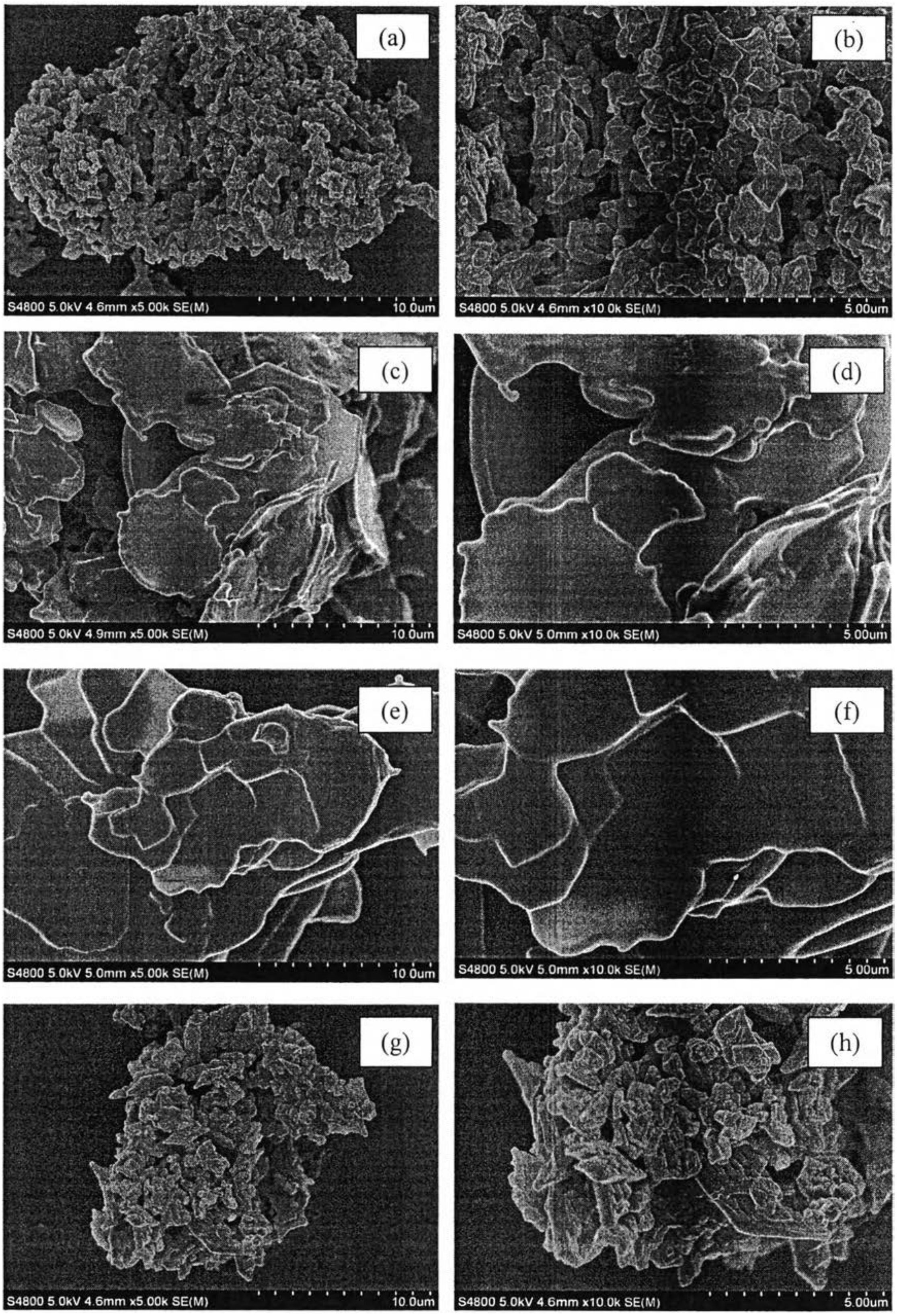


Figure 4.5 SEM images of calcium stearate (a, b), magnesium stearate (c, d), 4:1 Ca/Mg stearate (e, f) and stearic acid in natural hard water (g,h).

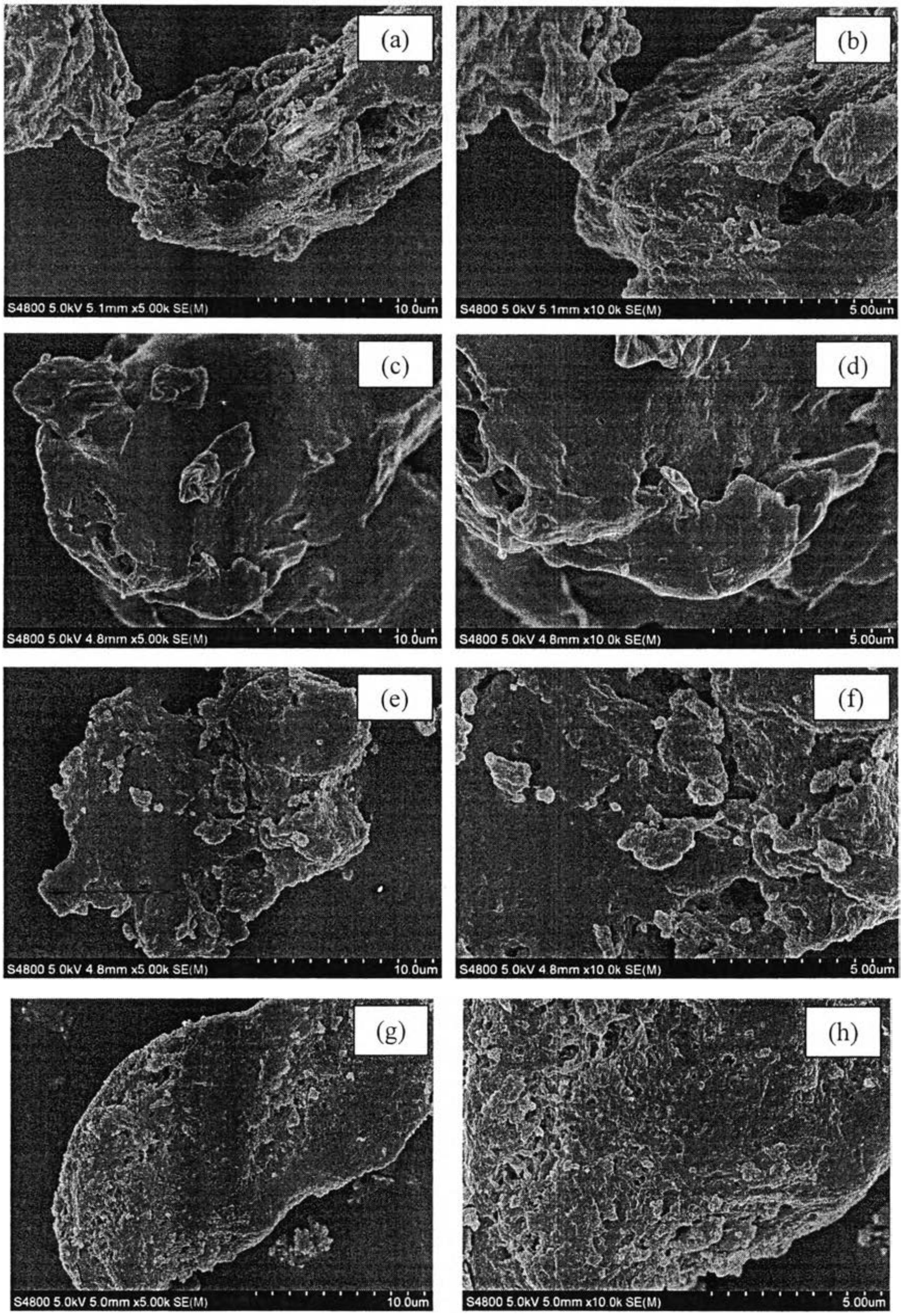


Figure 4.6 SEM image of commercial soap in pure calcium (a, b), pure magnesium (c, d), 4:1 Ca/Mg (e, f) and natural hard water (g, h).

In figure 4.5 and 4.6 show the SEM images of synthesized soap scums shown that soap scums synthesized from stearic acid had smooth and non-porous surface scum synthesized from commercial soap had rough and non-porous surface. However, the calcium and magnesium stearate soap scum had smaller sized than commercial soap scum that confirmed the result from particle sized. For calcium and magnesium stearate in hard water, the surface morphologies are also smooth and non-porous that was consistently with the previous work (Itsadanont *et al.*, 2013).

The FTIR patterns of stearic acid were shown in figure 4.7-4.8. The stearic acid reacted completely with calcium and magnesium ion in pure calcium, pure magnesium,4:1Ca/Mg and hard water because of no peak of –OH of carboxylic group. The peak at 1576.41and 1576.55 indicated COO^-in the carboxylic salts (Lambert *et al.*, 2010). These result can confirm that calcium and magnesium ions reacting with stearicacid completely and produce calcium and magnesium stearate. But in the case of soap scum synthesized from commercial soap shown in Figure 4.9 - 4.10, there were still found peak of –OH in all system including natural hard water, $CaCl_2$, $MgCl_2$and 4:1 Ca/Mg. It means that the reaction was not complete. The explanation is soap scum may agglomerate to bigger size then wrapping the remaining reactant inside the particle before the entirely reaction. Another one is the remaining reactant like to attach the soap scum so it is hard to wash out.That can cause the peak –OH at 3700-3100cm^{-1}. For other peaks, CH_3 and - CH_2in aliphatic compounds (CH-antisym and CH-sym stretching) presented at 2990-2850 cm^{-1} (Lambert *et al.*, 2010).

Figure 4.11 – 4.12 showed XRD analysis of soap scum synthesized from stearic acid, the crystalline size of calcium stearate (36.89 nm) was smaller than magnesium stearate (57.02 nm) and also in the mixed 4:1 Ca/Mg stearate (39.40 vs 56.01nm respectively). Except in natural hard water, the size of both calcium stearate and magnesium are nearly the same (39.53 vs. 39.85 nm, respectively). The crystalline sizes of calcium stearate and magnesium stearate in commercial soap (Figure 4.13) are 18.20 and 22.67 nm respectively. Moreover, the calcium and magnesium stearate in commercial soap scumwith 4:1 Ca/Mg shown in Figure 4.14 are 19.04 and 20.15 nm respectively which has nearly size in commercial soap scum

with natural hard water (16.11 vs 16.31 nm, respectively).Therefore, the ingredients of commercial soap and also mineral in natural hard water affect to the crystalline arrangement by decreasing the crystalline sized of calcium and magnesium stearate.

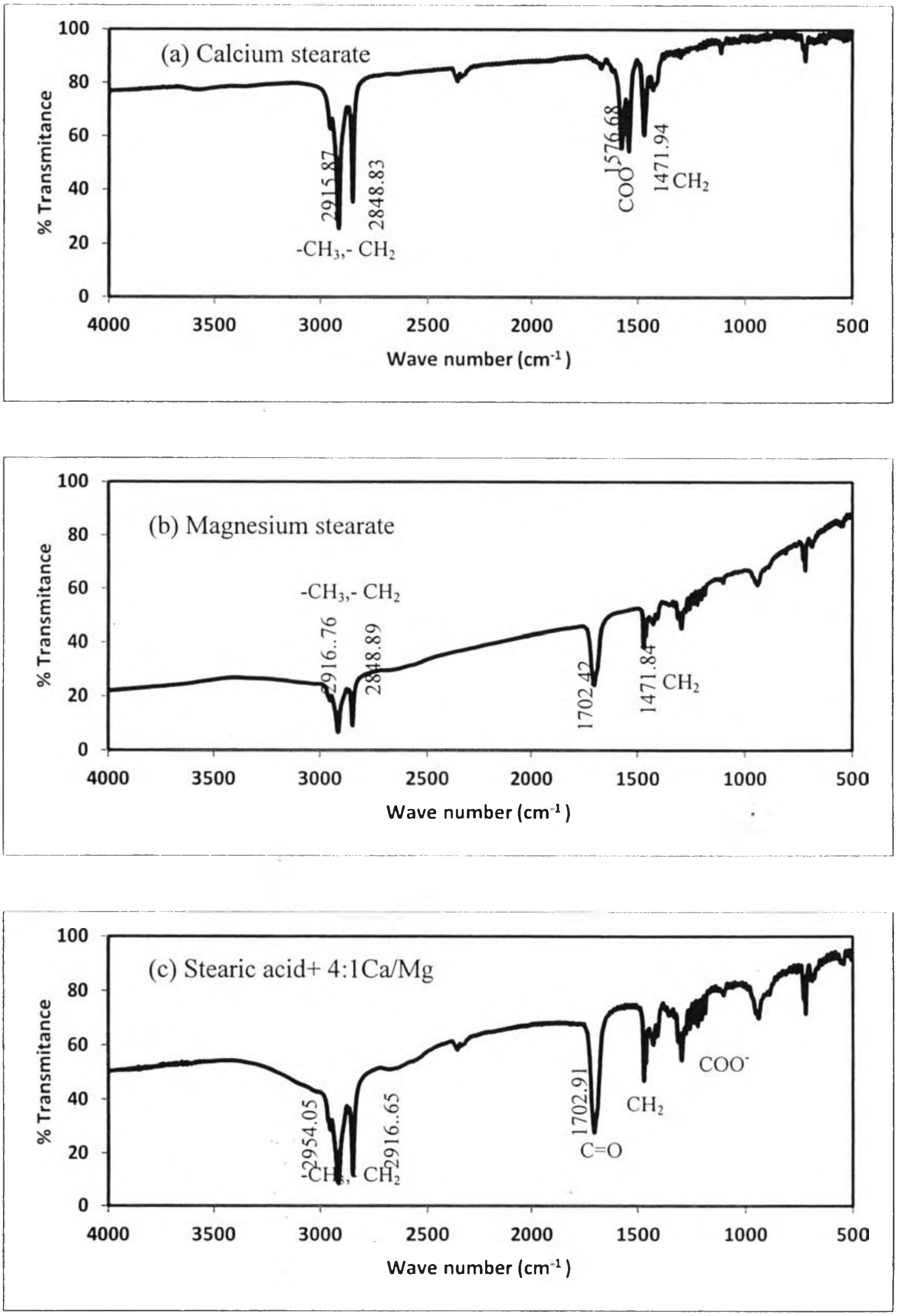


Figure 4.7 FTIR spectra of soap scums synthesized from stearic acid in pure calcium (a) pure magnesium (b) and 4:1 Ca/Mg (c).

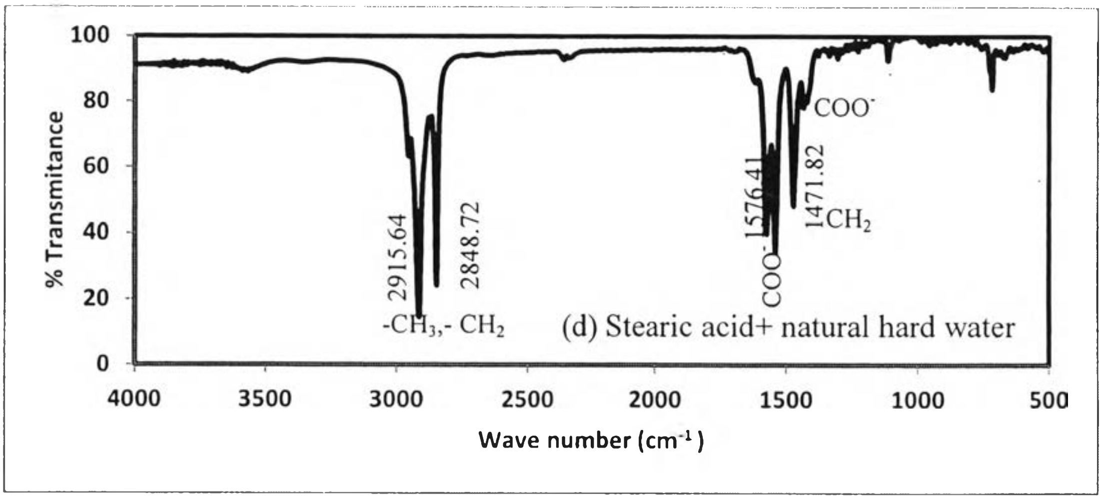


Figure 4.8 FTIR spectra of soap scum synthesized from stearic acid in natural hard water (d).

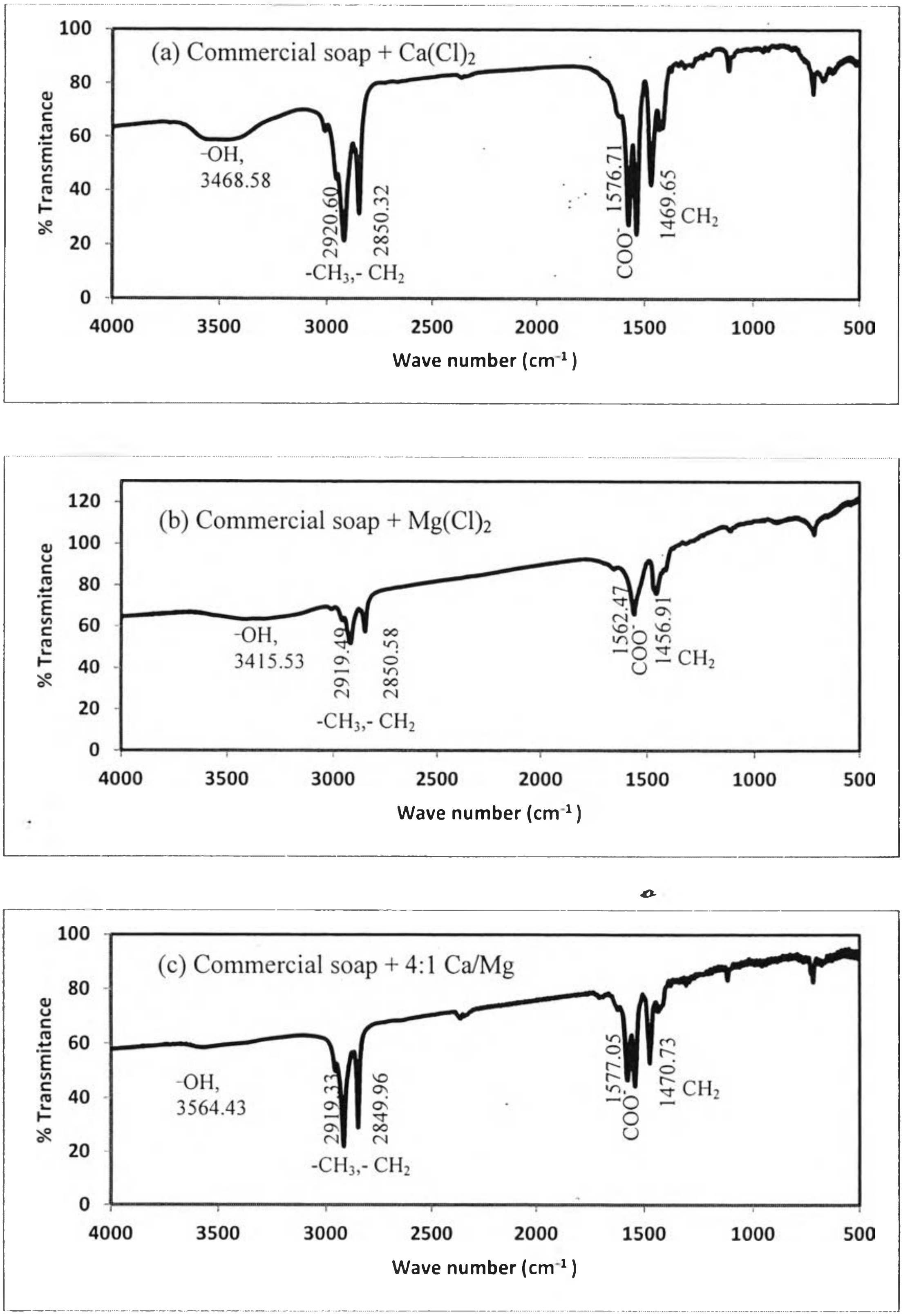


Figure 4.9 FTIR spectra of soap scums synthesized from commercial soap in pure calcium (a), pure magnesium (b) and 4:1 Ca/Mg (c).

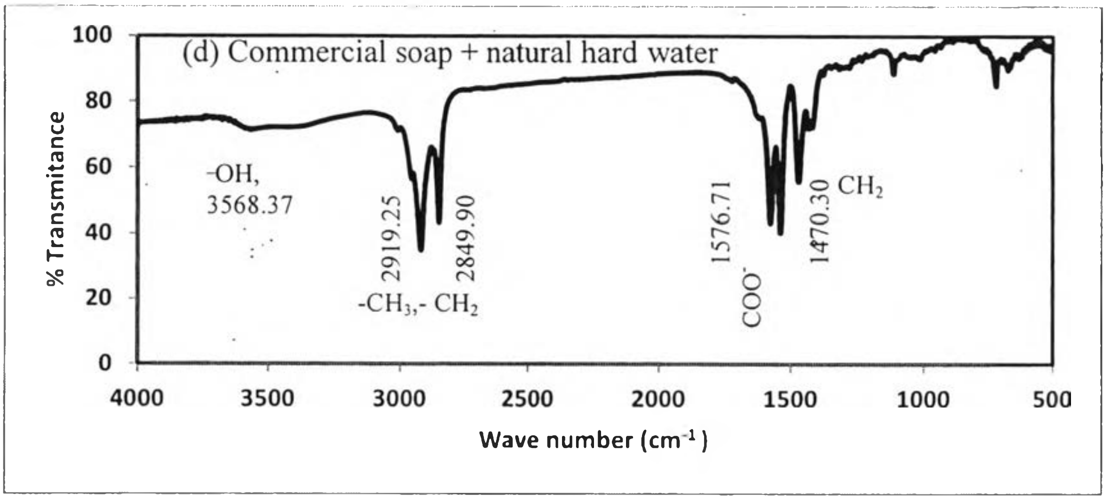
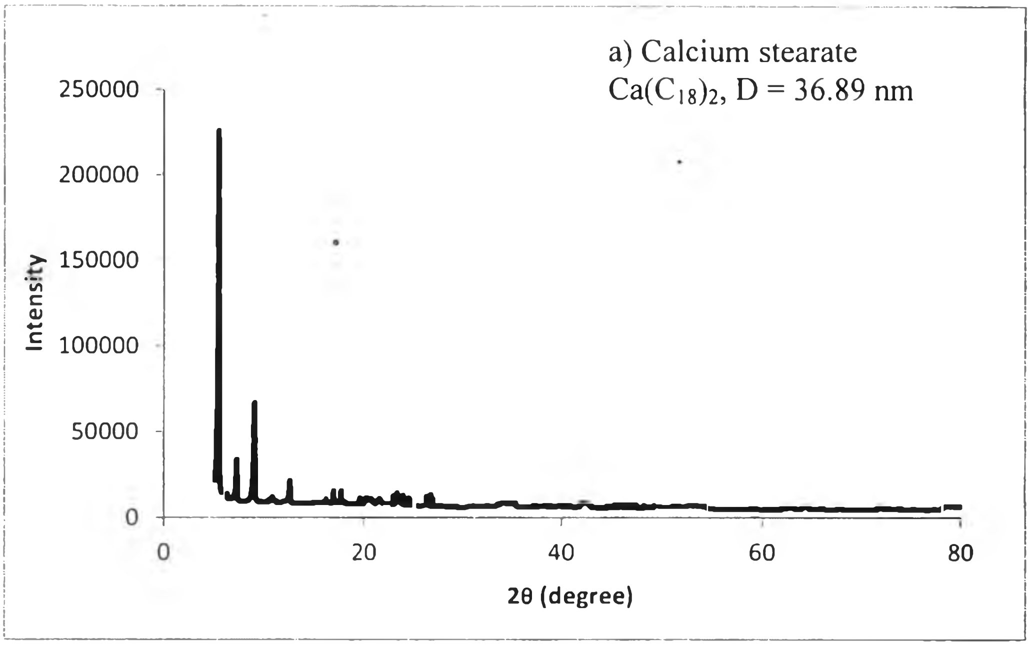


Figure 4.10 FTIR spectra of soap scum synthesized from commercial soap in natural hard water (d).



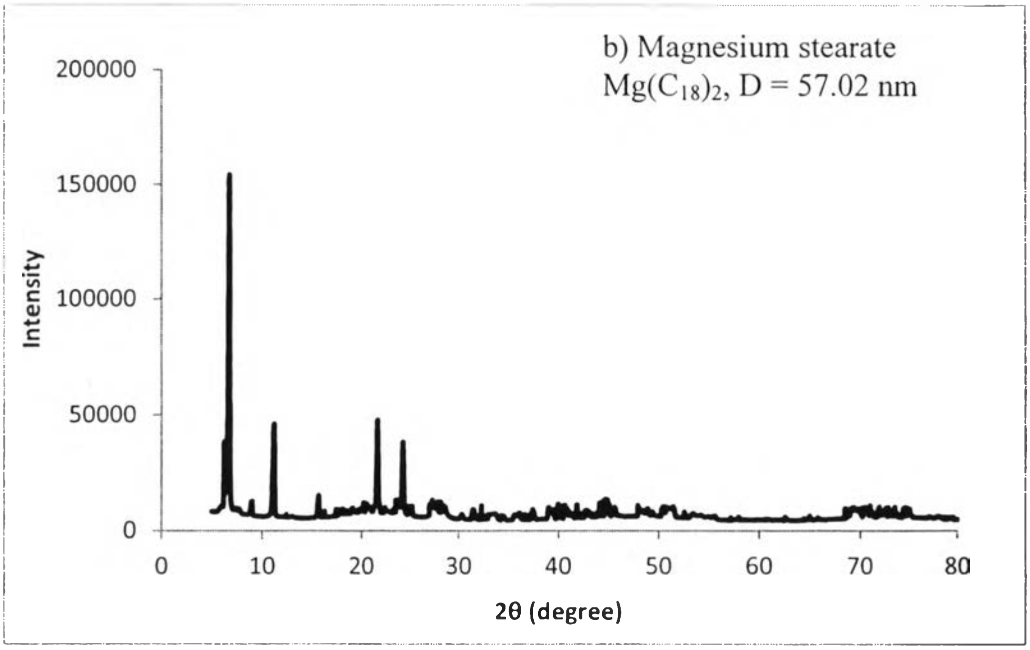
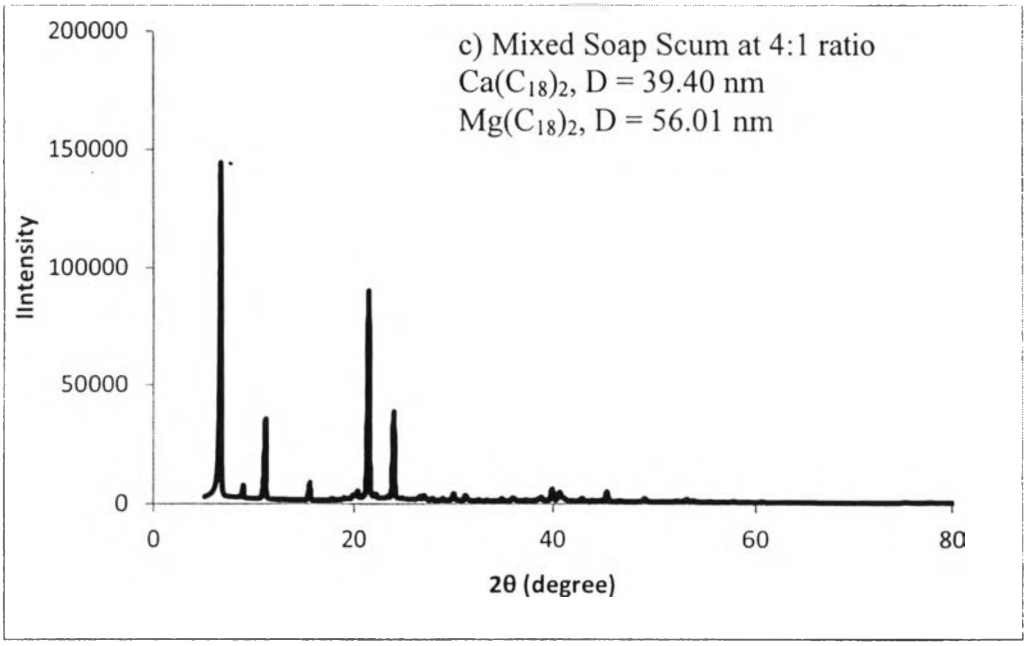


Figure 4.11 XRD diffraction patterns of calcium state (a) and magnesium stearate (b).



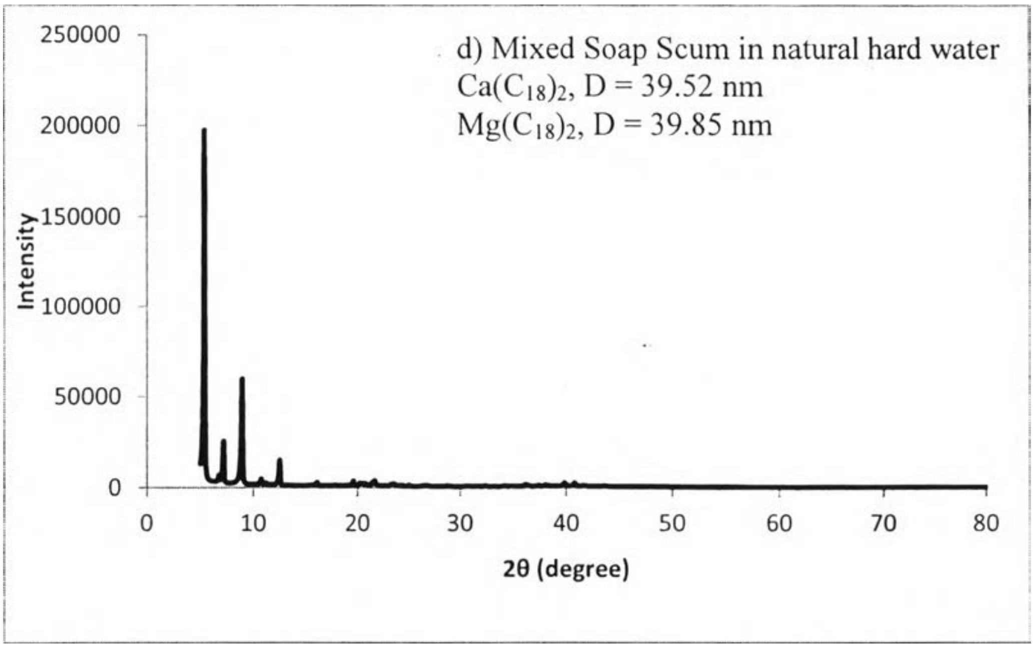
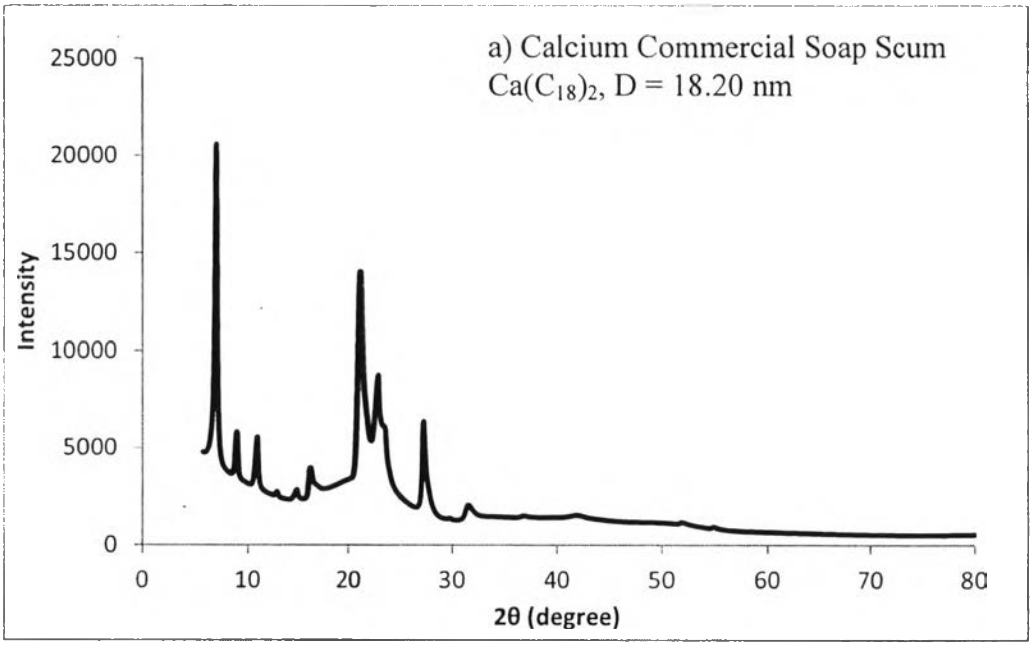


Figure 4.12 XRD diffraction patterns of soap scum synthesize from stearic acid in 4:1 Ca/Mg (c) and natural hard water (d).



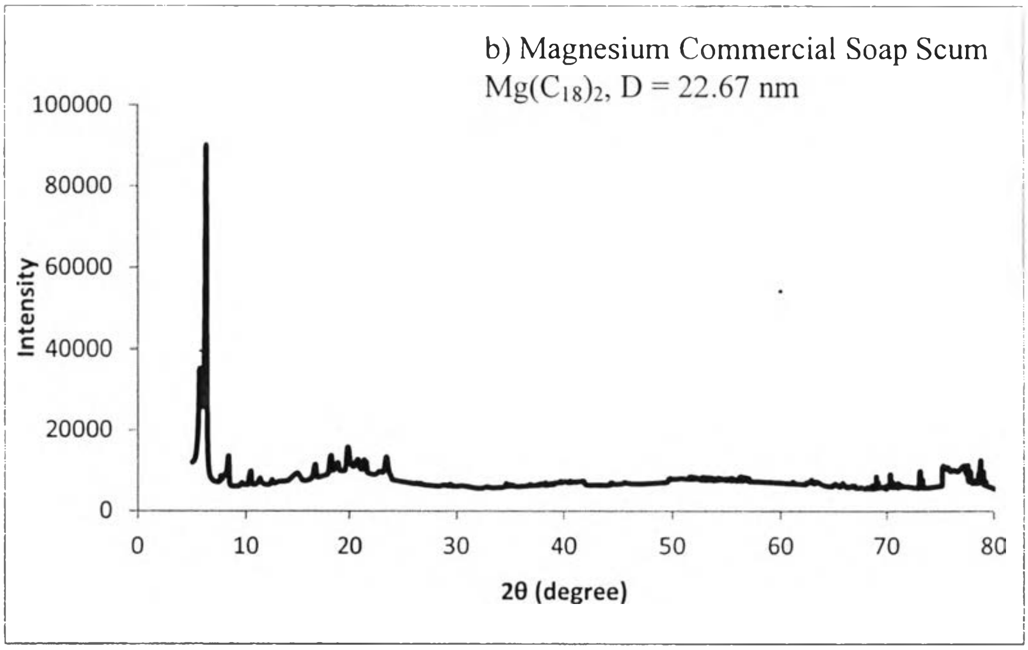
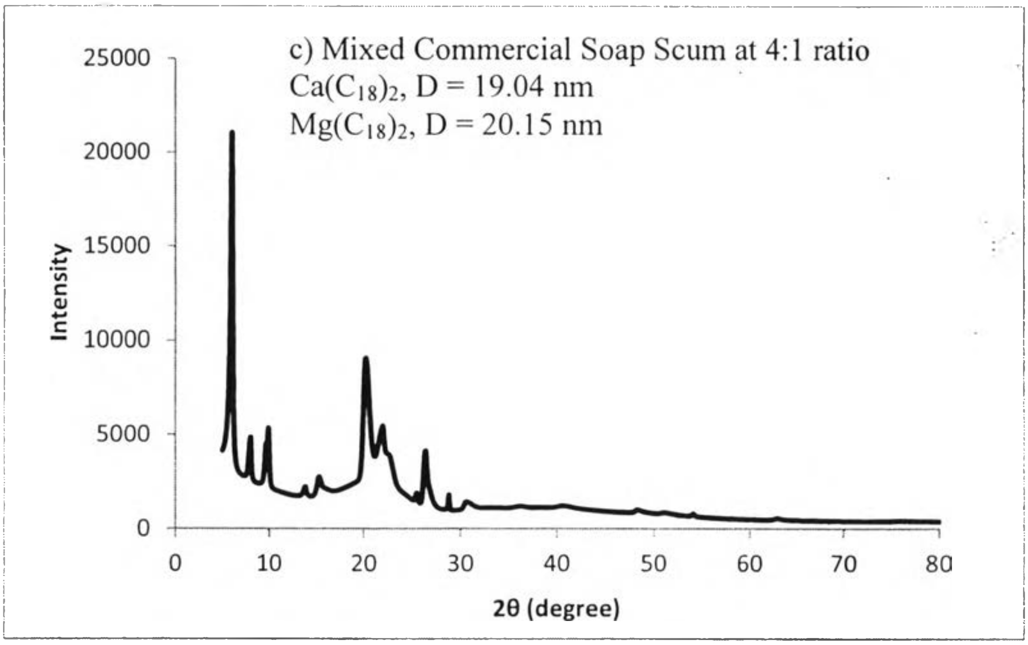


Figure 4.13 XRD diffraction patterns of soap scums synthesize from commercial soap in pure calcium (a) and pure magnesium (b).



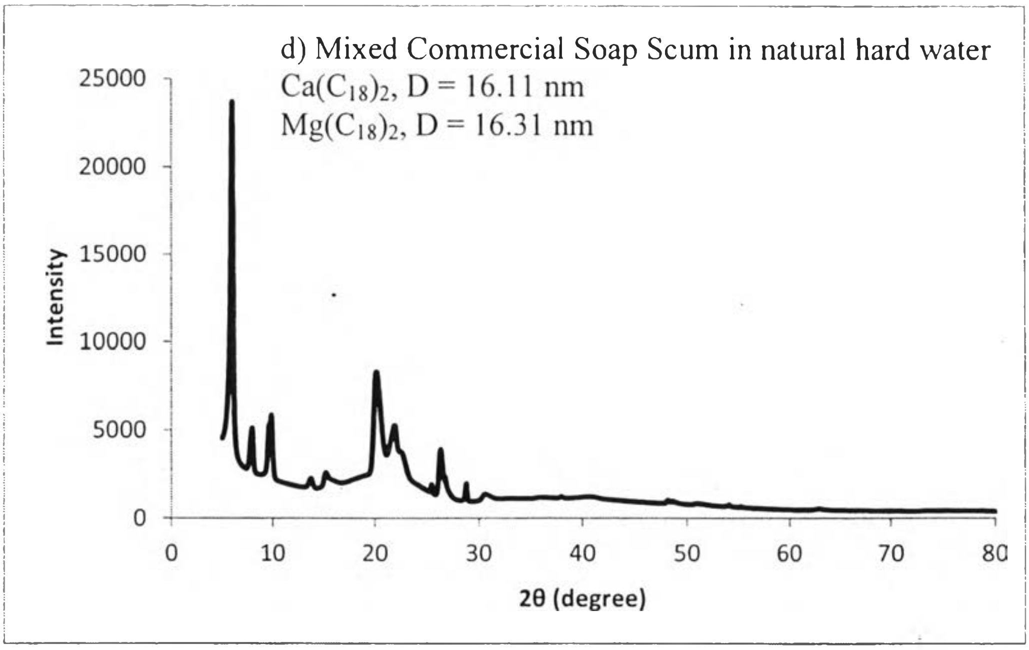


Figure 4.14 XRD diffraction patterns of soap scums synthesize from commercial soap in 4:1 Ca/Mg (c) and natural hard water (d).

4.3 Equilibrium Solubility of Pure Soap Scum

Figure 4.15 and 4.16 show the equilibrium solubility of pure calcium soap scumand pure magnesium soap scum in different optimum solution systems including pure water at pH 4, DDAO/Na_2EDTA at pH 11 and DDAO/Na_4GLDA at pH 11 under a constant temperature of 25 °C.

From previous work, the highest equilibrium solubility of calcium stearate and magnesium stearate in water were observed at pH 4. So, this condition without surfactant was used as one of the solution systems. This study found that not only calcium and magnesium stearate in pure water pH 4 has lower equilibrium solubility than in the presence of surfactant and chelating agent at pH 11 but also the same trend of calcium and magnesium commercial soap scum. Because the structure of fatty acid depends on solution pH leading to the protonation. At low solution pH, soap scum will be protonated to nonionic fatty acid which has low solubility (K_{sp}).

In surfactant-chelating agent system, the effect of DDAO surfactant in the presence of chelating agent (Na_2EDTA or Na_4GLDA) was investigated at optimum pH 11. The result showed that the equilibrium solubility of calcium stearate is as high as calcium commercial soap scum in DDAO/Na_2EDTA and DDAO/Na_4GLDA. For magnesium stearate, the equilibrium solubility is very low compared to magnesium commercial soap scum. This means magnesium commercial soap scum from various fatty acid can enhance the equilibrium solubility than magnesium stearate obviously. However, the equilibrium solubility of magnesium were lower than calcium due to the lower stability constant of Na_2EDTA or Na_4GLDA in magnesium metal. The mechanism of soap scum dissolution in the DDAO surfactant mixed with Na_2EDTA or Na_4GLDA can be explained as at high solution pH, the chelating agent in most effective form (Y^{4-}) binds with divalent cation (Ca^{2+} and Mg^{2+}), the remaining anionic of fatty acid will co-micellize with surfactant in zwitterionic form. Therefore, the equilibrium solubility of soap scum can improve. The calcium soap scum is easily soluble in all solution systems compared to magnesium soap scum from both stearic acid and commercial soap scum.

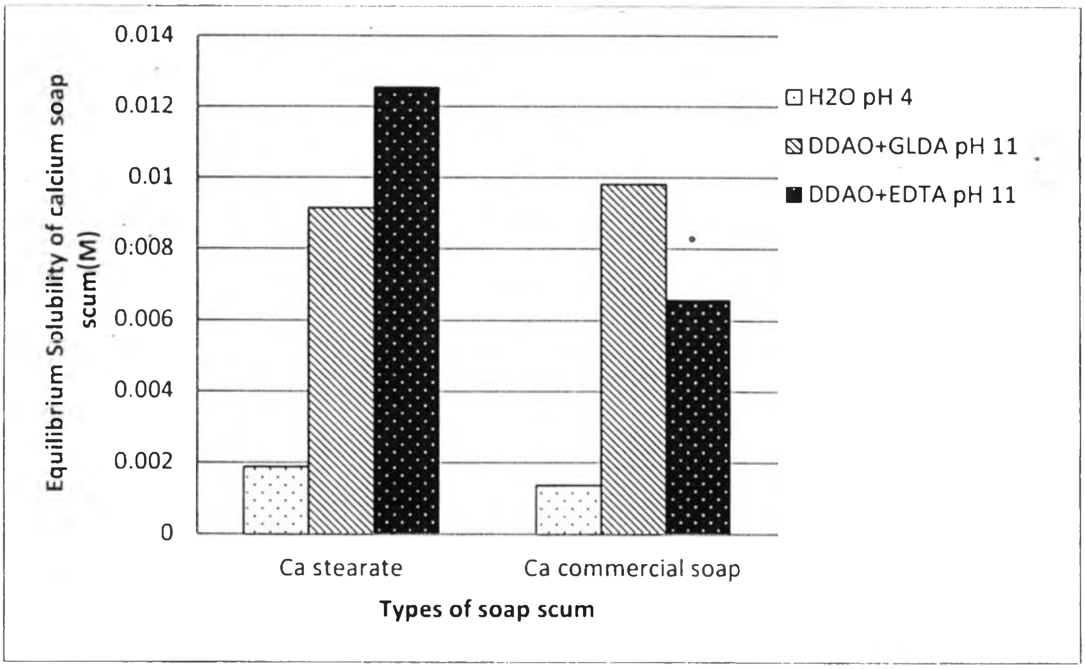


Figure 4.15 Equilibrium solubility of pure calcium soap scumin different optimum systems and a temperature of 25 °C.

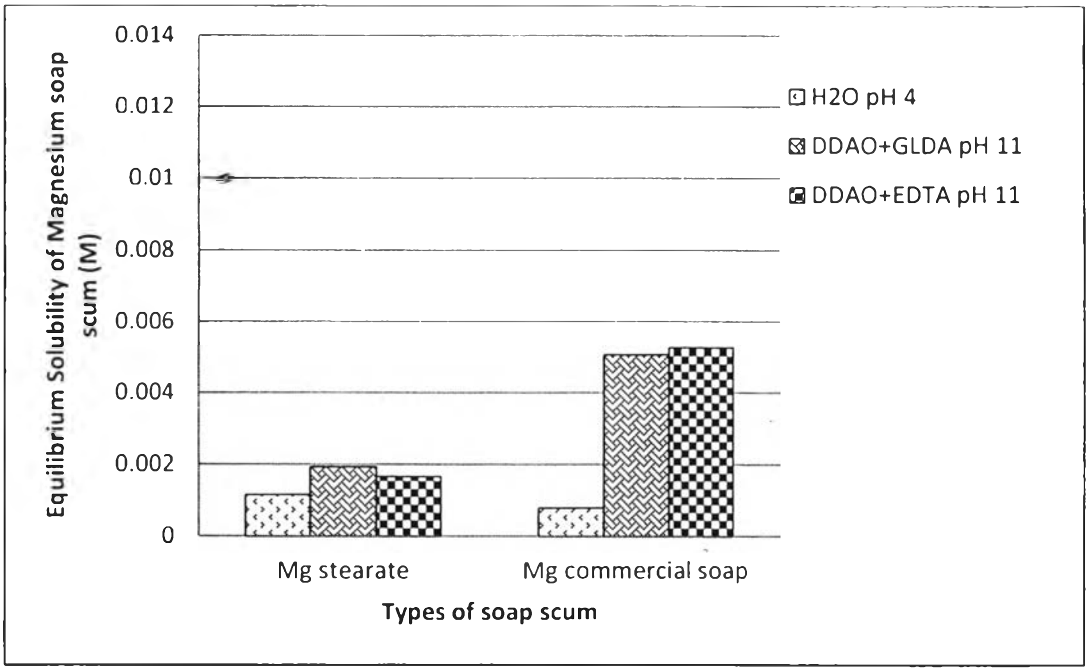


Figure 4.16 Equilibrium solubility of pure magnesium soap scumin different optimum systems and a temperature of 25 °C.

4.4 Equilibrium Solubility of Mixed Soap Scum

The equilibrium solubility of individual calcium and magnesium mixed soap scum synthesized from 4:1 Ca/Mg ratio and natural hard water are shown in figure 4.17 – 4.18 and 4:19 – 4.20 respectively. The result showed that calcium mixed commercial soap scum in 4:1 Ca/Mg ratio is higher equilibrium solubility than calcium mixed stearate soap scum since various fatty acids can improve the dissolution greater than calcium stearate. But both of calcium mixed stearate soap scum and calcium mixed commercial soap scum synthesized from natural hard water were insignificant different. This can discuss by the effect of impurity in natural hard water affecting to the solubility more than types of fatty acid. The trend in pure water is still lower than DDAO/Na_2EDTA and DDAO/Na_4GLDA which are nearly the same.

Due to the low solubility and the small amount of magnesium soap scum in 4:1 Ca/Mg ratio and natural hard water, the equilibrium solubility was not much different in pure water at pH 4, DDAO/Na_2EDTA at pH 11 and DDAO/Na_4GLDA at pH 11. The magnesium mixed stearate soap scum and magnesium mixed commercial soap scum gave the low equilibrium solubility.

The total equilibrium solubility of calcium and magnesium mixed commercial soap scum in 4:1 Ca/Mg ratio and natural hard water showed in Figure 4.21 and 4.22 respectively. For mixed soap scum, the total equilibrium solubility of calcium and magnesium mixed stearate soap scum in 4:1 Ca/Mg ratio was the lowest equilibrium solubility among those of mixed soap scums.

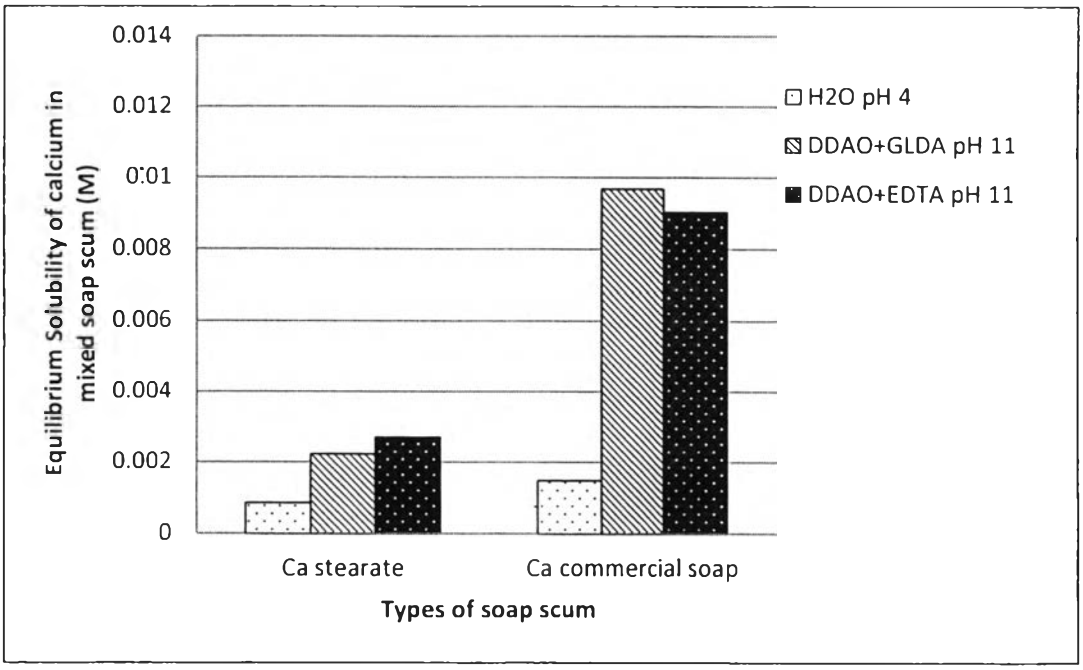


Figure 4.17 Equilibrium solubility of calcium mixed soap scum at 4:1 Ca/Mg ratio in different optimum systems and a temperature of 25 °C.

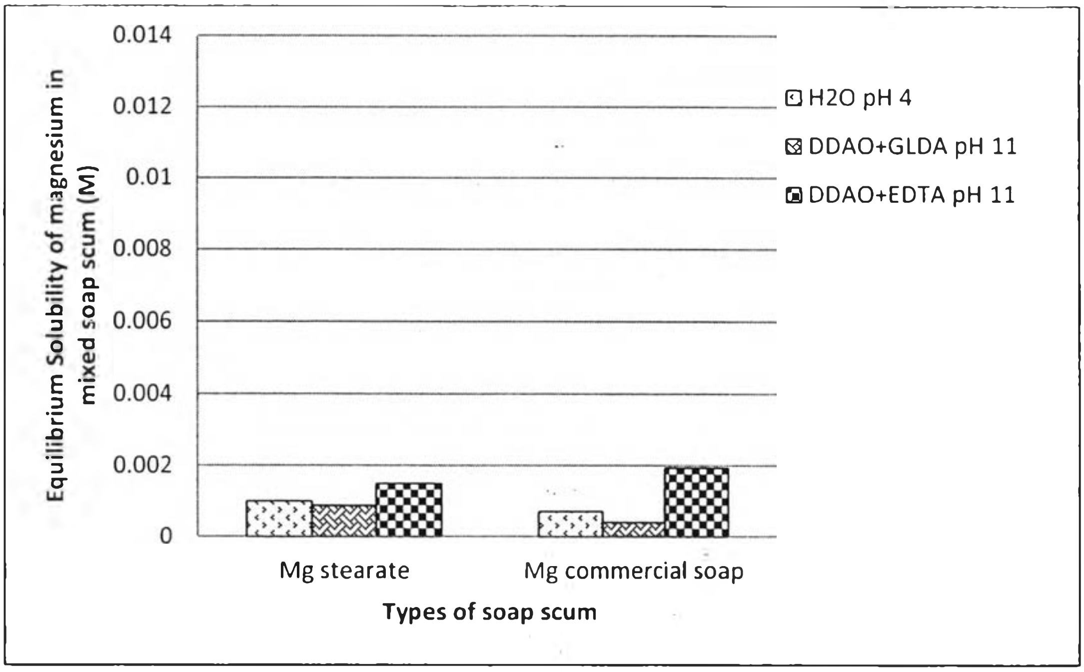


Figure 4.18 Equilibrium solubility of magnesium mixed soap scum at 4:1 Ca/Mg ratio in different optimum systems and a temperature of 25 °C.

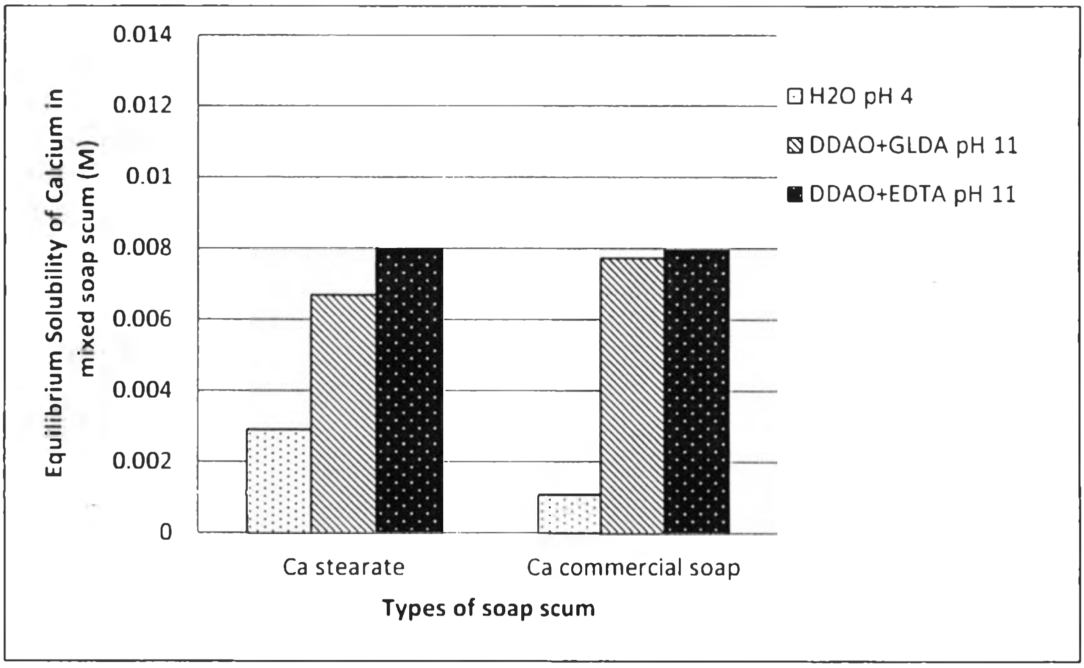


Figure 4.19 Equilibrium solubility of calcium mixed soap scum synthesized from natural hard water in different optimum systems and a temperature of 25 °C.

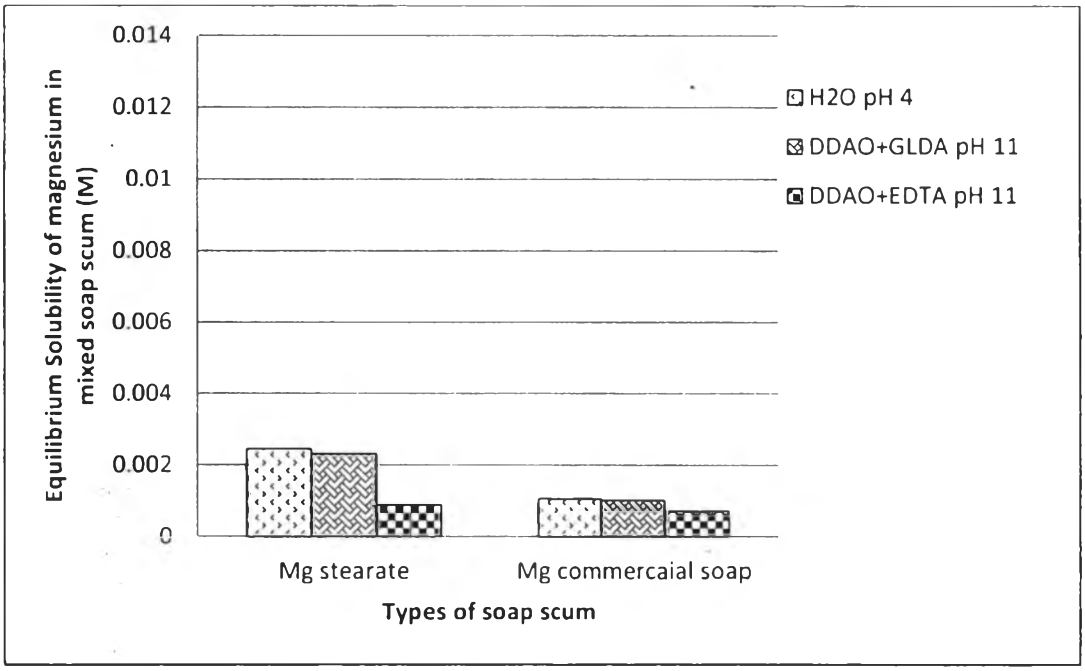


Figure 4.20 Equilibrium solubility of magnesium mixed soap scum synthesized from natural hard water in different optimum systems and a temperature of 25 °C.

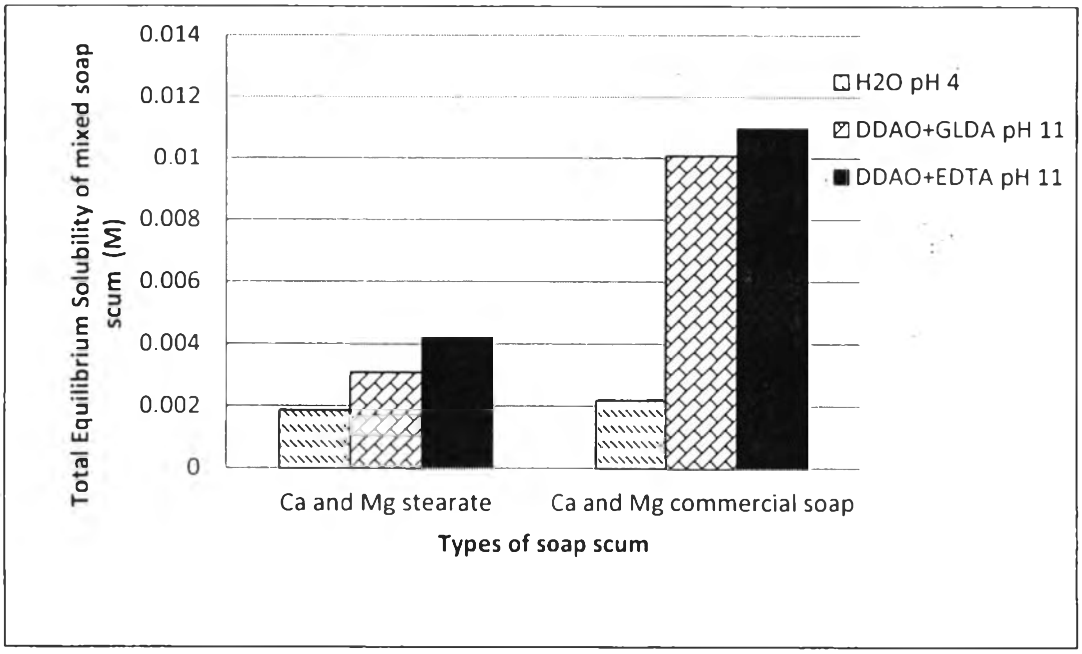


Figure 4.21 Total equilibrium solubility of calcium and magnesium mixed soap scum at 4:1 Ca/Mg ratio in different optimum systems and a temperature of 25 °C.

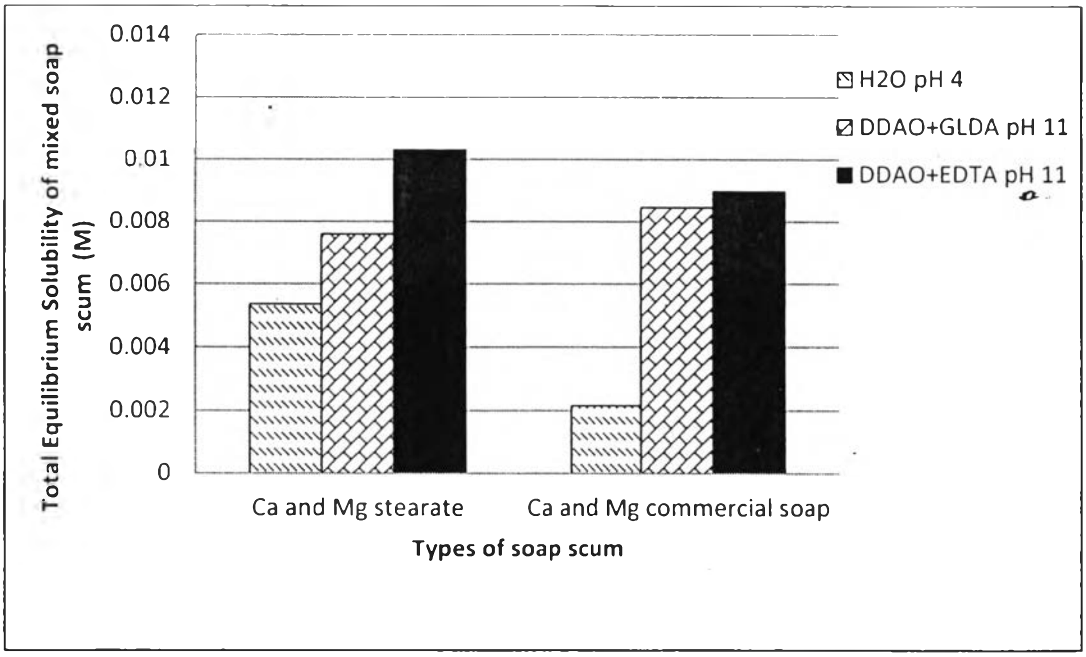


Figure 4.22 Total equilibrium solubility of calcium and magnesium mixed soap scum synthesized from natural hard water in different optimum systems and a temperature of 25 °C.

4.5 Equilibrium Solubility of Stearic Acid and Commercial Soap

In a comparison of two soap scum models according to Figure 4.23, the equilibrium solubility of stearic acid soap scums in the DDAO/Na_2EDTA and DDAO/Na_4GLDA at pH 11 was in the order of Ca-S > NHW-S > 4:1 Ca/Mg-S > Mg-S. For commercial soap scums, the equilibrium solubility in the Na_2EDTA/DDAO was in the order of 4:1 Ca/Mg-CS > NHW-CS > Ca-CS > Mg-CS and in the Na_4GLDA/DDAO was in the order of 4:1 Ca/Mg-CS ≈ Ca-CS > NHW-CS > Mg-CS. The synthesized commercial soap scum between pure and mixed soap scum are not much different compared to pure and mixed stearate soap scum. Moreover, the equilibrium solubility of commercial soap scum seems to equal or higher than stearate soap scum. So, the model of stearate soap scum can be representative of commercial soap scum. A comparison between Na_4GLDA and Na_2EDTA systems indicates that both chelating agents can competitive in pure and mixed soap scum. So, Na_4GLDA biodegradable chelating agent can used to replace Na_2EDTA.

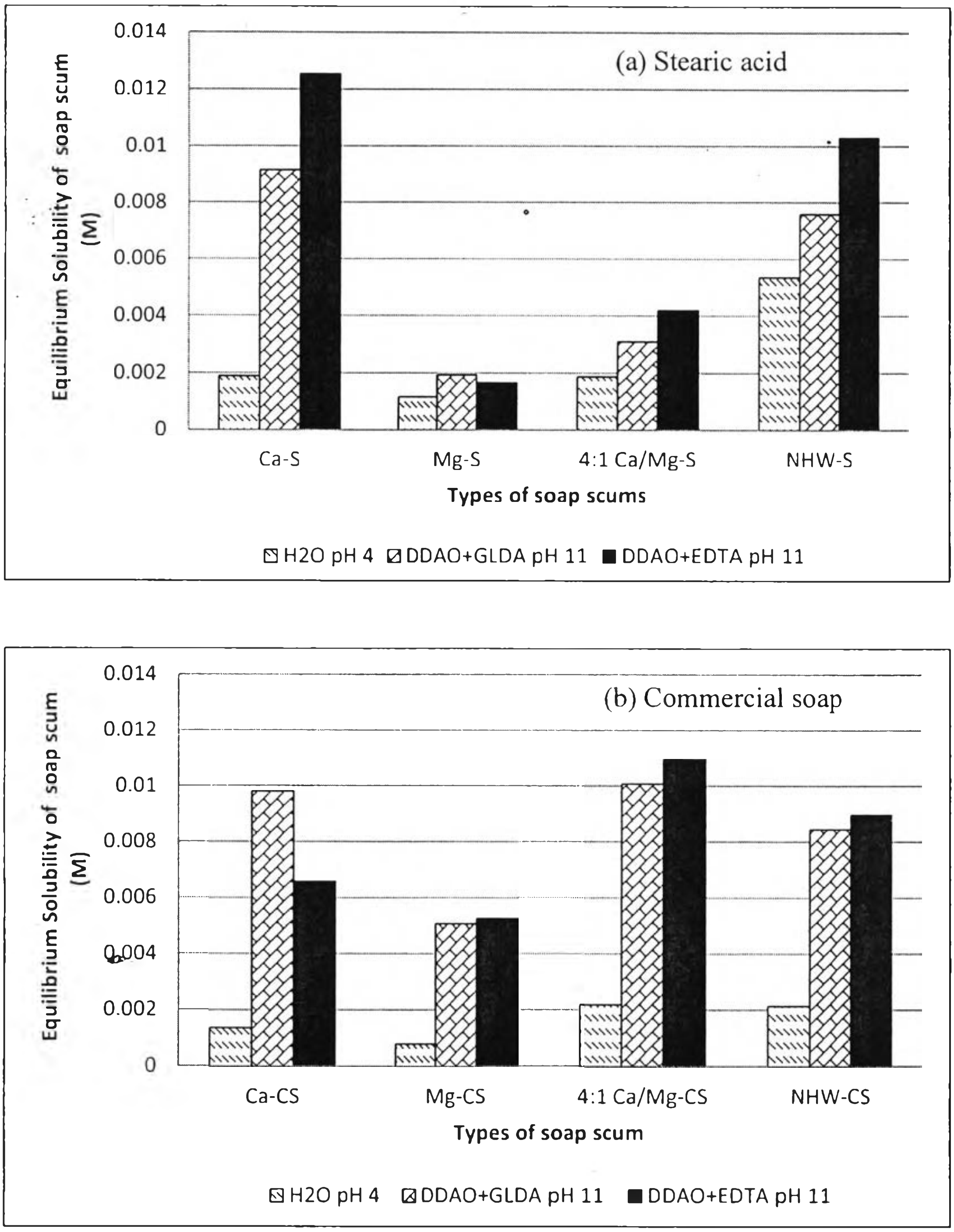


Figure 4.23 Equilibrium solubility of stearic acid (a) and commercial soap scum (b) in pure calcium , pure magnesium, 4:1 Ca/Mg and natural hard water in different optimum systems and a temperature of 25 °C.

4.6 Dissolution Rate of Mixed Soap Scum

The dissolution rate of soap scum was used the first order reaction as a model. The initial rate constant (k) was obtained from the first 10 minutes of experiment. The k value was calculated from the slope of the plot of $-\ln\left(\frac{M}{M_0}\right)$ with time. The dissolution rate of calcium and magnesium soap scum in NHW-S and NHW-CS is no significant different in both 0.1 M DDAO mixed with 0.1M Na_2EDTA and 0.1 M DDAO mixed with 0.1M Na_4GLDA (Figure 4.24 -4.25 and 4.26 -4.27 respectively).

By comparing calcium and magnesium mixed soap scum, the dissolution rate of calcium mixed soap scum is higher than that of magnesium soap scum for both NHW-S and NHW-CS shown in Table 4.2.

Table 4.2 Dissolution rate of calcium and magnesium in mixed soap scum synthesized from stearic acid or commercial soap with natural hard water in various solution pH 11 and a constant temperature of 25 °C

Solution	Initial rate constant (min^{-1}) of NHW-S		Initial rate constant (min^{-1}) of NHW-CS	
	Calcium	Magnesium	Calcium	Magnesium
0.1 M DDAO + 0.1M Na_2EDTA	0.071	0.039	0.099	0.035
0.1 M DDAO + 0.1 M Na_4GLDA	0.054	0.031	0.083	0.029

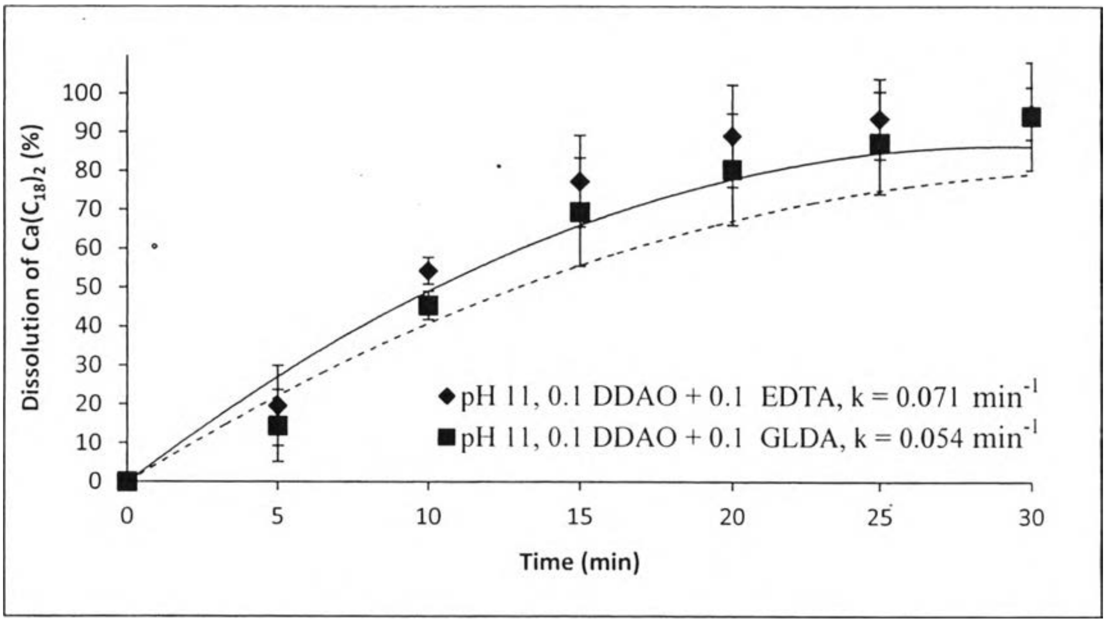


Figure 4.24 Dissolution rate of calcium stearate synthesized from natural hard water in 0.1 DDAO mixed with 0.1 Na_2EDTA or 0.1 Na_4GLDA at pH 11 and a constant temperature of 25 °C.

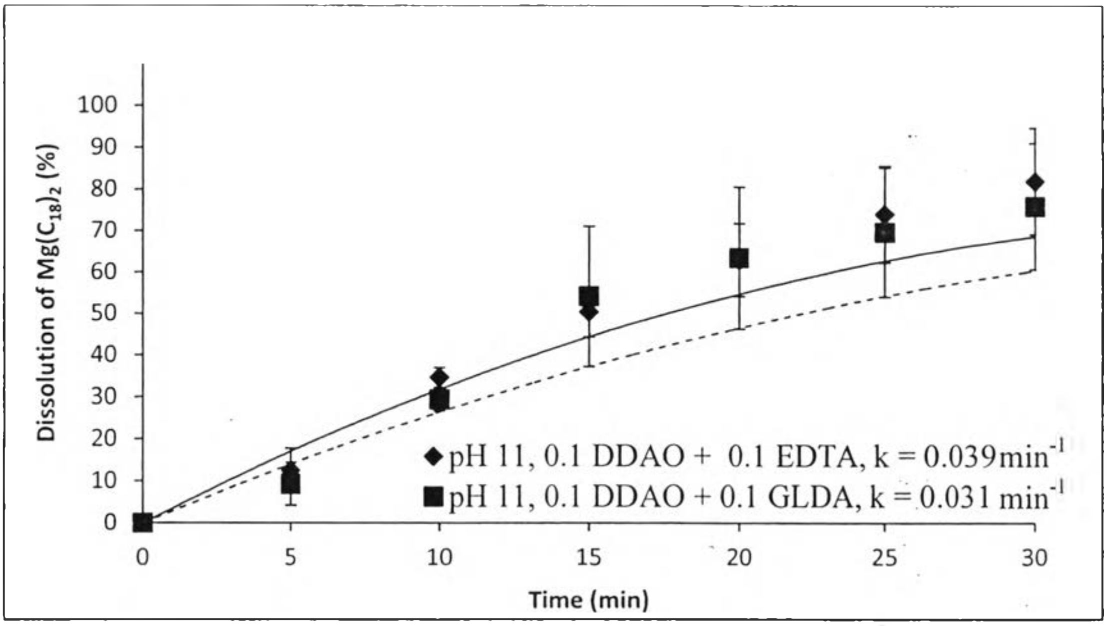


Figure 4.25 Dissolution rate of magnesium stearate synthesized from natural hard water in 0.1 DDAO mixed with 0.1 Na_2EDTA or 0.1 Na_4GLDA at pH 11 and a constant temperature of 25 °C.

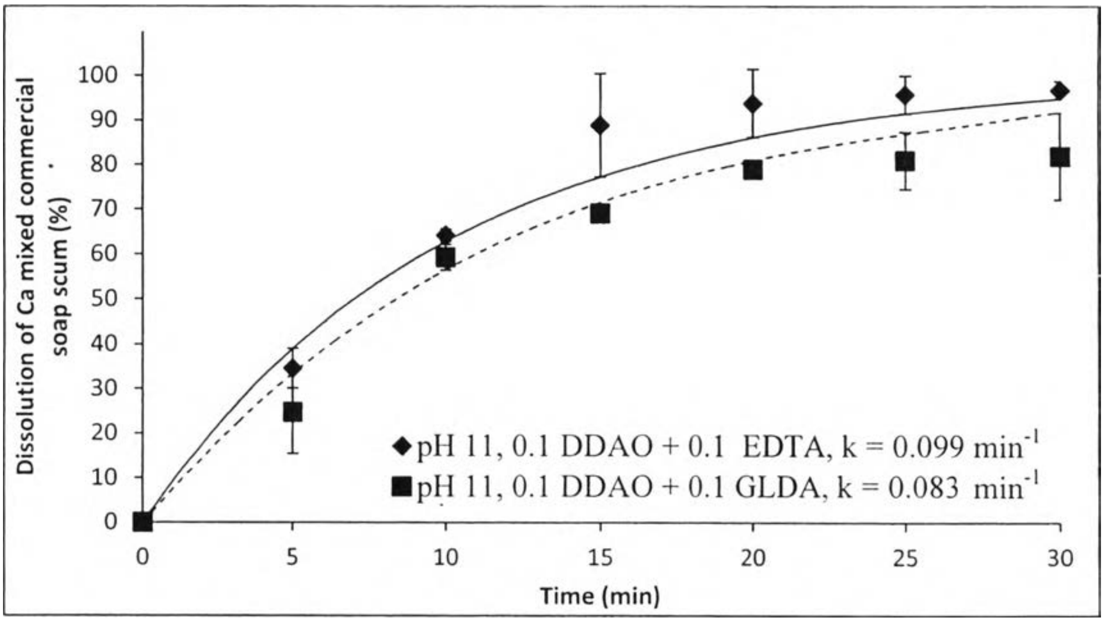


Figure 4.26 Dissolution rate of calcium mixed commercial soap scum synthesized from natural hard water in 0.1 DDAO mixed with 0.1 Na_2EDTA or 0.1 Na_4GLDA at pH 11 and a constant temperature of 25 °C.

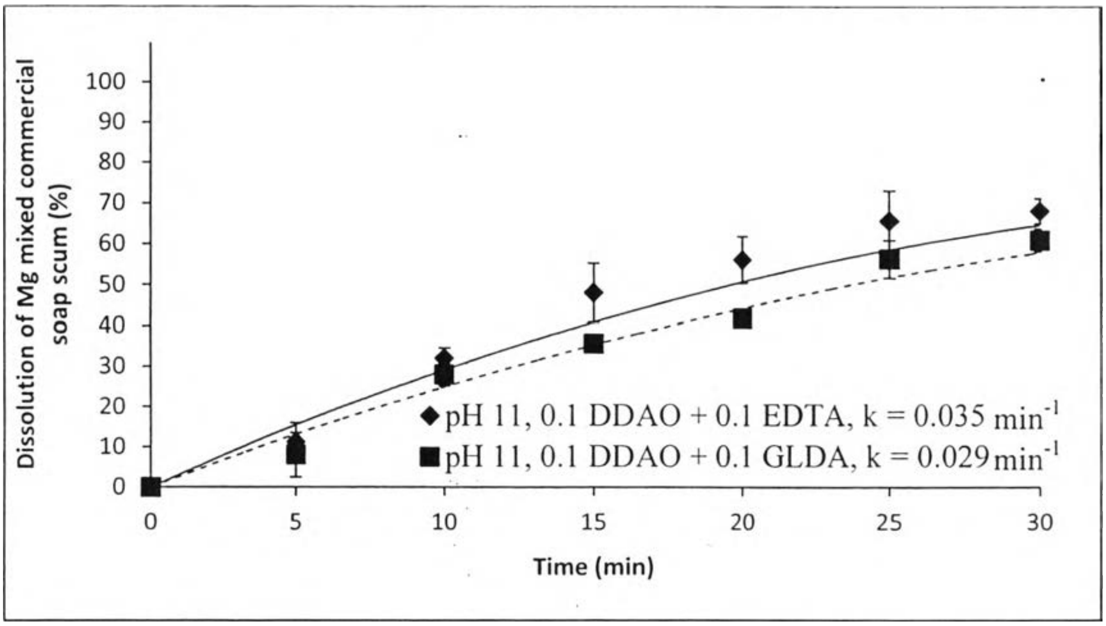


Figure 4.27 Dissolution rate of magnesium mixed commercial soap scum synthesized from natural hard water in 0.1 DDAO mixed with 0.1 Na_2EDTA or 0.1 Na_4GLDA at pH 11 and a constant temperature of 25 °C.