CHAPTER IV
RESULTS AND DISCUSSION

By following the procedure and all chemicals used in the experiments from the previous work, the amount of calcium and magnesium concentration have a typical molar ratio of 4:1. The equilibrium solubility and dissolution rate of synthesized soap scum samples at different Ca:Mg molar ratios (1:1 and 4:1) in different system (pure water, disodiumethylene diaminetetraacetate (Na_2EDTA), tetrasodium glutamatediacetate (Na_4GLDA), dimethyldodecylamine oxide (DDAO), DDAO/Na_2EDTA, and DDAO/Na_4GLDA) were investigated at different solution pH levels (4-12) and at a constant temperature of 25 °C.

4.1 Characteristics of Mixed Synthesized Soap Scum

The ratio of mixed soap scum was analyzed by AAS, the results indicated that the calcium to magnesium ratios of both mixed soap scum were consistent with the theory as 1 to 1 for Ca:Mg = 1:1 molar ratio and 4.19 to 1 for Ca:Mg = 4:1 molar ratio. Figure 4.1 showed the particle size distribution and average diameter of each mixed soap scum. Both of mixed soap scums had nearly the same particle size distribution in the range of 10 to 130 μm and the average diameters were 42.58 μm for 1:1 and 43.77 μm for 4:1 ratio of mixed soap scum. Figure 4.2 showed that the calcium stearate of both ratios had smaller crystalline size than the magnesium stearate. The crystalline size of calcium and magnesium was 39.28 nm and 51.80 nm for 1:1 ratio. For 4:1 ratio, the crystalline size of calcium and magnesium was 39.40 and 56.01 nm.

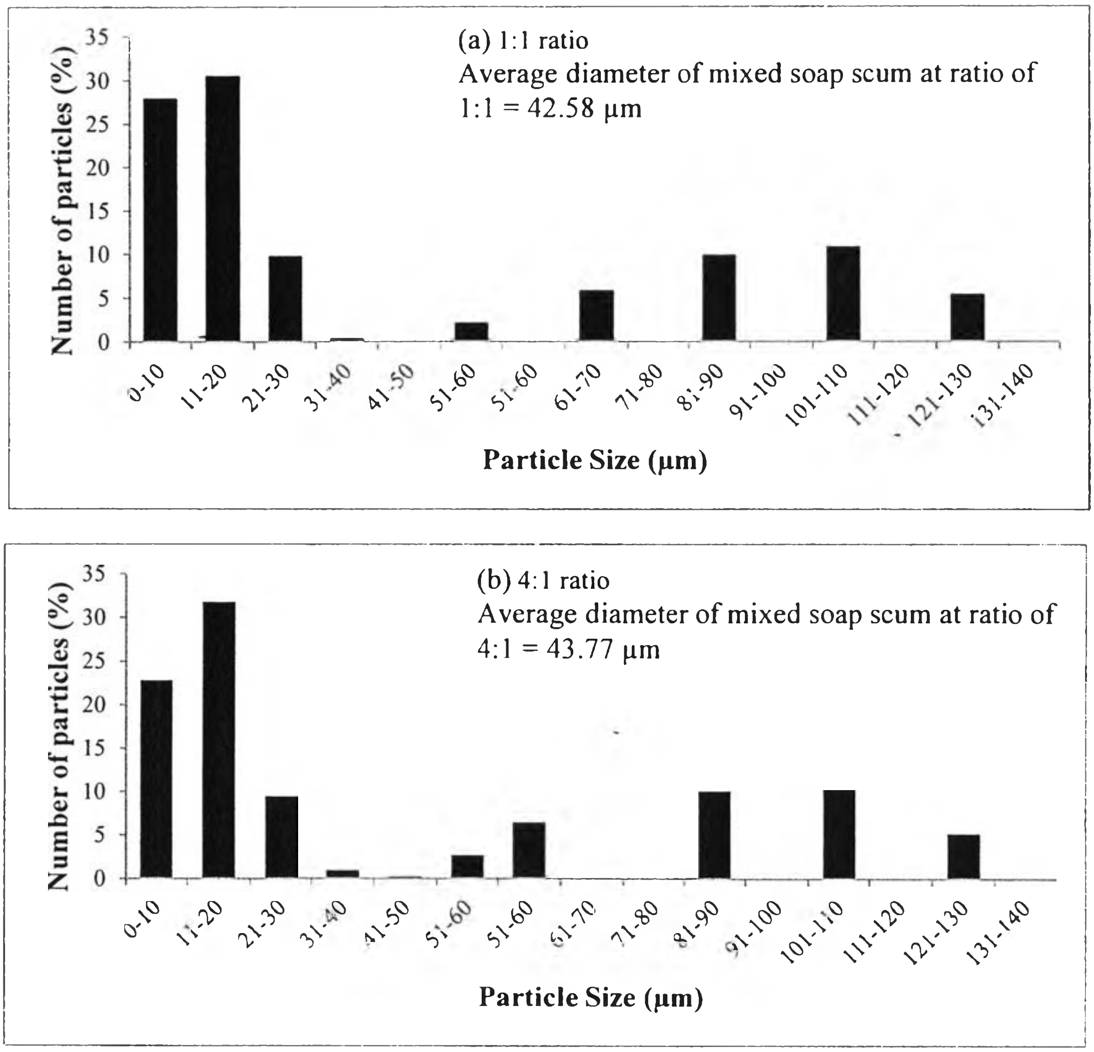


Figure 4.1 Particle size distribution and average diameter of two mixed calcium and magnesium soap scums at different ratios.

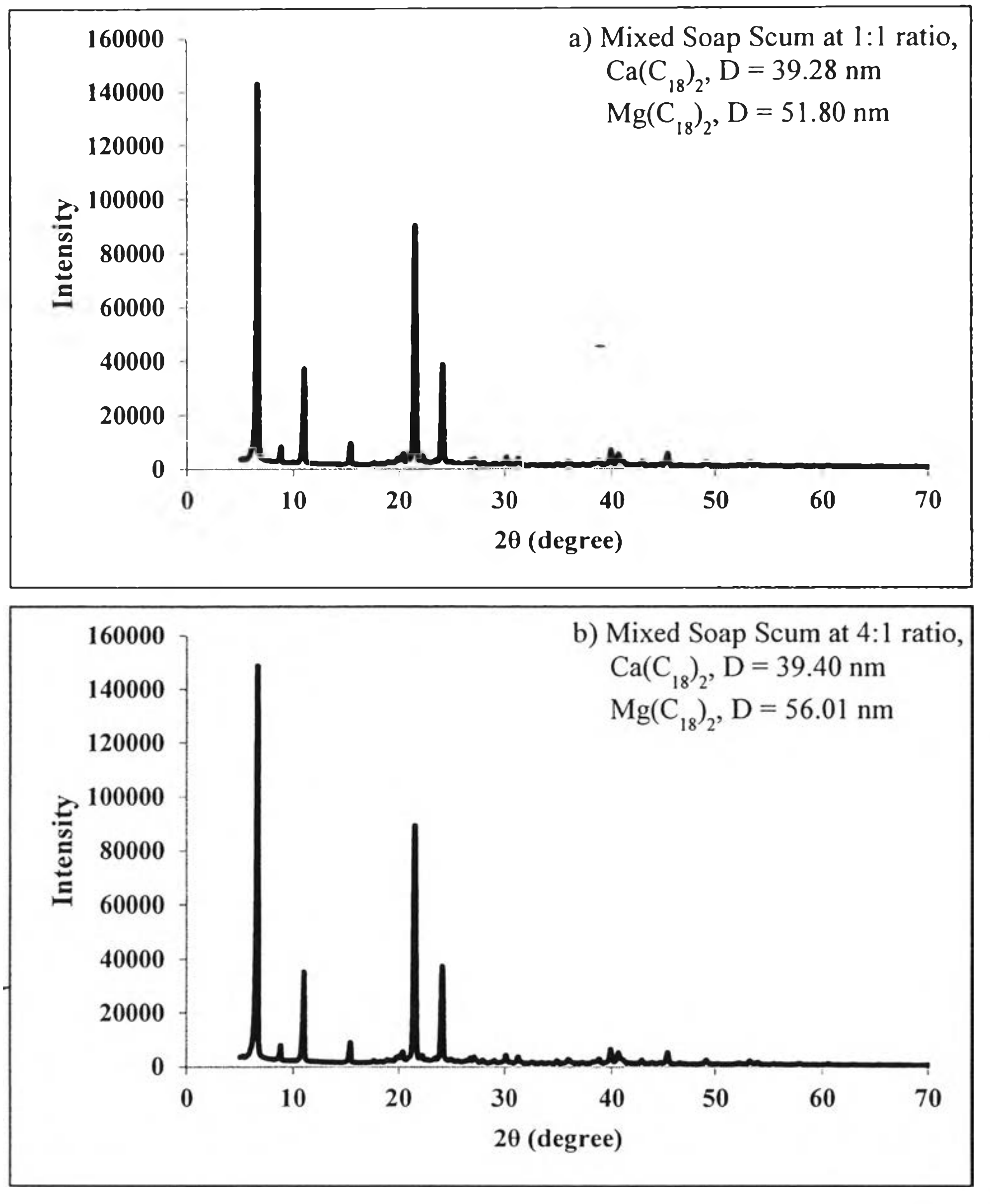


Figure 4.2 XRD diffraction patterns and crystalline size of mixed soap scums.

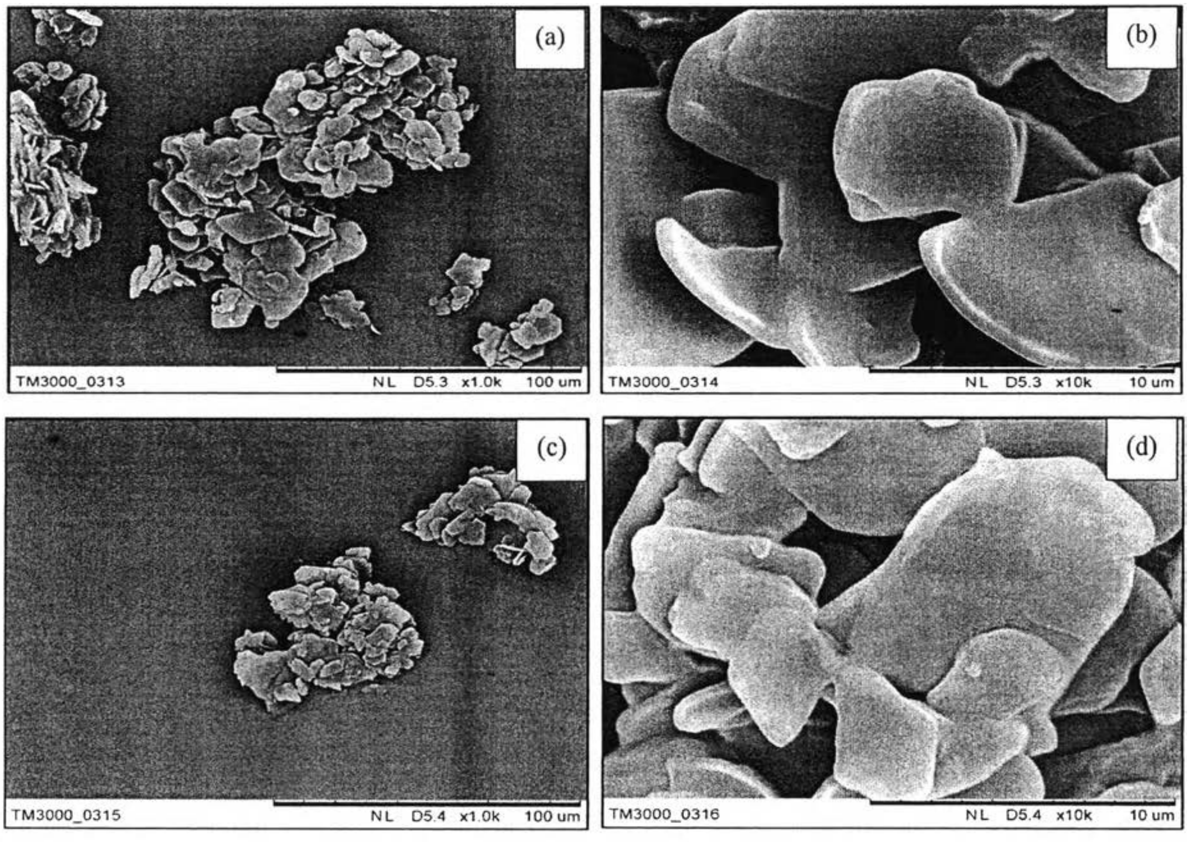


Figure 4.3 SEM images of two mixed calcium and magnesium soap scums at different ratios: (a),(b) 1:1 ratio ,and (c),(d) 4:1 ratio.

The SEM images were shown in Figure 4.3. Both of them had smooth and non-porous surfaces. For 4:1 ratio mixed soap scum had smaller sizes than 1:1 ratio because of the larger amount of Ca proportion that was consistent with the previous work (Itsadanont et al., 2013).

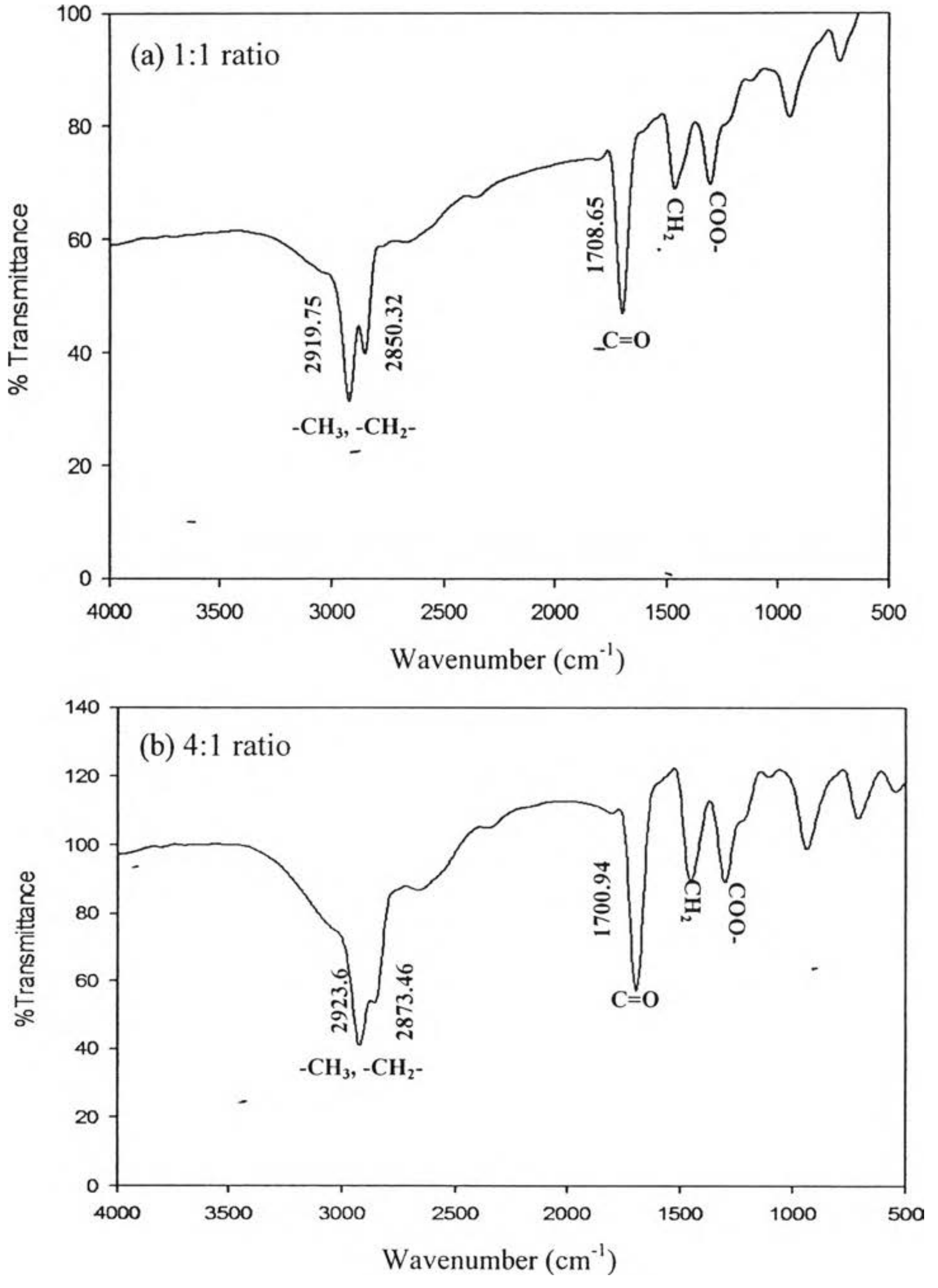


Figure 4.4 FT-IR spectra of two mixed calcium and magnesium soap scums at different ratios.

The FT-IR spectra of mixed soap scums were shown in Figure 4.4. The stearic acid absolutely reacted with calcium and magnesium ions because of no peak of –OH in carboxylic acid group present in FT-IR. The peak at 1708 cm^{-1} in the ratio of 1:1 and at 1700 cm^{-1} in the ratio of 4:1 indicated C=O in carboxylic acid ester stretching that wavenumbers present at 1710-1690 cm^{-1} (Lambert *et al.*, 2010, Silverstein *et al.*, 2012). These can confirm that calcium or magnesium ions can react with stearic acid to produce calcium and magnesium stearate completely. For other peaks, $-CH_3$ and $-CH_2-$ in aliphatic compounds (CH-antisym and CH-sym stretching) were found at 2990-2850 cm^{-1} (Lambert *et al.*, 2010).

4.2 Equilibrium Solubility of Mixed Soap Scum

Figures 4.5-4.8 showed the equilibrium solubility of both calcium and magnesium mixed soap scum in 1:1 and 4:1 ratios at different solution systems (pure water, Na_2EDTA, Na_4GLDA, DDAO, DDAO/Na_2EDTA, and DDAO/Na_4GLDA).

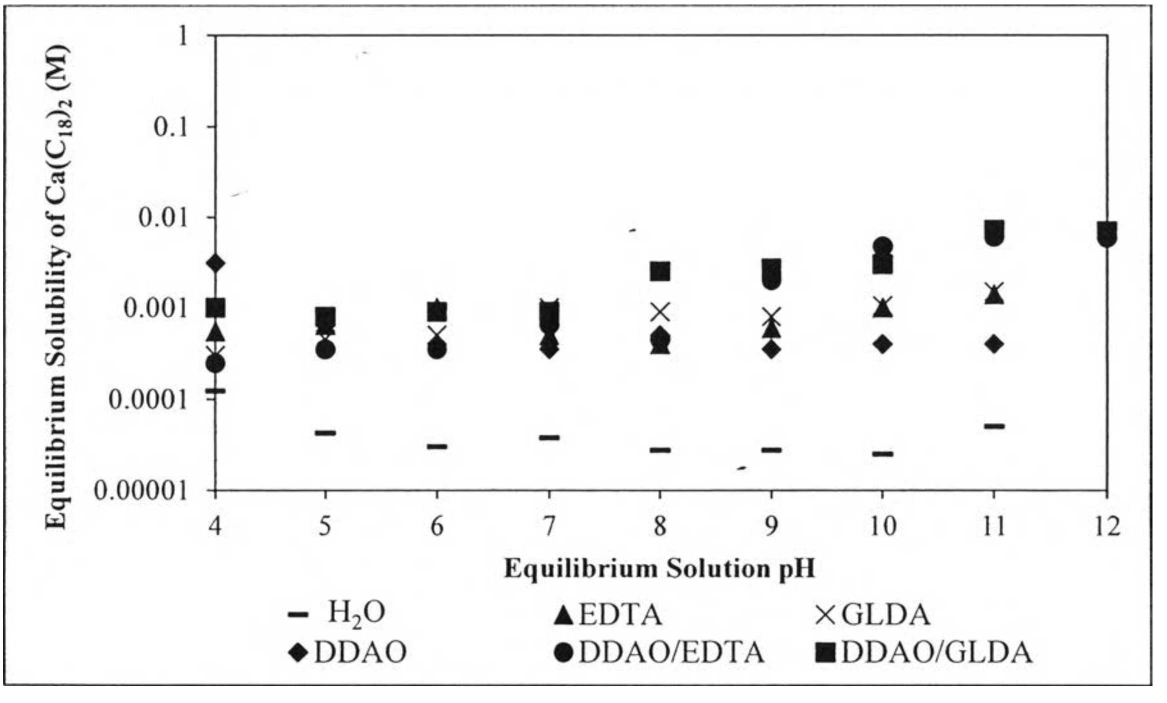


Figure 4.5 Equilibrium solubilities of calcium mixed soap scum at 1:1 ratio in different systems at different solution pH values and a temperature of 25 °C.

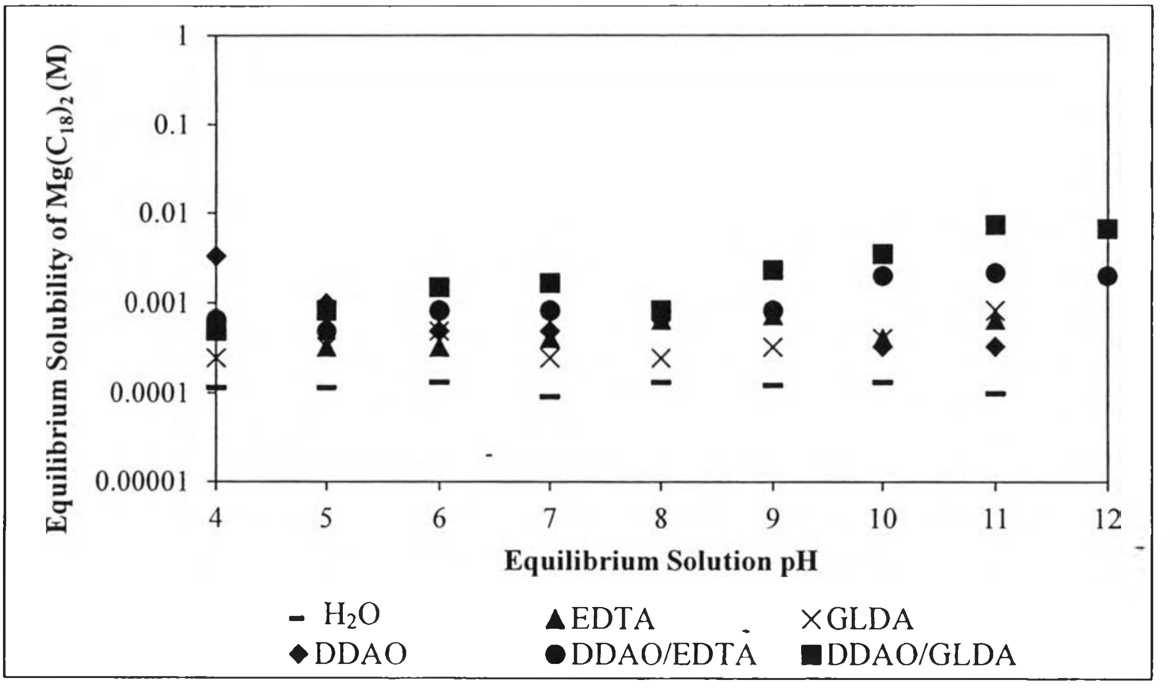


Figure 4.6 Equilibrium solubilities of magnesium mixed soap scum at 1:1 ratio in different systems at different solution pH values and a temperature of 25 °C.

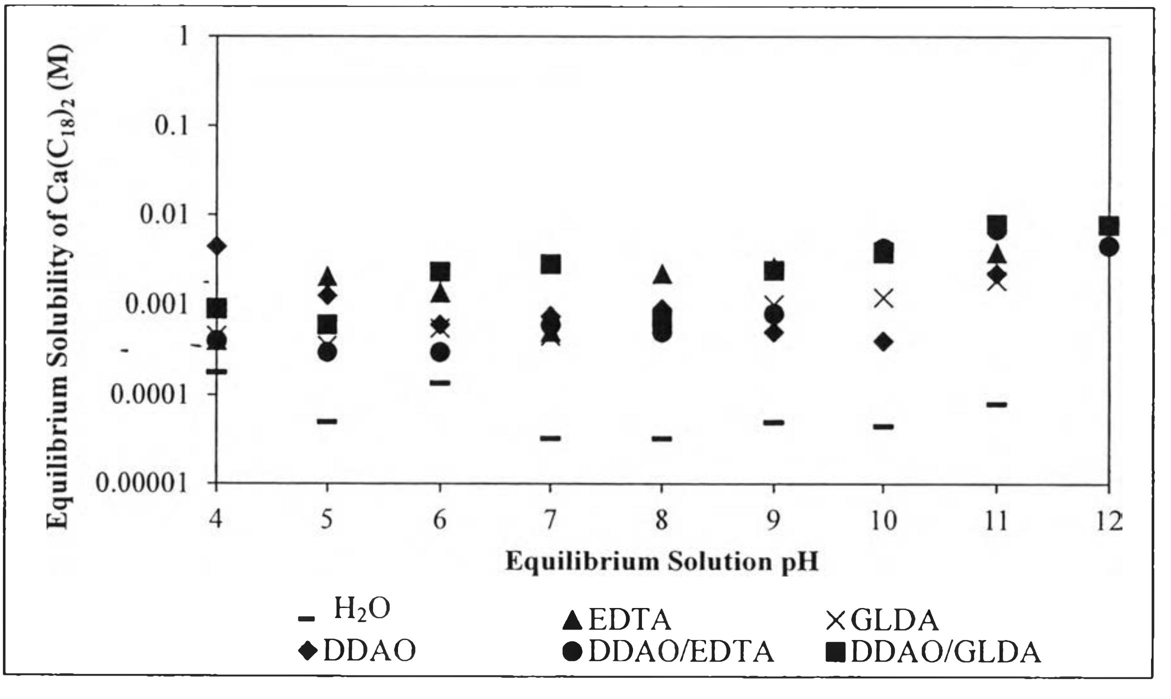


Figure 4.7 Equilibrium solubilities of calcium mixed soap scum at 4:1 ratio in different systems at different solution pH values and a temperature of 25 °C.

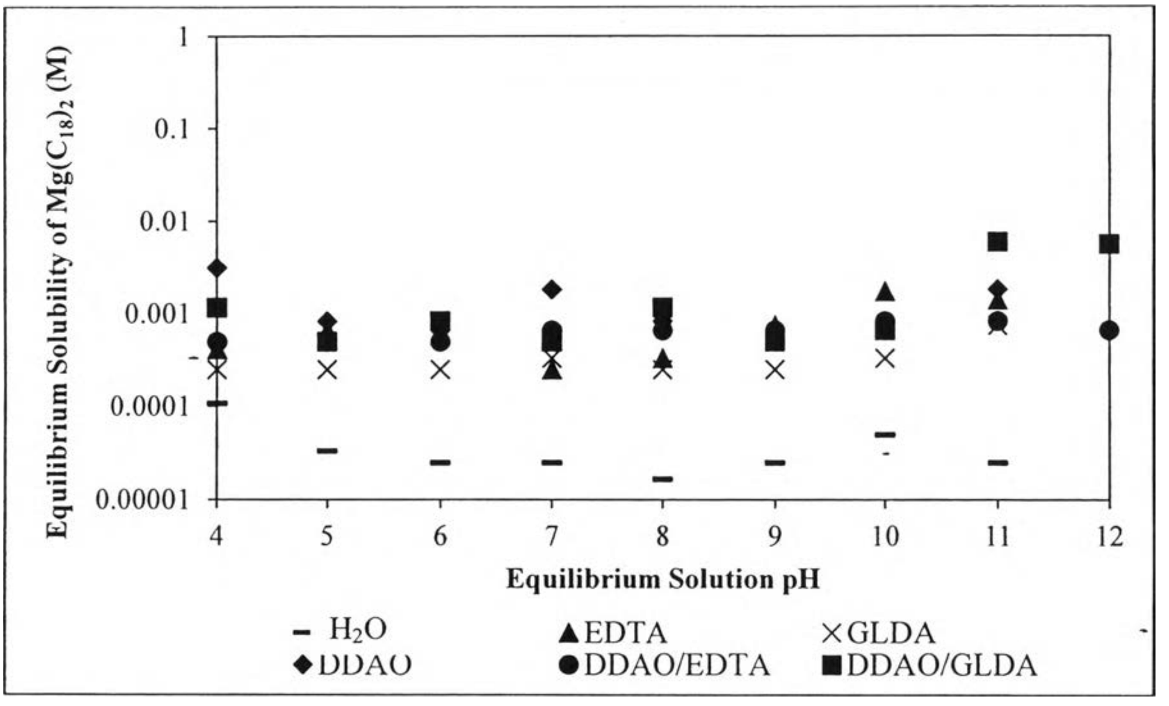


Figure 4.8 Equilibrium solubilities of magnesium mixed soap scum at 4:1 ratio in different systems at different solution pH values and a temperature of 25 °C.

4.2.1 Equilibrium Solubility of Mixed Soap Scum without Surfactant

In pure water, mixed soap scums had very low equilibrium solubility. Since calcium and magnesium stearate had a very low solubility (K_{sp}). The highest equilibrium solubilities of mixed calcium and magnesium were observed at pH 4 for both 1:1 and 4:1 ratios that was consistent with the previous work. The structure of the fatty acid depends on solution pH because of the protonation. The ratio between stearic acid and stearate anion increased with decreasing solution pH because protons exchanged with calcium or magnesium ion and formed stearic acid while stearate anion will form at high solution pH. As a consequence, stearic acid had higher solubility in water than stearate anion because of hydrogen bond (Itsadanont *et al.*, 2013).

The Na_2EDTA or Na_4GLDA alone had slightly effect on mixed soap scum solubility at low pH, but improved solubility as pH increases due to the increase in effectiveness of the complexation between the chelant and calcium or magnesium ions in both ratios. At low pH solution, soap scum will be protonated to the nonionic stearic acid whereas soap scum will be dissociated to the stearate anion at high pH solution. In the presence of chelant, the five forms of chelant depend on solution pH (H_4Y, H_3Y^-, H_2Y^{2-}, HY^{3-}, and Y^{4-}). The most effective form to bind with metal ions (calcium and magnesium ions) is Y^{4-} which appears in high pH value (Itsadanont *et al.*, 2013). Although the most effective chelant form appears at a high solution pH, the dissolution of soap scum was found to be very low because the stearate anion has a very low solubility (K_{sp}). The highest equilibrium solubilities of both calcium and magnesium were found at pH 11.

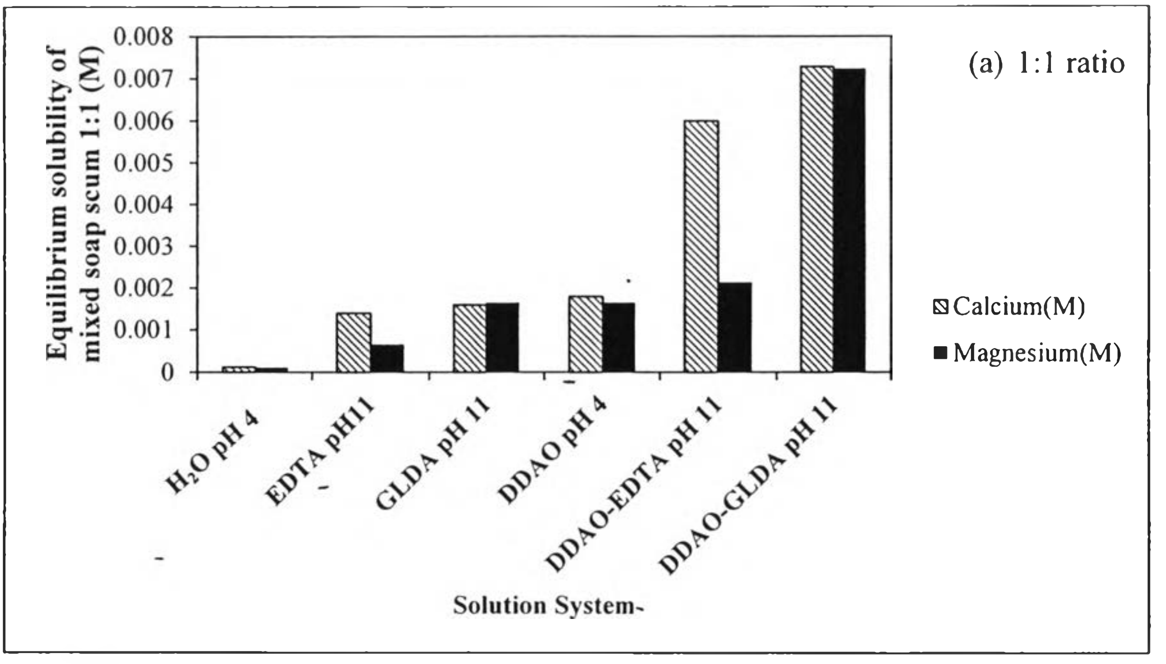
4.2.2 Equilibrium Solubility of Mixed Soap Scum with Surfactant

The highest equilibrium solubilities of mixed calcium and magnesium soap scum in DDAO solution were observed at pH 4 for both 1:1 and 4:1 ratios same as in water system. But in the presence of DDAO surfactant, the equilibrium solubility can be improved significantly. The presence of DDAO caused the equilibrium solubility of mixed calcium and magnesium soap scum decrease with increasing solution pH. Since DDAO amphoteric surfactant can form cationic or zwitterionic which depend on solution pH. At low solution pH, the cationic form dominants led to the formation of cationic (DDAO) and nonionic (stearic acid) mixed micelle. At high solution pH, the zwitterionic form dominants led to the formation of zwitterionic (DDAO) and anionic (stearate) mixed micelle. However, the formation of cationic (DDAO) and nonionic (stearic acid) mixed micelle had better synergism than the formation of zwitterionic (DDAO) and anionic (stearate) mixed micelle because the repulsion between head group of cationic (DDAO) and nonionic (stearic acid) mixed micelle was less. Therefore, the highest equilibrium solubility in DDAO surfactant was found in low pH solution.

The addition of chelant (Na_2EDTA or Na_4GLDA) caused dramatically increased the equilibrium solubilities of mixed calcium and magnesium soap scum. The trends were opposite with pure surfactant system. The presence of chelant in DDAO caused the equilibrium solubility of mixed calcium and magnesium soap scum increase with increasing solution pH. The effective pH value of Na_2EDTA is in the range of 4–11 (Itsadanont *et al.*, 2013) while Na_4GLDA has the effectiveness in the range of 4–12 (Brochure, 2007). However, the highest the equilibrium solubilities of mixed calcium and magnesium soap scum in DDAO/Na_2EDTA and DDAO/Na_4GLDA were observed at pH 11 for both 1:1 and 4:1 ratios. The most effective form of chelant is Y^{4-} for binding calcium and magnesium ions which observed at high pH solution and left the stearic acid and stearic anions to form mixed micelle with DDAO surfactant leading to dramatically increasing in the equilibrium solubility of mixed soap scum. By comparing DDAO/Na_2EDTA and DDAO/Na_4GLDA system, the calcium and magnesium ions can substitute in chelant vacancies. The Na_4GLDA had four vacancies substitution whereas the Na_2EDTA had lesser. Thus the equilibrium solubility of mixed soap scum in DDAO/Na_4GLDA was higher than DDAO/Na_2EDTA system which might have more the stability constant (Brochure, 2007).

4.2.3 Equilibrium Solubility in 1:1 and 4:1 Ratios

In a comparison of two soap scum models according to Figure 4.9a, for 1:1 ratio, it showed that the equilibrium solubility of both calcium and magnesium was insignificant different except in a solution containing Na_2EDTA which had low the equilibrium solubility of magnesium. These results can represent the competition between calcium and magnesium in mixed soap scum. But for 4:1 ratio, the equilibrium solubility of calcium is higher than that of magnesium in mixed soap scum as shown in Figure 4.9b because of the larger amount of calcium in solution.



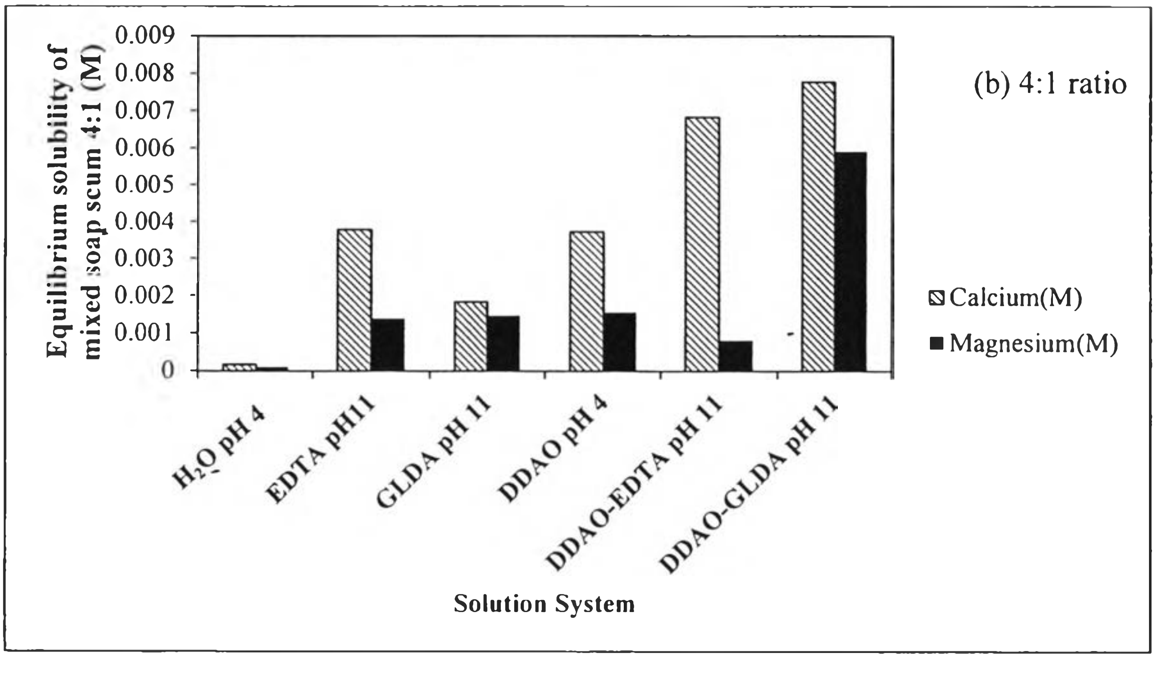


Figure 4.9 The highest equilibrium solubilities of calcium and magnesium mixed soap scum in different system at different solution pH values and a temperature of 25 °C.

4.3 Dissolution Rate of Mixed Soap Scum

The first order reaction was used as a model so k values were parameter to compare the dissolution rate in different systems. The rate constant or k-value was obtained from the first 10 min of the experiment. The k-value of each system was calculated from a slope of a plot of $\ln\left(\frac{M}{M_0}\right)$ versus time. The solution containing 0.1 M DDAO and 0.1 M Na_2EDTA at pH 11 was provided the higher dissolution rate of mixed calcium and magnesium soap scum than the solution of 0.1 M DDAO and 0.1 M Na_4GLDA at pH 11 for both 1:1 and 4:1 ratios as shown in Figure 4.10 to 4.13 and Table 4.1. Since the stability constant-of Na_2EDTA was higher than that of Na_4GLDA chelating agent.

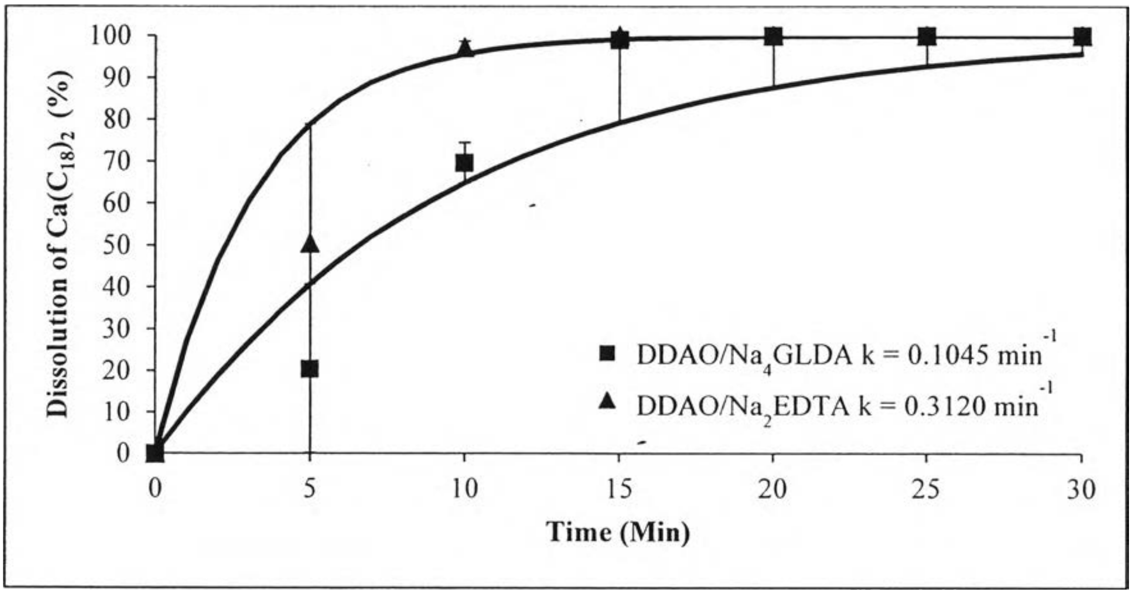


Figure 4.10 Dissolution rate of calcium mixed soap scum at 1:1 ratio in 0.1 M DDAO mixed with 0.1 M Na_2EDTA or 0.1 M Na_4GLDA at pH 11 and a constant temperature of 25°C.

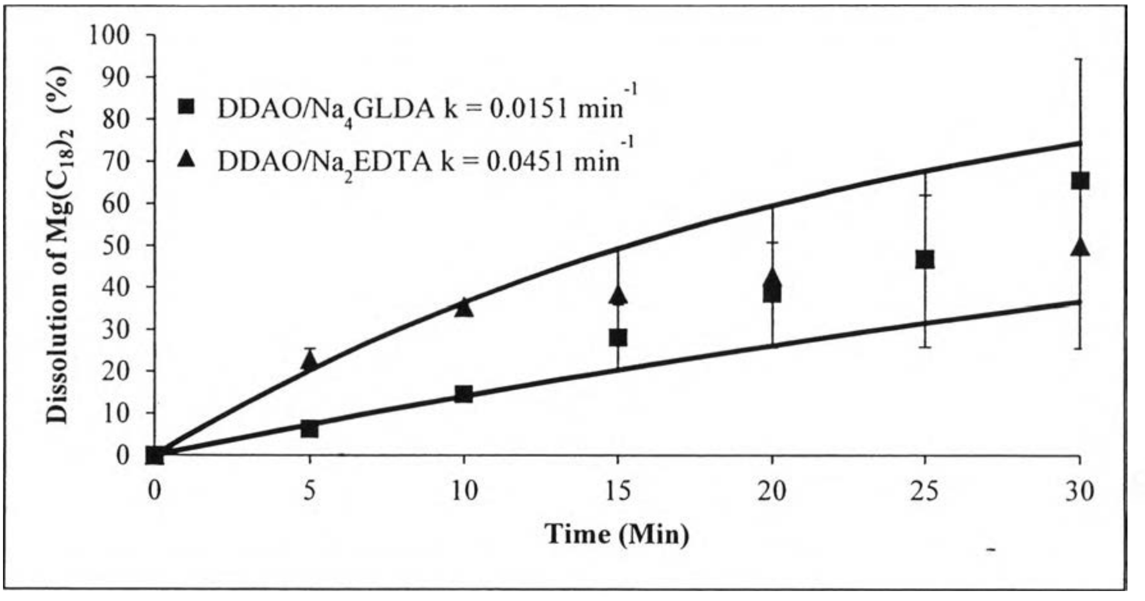


Figure 4.11 Dissolution rate of magnesium mixed soap scum at 1:1 ratio in 0.1 M DDAO mixed with 0.1 M Na_2EDTA or 0.1 M Na_4GLDA at pH 11 and a constant temperature of 25°C.

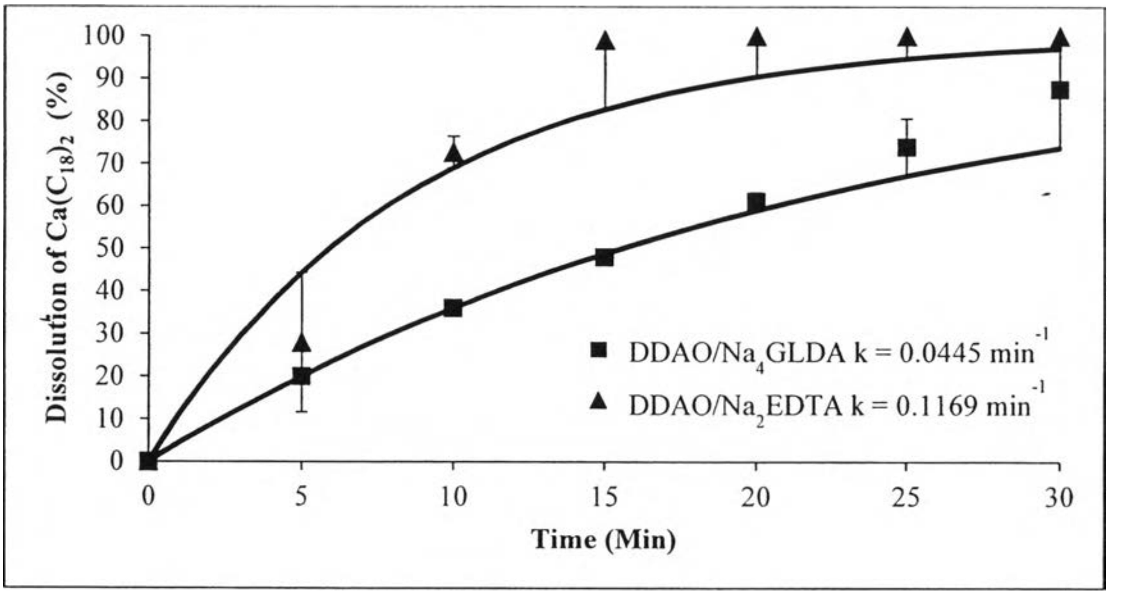


Figure 4.12 Dissolution rate of calcium mixed soap scum at 4:1 ratio in 0.1 M DDAO mixed with 0.1 M Na_2EDTA or 0.1 M Na_4GLDA at pH 11 and a constant temperature of 25°C.

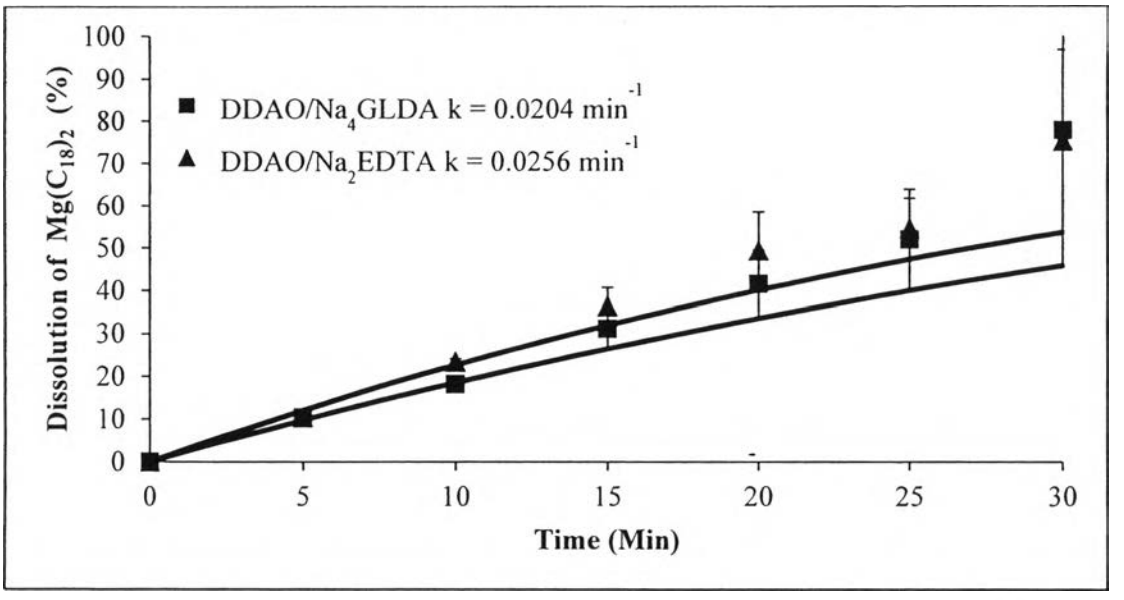


Figure 4.13 Dissolution rate of magnesium mixed soap scum at 4:1 ratio in 0.1 M DDAO mixed with 0.1 M Na_2EDTA or 0.1 M Na_4GLDA at pH 11 and a constant temperature of 25°C.

Table 4.1 Dissolution rate of calcium and magnesium in mixed soap scum at 1:1 and 4:1 ratio in various solutions pH 11 and a constant temperature of 25°C

Solution	Initial rate constant (min^{-1}) of 1:1 Ratio		Initial rate constant (min^{-1}) of 4:1 Ratio	
	Calcium	Magnesium	Calcium	Magnesium
0.1 M DDAO + 0.1M Na_2EDTA	0.3120	0.0451	0.1169	0.0256
0.1 M DDAO + 0.1M Na_4GLDA	0.1045	0.0151	0.0445	0.0204

By comparing calcium and magnesium mixed soap scum, the dissolution rate of calcium mixed soap scum is higher than that of magnesium mixed soap scum for both 1:1 and 4:1 ratios. Especially, the calcium dissolution rate at 4:1 ratio had significant higher than the magnesium since calcium ion forms a more stable complex with EDTA than magnesium.