CHAPTER IV
RESULTS AND DISCUSSION

The equilibrium solubility and dissolution rate of calcium soap scum ($Ca(C_{18})_2$) were investigated at constant temperature of 25 °C by using amphoteric surfactant (DDAO) with various solution pHs and NaCl concentrations.

4.1 Equilibrium Solubility of Calcium Soap Scum

4.1.1 Effect of NaCl Concentrations

The presence of NaCl in DDAO system caused the equilibrium solubility of soap scum decreased with increasing solution pH which was a similar trend to the equilibrium solubility of soap scum in DDAO system as shown in Figure 4.1

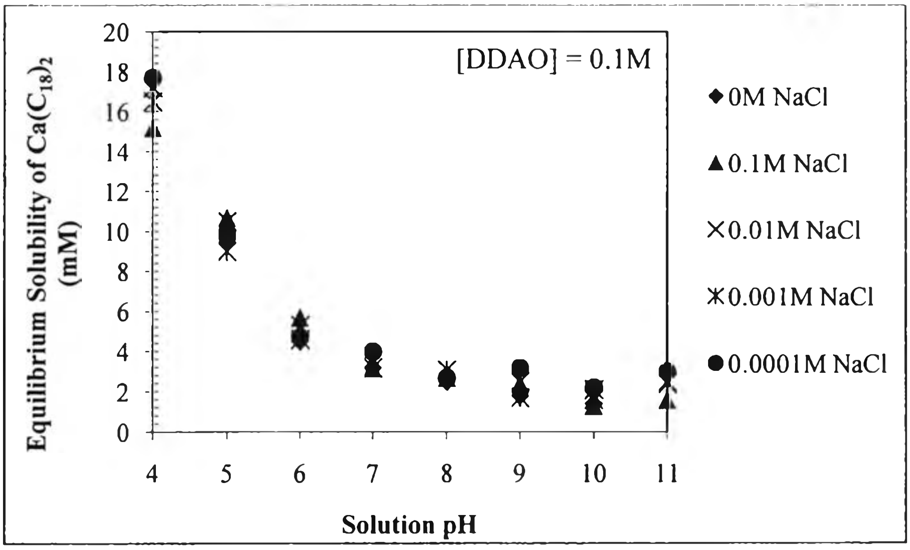


Figure 4.1 Equilibrium solubility of calcium soap scum in DDAO surfactant at various solution pHs and NaCl concentrations at constant temperature of 25 °C.

According to the theoretical, the NaCl could help to reduce the repulsive force among head group of mixed micelle between soap scum molecules (stearic acid or stearate) and DDAO surfactants (cationic or zwitterionic) lead to an increasing on the equilibrium solubility of soap scum (Rosen, 2004). But from the result, the addition of NaCl had insignificant effect on equilibrium solubility of soap scum that could be due to the formation of nonionic (stearic acid) and cationic (DDAO) mixed micelles at low solution pH.

4.1.2 Effect of Chelant and NaCl

The equilibrium solubility of soap scum in DDAO with chelant system increased with increasing solution pH which was the opposite trend when compared with DDAO system. In addition, the presence of NaCl in DDAO with chelant system caused the reducing in the equilibrium solubility of soap scum as showed in Figure 4.2.

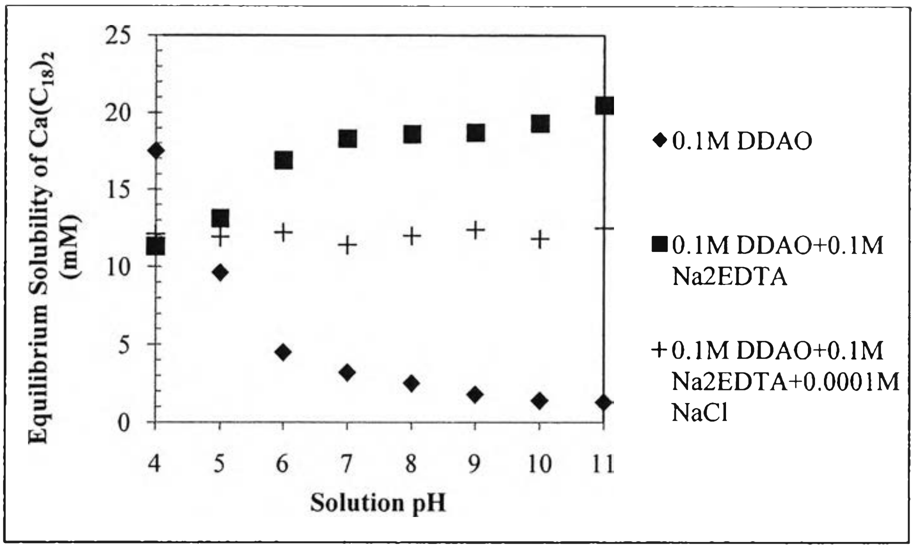


Figure 4.2 Equilibrium solubility of calcium soap scum in DDAO surfactant at various solution pHs with and without chelant and NaCl at constant temperature of 25 °C.

There are five forms of chelant that depends on solution pH (H_4Y, H_3Y^-, H_2Y^{2-}, HY^{3-} and Y^{4-}) (Soontravanich, 2010) and the most effective form to bind with calcium ions is Y^{4-} that present at high solution pH and left the stearic acid and stearate anion to form mixed micelle with DDAO surfactant leading to significantly increasing in the equilibrium solubility of soap scum. However, when

NaCl present in DDAO with chelant system, the equilibrium solubility of soap scum decreased especially at high solution pH because chelant had to form bond with both Ca^{2+} and Na^{+} ions instead of only Ca^{2+} ions.

4.2 Dissolution Rate of Calcium Soap Scum

Initial rate constant was needed in order to compare the dissolution rate in different systems. The Initial rate constant (k) was obtained from the first 10 minutes of dissolution data and calculated from the slope of the plot of $-\ln(M/M_0)$ with time.

4.2.1 Effect of Solution pH

4.2.1.1 Water Solution

The dissolution rate of soap scum in water was very low and the highest dissolution rate of soap scum in water solution was observed at pH 4 and followed by pH 7 and pH 11 respectively as shown in Figure 4.3.

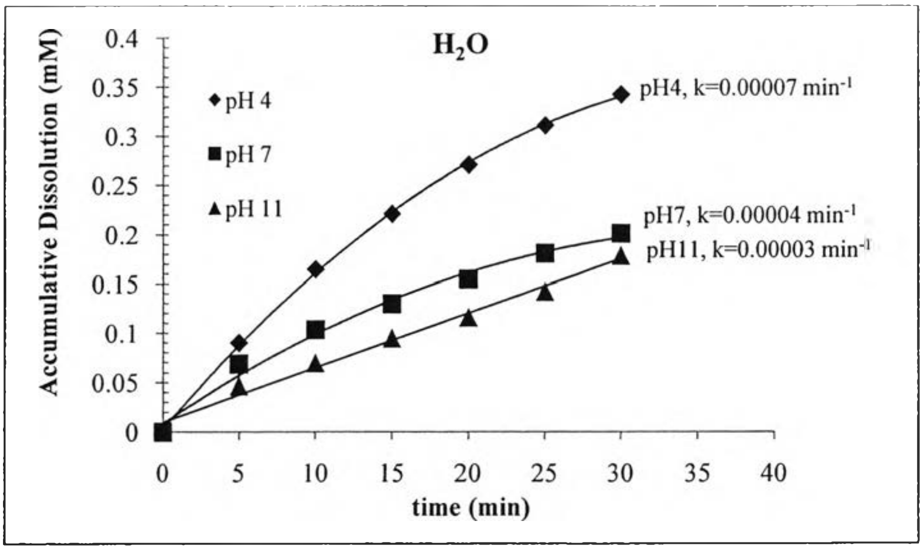


Figure 4.3 Accumulative dissolution and dissolution rate of calcium soap scum in de-ionized water at various solution pHs and at constant temperature of 25 °C.

Structure of the fatty acid depends on solution pH due to the protonation. The ratio between stearic acid to stearate anion increased with decreasing solution pH because protons exchanged with calcium ion and formed stearic acid while stearate anion will be formed at high solution pH. As a consequence, stearic acid has higher solubility in water than stearate anion because of hydrogen bond.

4.2.1.2 DDAO Solution

The dissolution of soap scum in DDAO system showed the similar trend as in water system. However, in the presence of DDAO surfactant dramatically increased the dissolution rate of soap scum as shown in Figure 4.4.

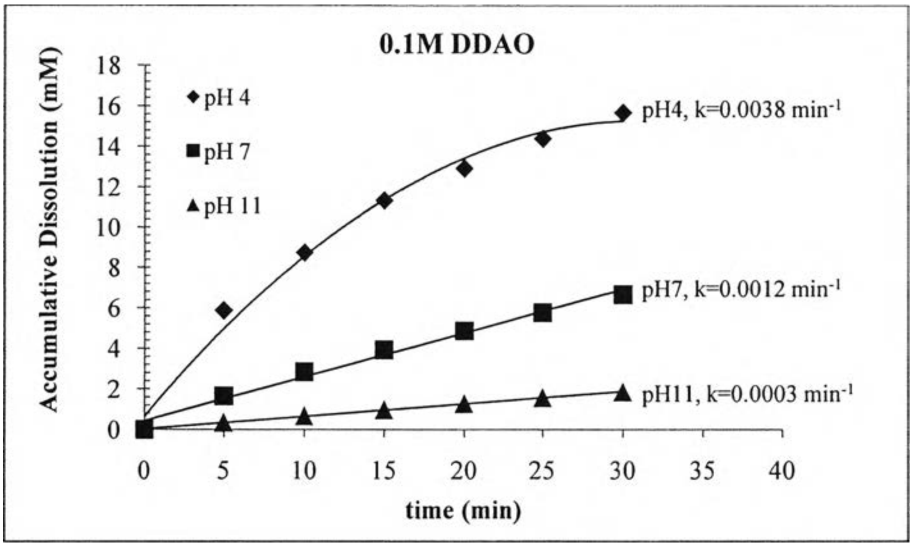
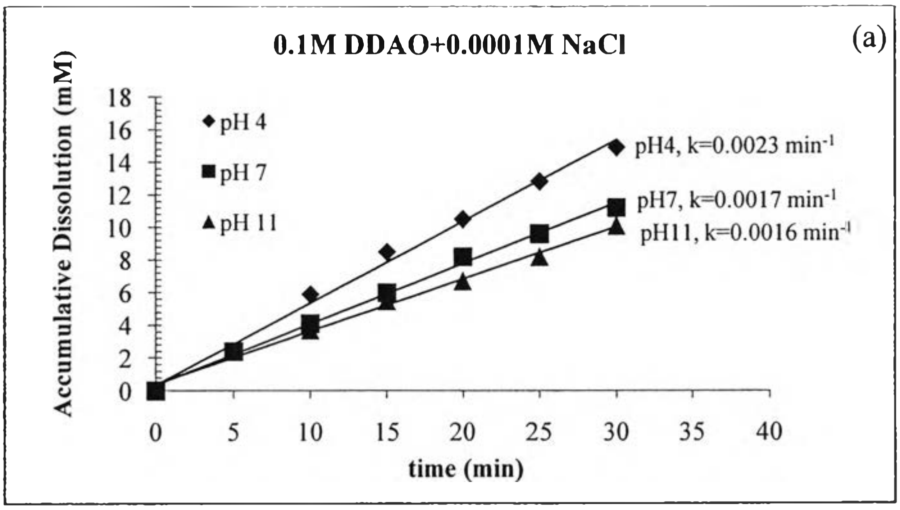


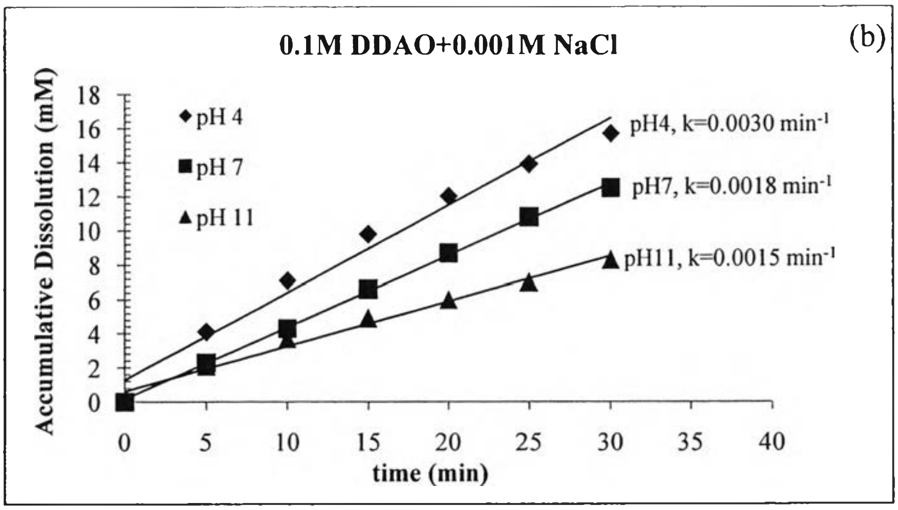
Figure 4.4 Accumulative dissolution and dissolution rate of calcium soap scum in 0.1M DDAO surfactant at various solution pHs and at constant temperature of 25 °C.

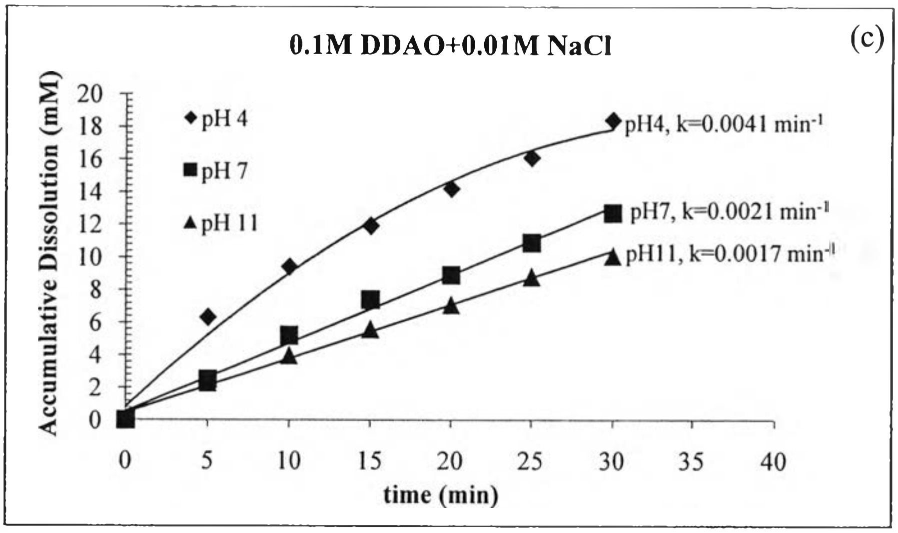
Not only the form of fatty acid but solution pH also affected the form of DDAO surfactant whether cationic or zwitterionic form because DDAO is an amphoteric surfactant. At low solution pH, the cationic form dominants led to the formation of cationic (DDAO) and nonionic (stearic acid) mixed micelle. At high solution pH, the zwitterionic form dominants led to the formation of zwitterionic (DDAO) and anionic (stearate) mixed micelle. Therefore, the highest dissolution rate of soap scum was found at low solution pH because the formation of cationic (DDAO) and nonionic (stearic acid) mixed micelle had a better synergism than zwitterionic (DDAO) and anionic (stearate) mixed micelle due to a less repulsive force among head group of cationic (DDAO) and nonionic (stearic acid) mixed micelle.

4.2.1.3 Mixture of DDAO and NaCl Solution

Various NaCl concentrations showed the similar trend on the dissolution rate of soap scum where the highest dissolution rate of soap scum was found at solution pH of 4 as shown in Figure 4.5







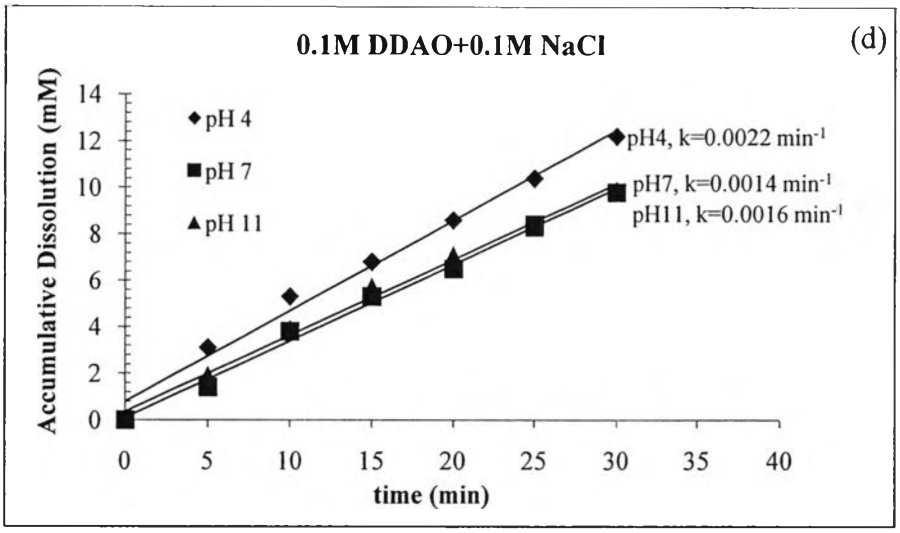


Figure 4.5 Accumulative dissolution and dissolution rate of calcium soap scum in 0.1M DDAO surfactant at various NaCl concentrations; (a) 0.0001M NaCl; (b) 0.001M NaCl; (c) 0.01M NaCl; (d) 0.1M NaCl at various solution pHs at constant temperature of 25 °C.

At low solution pH, stearic acid could occur due to the exchange ion between calcium ion and proton and further exchanged with sodium ion led to the formation of stearate anion. As a result, nonionic (stearic acid) and cationic (DDAO) or anionic (stearate) and cationic (DDAO) mixed micelle could occur while at high solution pH, there was only anionic (stearate) and zwitterionic (DDAO) mixed micelle. The synergism between nonionic (stearic acid) and cationic

(DDAO) or anionic (stearate) and cationic (DDAO) mixed micelle was better than anionic (stearate) and zwitterionic (DDAO) mixed micelle resulted in higher dissolution of soap scum.

4.2.1.4 Mixture of DDAO and Na_2EDTA Solution

The dissolution rate of soap scum in DDAO with Na_2EDTA was the opposite trend with previous systems. The highest dissolution rate of soap scum was found at pH 11 as shown in Figure 4.6

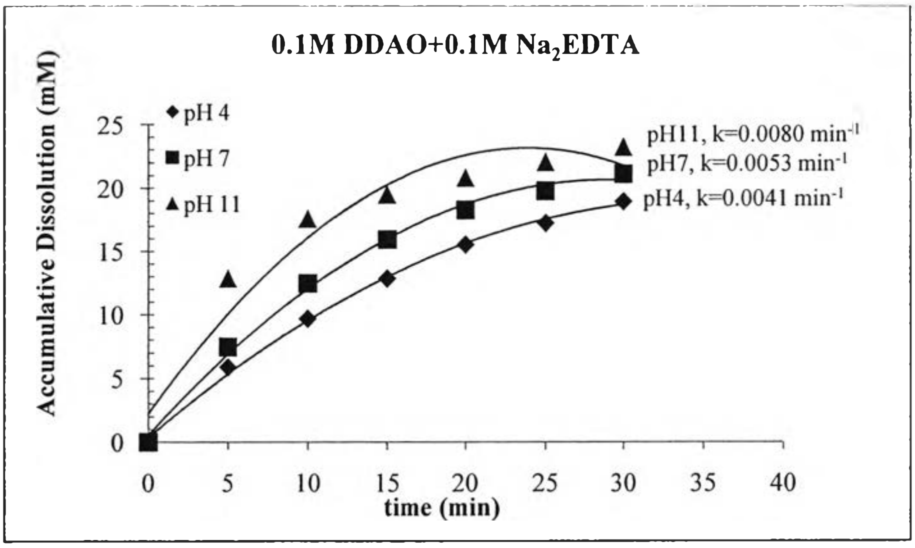


Figure 4.6 Accumulative dissolution and dissolution rate of calcium soap scum in 0.1M DDAO mixed with 0.1M Na_2EDTA at various solution pHs and at constant temperature of 25 °C.

There are 5 forms of chelant depending on solution pH (H_4Y, H_3Y^-, H_2Y^{2-}, HY^{3-} and Y^{4-}). In order to form bond with Ca^{2+} ions, Y^{4-} is the most effective form which found at high solution pH and the effectiveness of chelant decreased with decreasing solution pH because of the protonation of active sites on the Na_2EDTA. Consequently, the highest dissolution rate of soap scum was found at pH 11.

4.2.1.5 Mixture of DDAO, Na_2EDTA and NaCl Solution

The solution pH had insignificant effect on the dissolution of soap scum in the mixture of DDAO, Na_2EDTA and NaCl solution as shown in Figure 4.7.

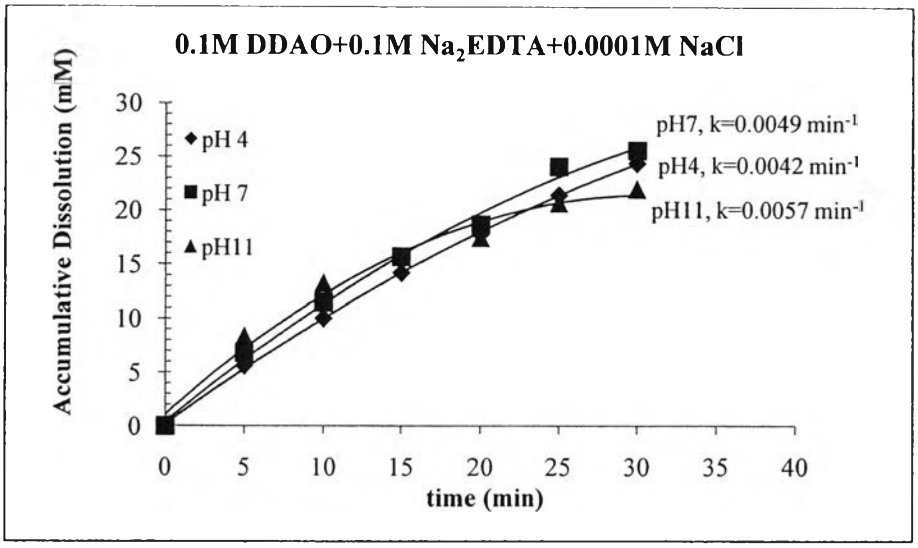


Figure 4.7 Accumulative dissolution and dissoloution rate of calcium soap scum in 0.1M DDAO mixed with 0.1M Na_2EDTA and 0.0001M NaCl at various solution pHs and at constant temperature of 25 °C.

Even though, chelant has the most effective form to bind with Ca^{2+} ions at high solution pH but in the presence of NaCl, the effectiveness of chelant to form with Ca^{2+} ions was decreased because the presence of NaCl provided less active sites of chelant to form bond with calcium ions. Therefore, the dissolution rate of soap scum was nearly the same for all studied solution pH.

4.2.2 Effect of NaCl Concentration

4.2.2.1 Solution pH of 4

The optimum NaCl concentration on the dissolution rate of soap scum was found at 0.01M which showed the highest dissolution rate of soap scum as shown in Figure 4.8 and Table 4.1.

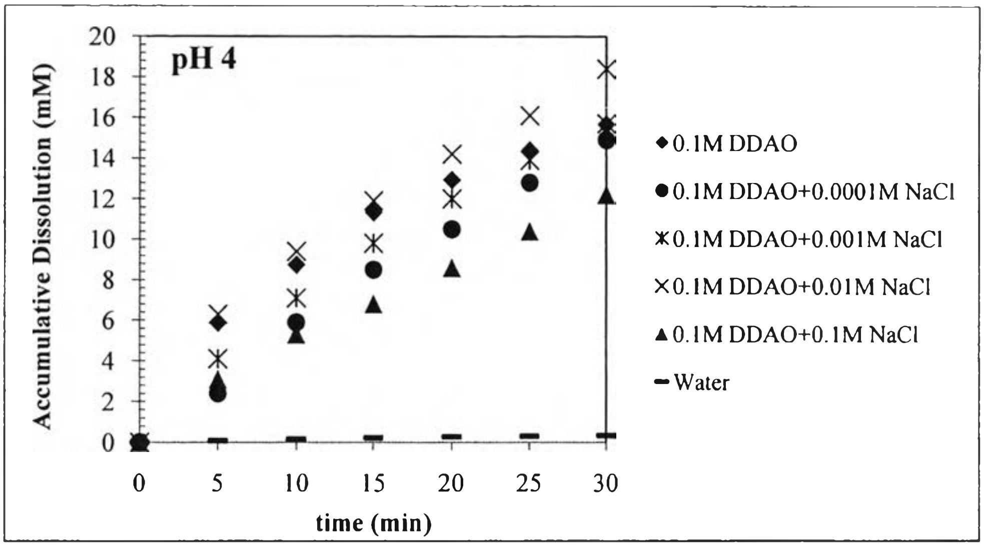


Figure 4.8 Accumulative dissolution of calcium soap scum in 0.1M DDAO at various NaCl concentrations at pH 4 and constant temperature of 25 °C.

Table 4.1 Dissolution rate of calcium soap scum in various solutions at pH 4 and constant temperature of 25 °C

Solution	Initial rate constant (10^3 min^{-1})
H_2O	0.07
0.1M DDAO	3.80
0.1M DDAO + 0.0001M NaCl	2.30
0.1M DDAO + 0.001M NaCl	3.00
0.1M DDAO + 0.01M NaCl	4.10
0.1M DDAO + 0.1M NaCl	2.20

At NaCl concentration less than 0.01M, the dissolution rate of soap scum decreased as compared to DDAO system because sodium ions from NaCl can exchanged with proton in stearic acid and caused stearate anion led to the formation of anionic (stearate) and cationic or zwitterionic (DDAO) mixed micelles which have a higher electrostatic repulsion between the head group than nonionic (stearic acid) and cationic or zwitterionic (DDAO) mixed micelles. At the optimum concentration of NaCl (0.01M), the dissolution rate of soap scum increased because amount of NaCl had high enough for balancing charges among the head group of mixed micelles. However, further increasing NaCl, the dissolution rate of soap scum decreased because of high repulsive force among the head group of mixed micelles.

4.2.2.2 Solution pH of 7

At this solution pH, the addition of NaCl increased the dissolution rate of soap scum and 0.01M NaCl was the optimum concentration which gave the highest dissolution rate of soap scum as shown in Figure 6.9 and Table 4.2

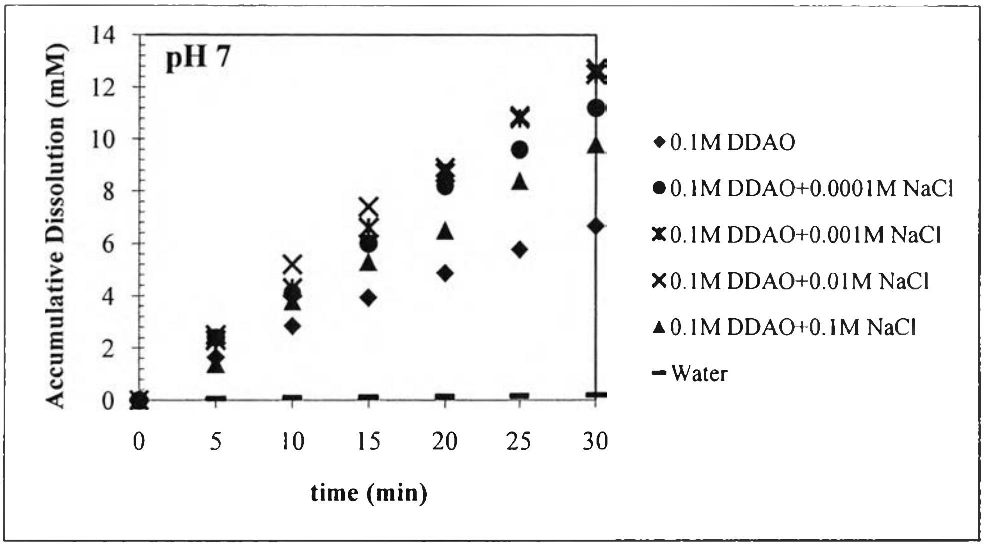


Figure 4.9 Accumulative dissolution of calcium soap scum in various solutions at pH 7 and constant temperature of 25 °C.

Table 4.2 Dissolution rate of calcium soap scum in various solutions at pH 7 and constant temperature of 25 °C

Solution	Initial rate constant (10^3 min^{-1})
H_2O	0.04
0.1M DDAO	1.20
0.1M DDAO + 0.0001M NaCl	1.70
0.1M DDAO + 0.001M NaCl	1.80
0.1M DDAO + 0.01M NaCl	2.10
0.1M DDAO + 0.1M NaCl	1.40

Without NaCl, the formation of anionic (stearate) and zwitterionic (DDAO) occurred. But the addition of NaCl provided sodium ion to balance the charge between head group of mixed micelles led to an increasing in dissolution rate of soap scum. Moreover, increasing NaCl concentration, the dissolution rate increased until reaching the optimum concentration because of high enough ions for balancing the charged between the head group of mixed micelles. However, adding higher NaCl concentration beyond the optimum concentration, the more stearate was obtained leading to decrease on the dissolution rate of soap scum due to a high electrostatic repulsion among the head group of mixed micelles.

4.2.2.3 Solution pH of 11

The addition of NaCl significantly increased the dissolution of soap scum and the highest dissolution rate of soap scum was found in 0.1M DDAO mixed with 0.01M NaCl system as shown in Figure 4.10 and Table 4.3.

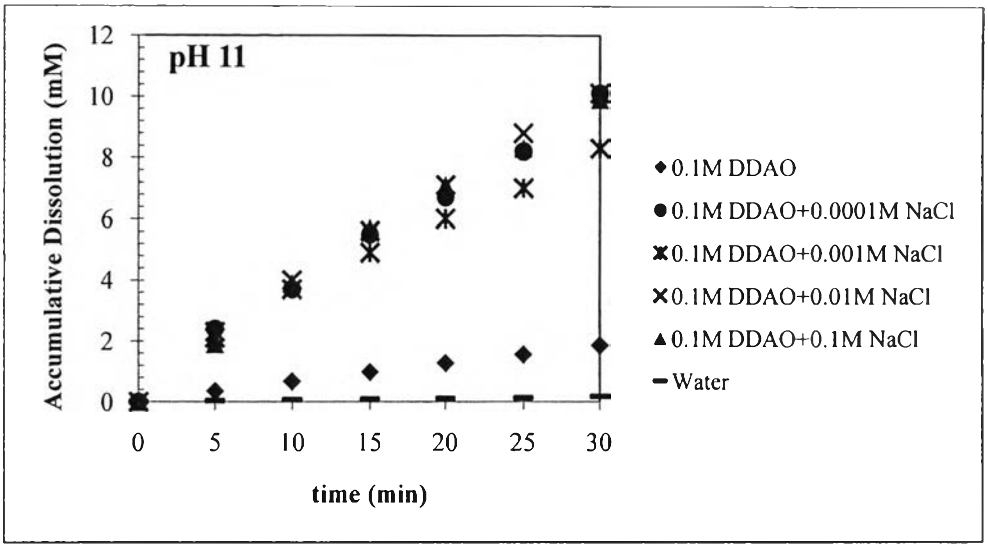


Figure 4.10 Accumulative dissolution of calcium soap scum in various solutions at pH 11 and constant temperature of 25 °C.

Table 4.3 Dissolution rate of calcium soap scum in various solutions at pH 11 and concstant temperature of 25 °C

Solution	Initial rate constant (10^3 min^{-1})
H_2O	0.03
0.1M DDAO	0.30
0.1M DDAO + 0.0001M NaCl	1.60
0.1M DDAO + 0.001M NaCl	1.50
0.1M DDAO + 0.01M NaCl	1.70
0.1M DDAO + 0.1M NaCl	1.60

Due to an increasing of anionic (stearate) and zwitterionic (DDAO) mixed micelle in DDAO system which had high electrostatic repulsion between head group of mixed micelles leading to low dissolution rate of soap scum. But the dissolution rate of soap scum can be improved by adding NaCl because NaCl provided sodium ion for balancing the charge between head group of mixed micelles.

4.2.3 Effect of Chelant

4.2.3.1 Solution pH of 4

The addition of chelant in both DDAO and DDAO with NaCl system had slightly effect on the dissolution rate of soap scum as compare to DDAO and DDAO with NaCl systems as shown in Figure 4.11 and Table 4.4.

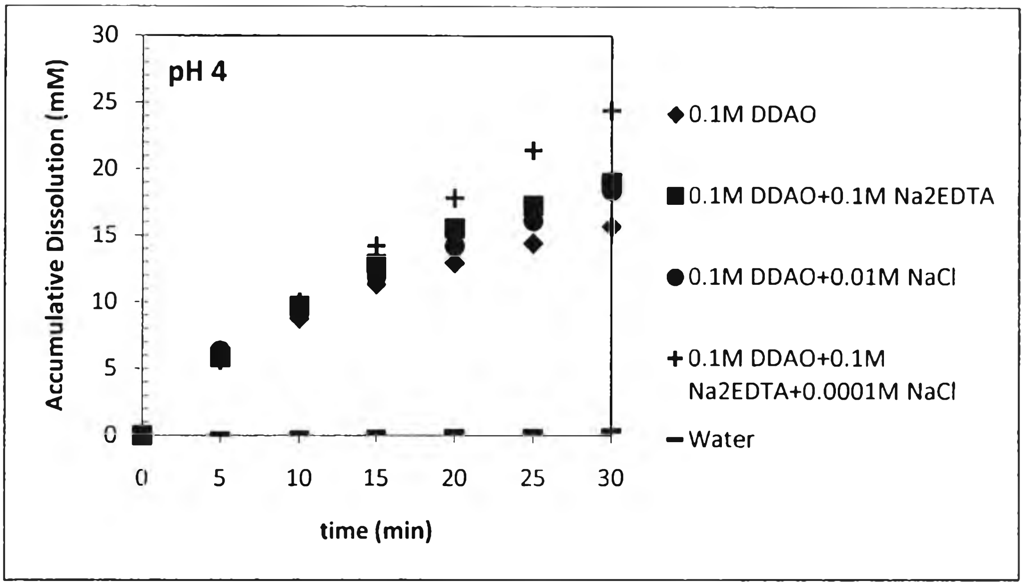


Figure 4.11 Accumulative dissolution of calcium soap scum in various solutions at pH 4 and constant temperature of 25 °C.

Table 4.4 Dissolution rate of calcium soap scum in various solutions at pH 4 and constant temperature of 25 °C

Solution	Initial rate constant (10^3 min^{-1})
H_2O	0.07
0.1M DDAO	3.80
0.1M DDAO + 0.1M Na_2EDTA	4.10
0.1M DDAO + 0.01M NaCl	4.10
0.1M DDAO + 0.1M Na_2EDTA + 0.0001M NaCl	4.20

The dissolution rate of soap scum in DDAO, DDAO with chelant, DDAO with salt and DDAO with chelant and salt showed nearly the same rate because chelant had ineffective form and less active site to form bond with calcium ions at this solution pH.

4.2.3.2 Solution pH of 7

The presence of chelant greatly improved the dissolution rate of soap scum as shown in Figure 4.12 and Table 4.5.

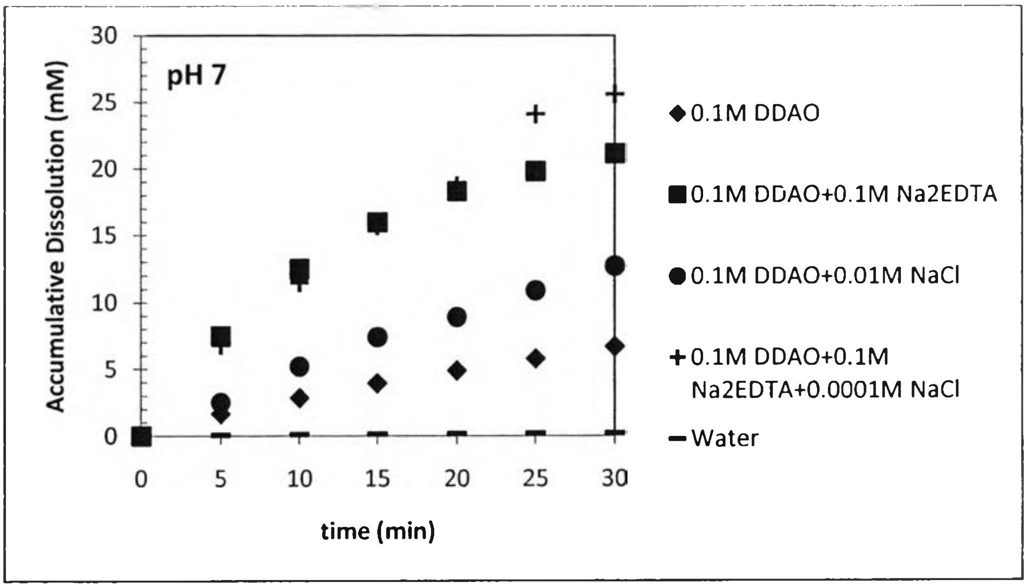


Figure 4.12 Accumulative dissolution of calcium soap scum in various solutions at pH 7 and constant temperature of 25 °C.

Table 4.5 Dissolution rate of calcium soap scum in various solutions at pH 7 and constant temperature of 25 °C

Solution	Initial rate constant (10^3 min^{-1})
H_2O	0.04
0.1M DDAO	1.20
0.1M DDAO + 0.1M Na_2EDTA	5.30
0.1M DDAO + 0.01M NaCl	2.10
0.1M DDAO + 0.1M Na_2EDTA + 0.0001M NaCl	4.90

The addition of chelant greatly aided the dissolution rate of soap scum because, at this solution pH, chelant had quite effective form to bind with calcium ions and left the stearate anion to form mixed micelle with DDAO surfactant and NaCl also helped on balancing the charged between head group of mixed micelles. However, when NaCl present in DDAO with Na_2EDTA system, the dissolution rate of soap scum slightly decreased as compare to DDAO with Na_2EDTA system because the presence of NaCl provided less active site of chelant to bind with calcium ions.

4.2.3.3 Solution pH 11

The addition of chelant caused a significantly improvement of soap scum dissolution rate. However, when both chelant and NaCl present in the DDAO system, the dissolution rate of soap scum was decreased as shown in Figure 4.13 and Table 4.6.

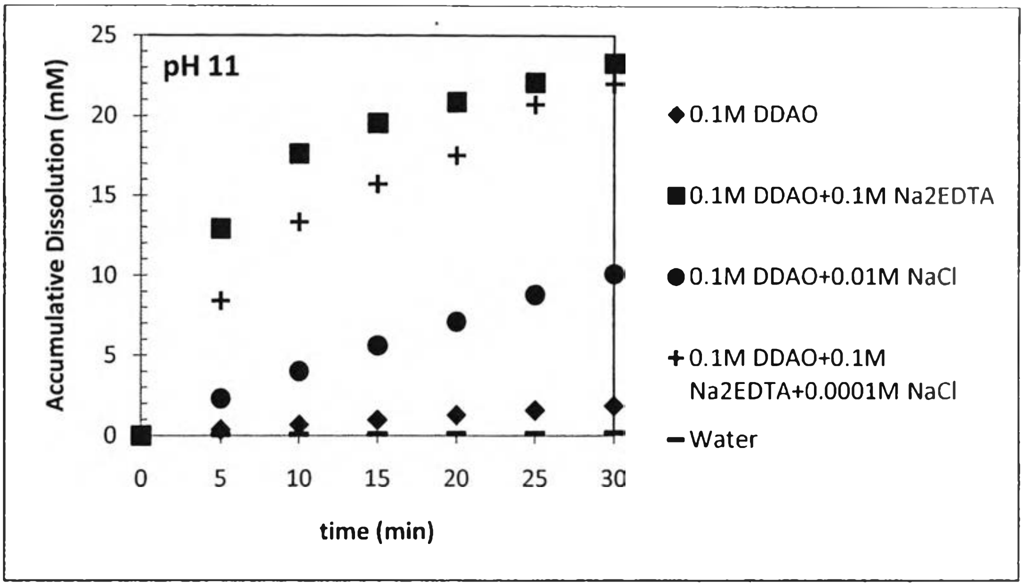


Figure 4.13 Accumulative dissolution of calcium soap scum in various solutions at pH 11 and constant temperature of 25 °C.

Table 4.6 Dissolution rate of calcium soap scum in various solution at pH 11 and constant temperature of 25 °C

Solution	Initial rate constant (10^3 min^{-1})
H_2O	0.03
0.1M DDAO	0.30
0.1M DDAO + 0.1M Na_2EDTA	8.00
0.1M DDAO + 0.01M NaCl	1.70
0.1M DDAO + 0.1M Na_2EDTA + 0.0001M NaCl	5.70

The highest dissolution rate of soap scum was found in DDAO with chelant system follow by DDAO with chelant and NaCl, DDAO with NaCl, DDAO and the water respectively. At this solution pH, the most effective form of chelant was found led to significantly increase the dissolution rate of soap scum. But when chelant and NaCl present in the DDAO system, the dissolution rate was decreased because the presence of sodium ions from NaCl provided less active sites of chelant to form with calcium ions.