

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Critical Micelle Concentration (CMC) Measurement

The critical micelle concentration (CMC) is an important parameter to determine the effectiveness of surfactant system. At the CMC is the lowest surfactant concentration starting to form micelle, below the CMC, surfactant solution has much less efficient solubilization than higher CMC value. The CMC is determined by the plot between surface tension (mN/m) and logarithmic surfactant concentration (μM). The transition point (interception point) of the plot is the CMC value of the surfactant system as shown in Figure 4.1.

The CMC values were investigated with the effect of salinity or salt concentration, number of EO group in nonionic surfactant and synergism interaction of mixed anionic and nonionic systems.

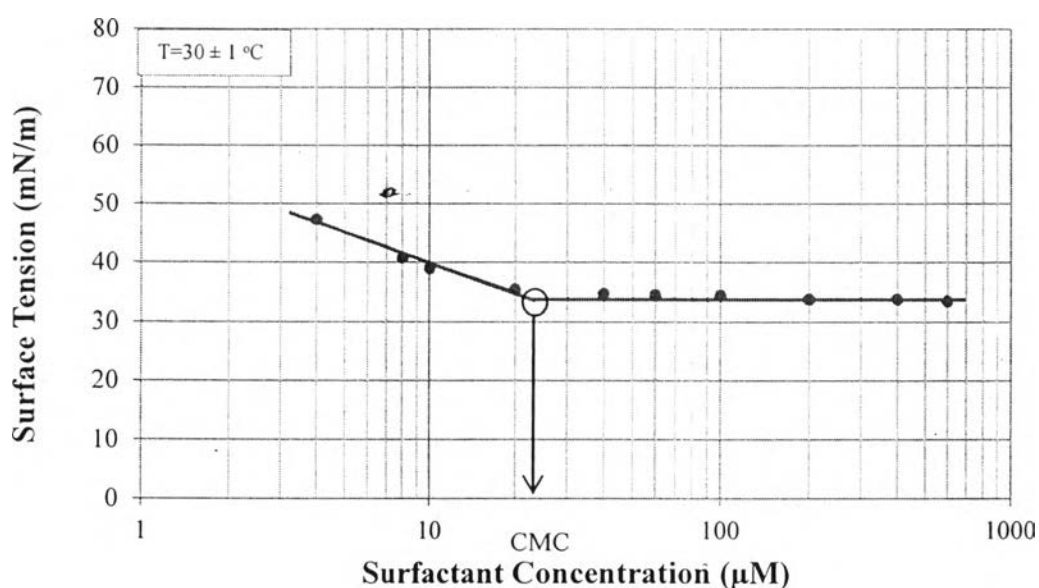


Figure 4.1 The determination of critical micelle concentration (CMC).

4.1.1 The Effect of NaCl

The result showed that the presence of NaCl significantly decreased the CMC value of anionic extended surfactant [$C_{14-15}H_{29-31}-(PO)_8-SO_4Na$] from about 20 to just 10 μM without and with 4.6 % NaCl, respectively as shown in Figure 4.2. The mixed surfactant systems showed the same trend as single anionic surfactant, the mixed surfactant systems with $C_{14-15}H_{29-31}-(PO)_8-SO_4Na$ and $C_{12-14}H_{25-29}-(EO)_3-OH$ at 1:1 by molar ratio without and with NaCl (4.6 %w/v) indicated the CMC values of 20 and 6.1 μM , respectively as shown in Figure 4.3. This is because NaCl or electrolyte addition reduces the repulsion between anionic charges of surfactant head group. As a consequence, the aggregation number of surfactants increases, with increasing ability of the aggregates to form micelle comfortably and leads to a reduction in the CMC value (Rosen, 2012).

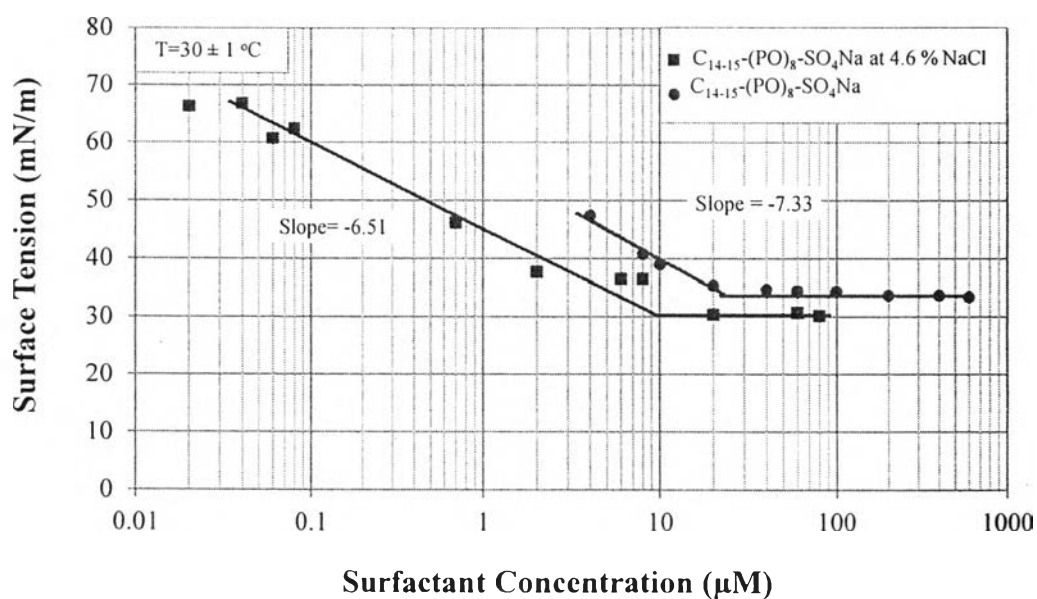


Figure 4.2 The CMC values of $C_{14-15}H_{29-31}-(PO)_8-SO_4Na$ with and without NaCl added.

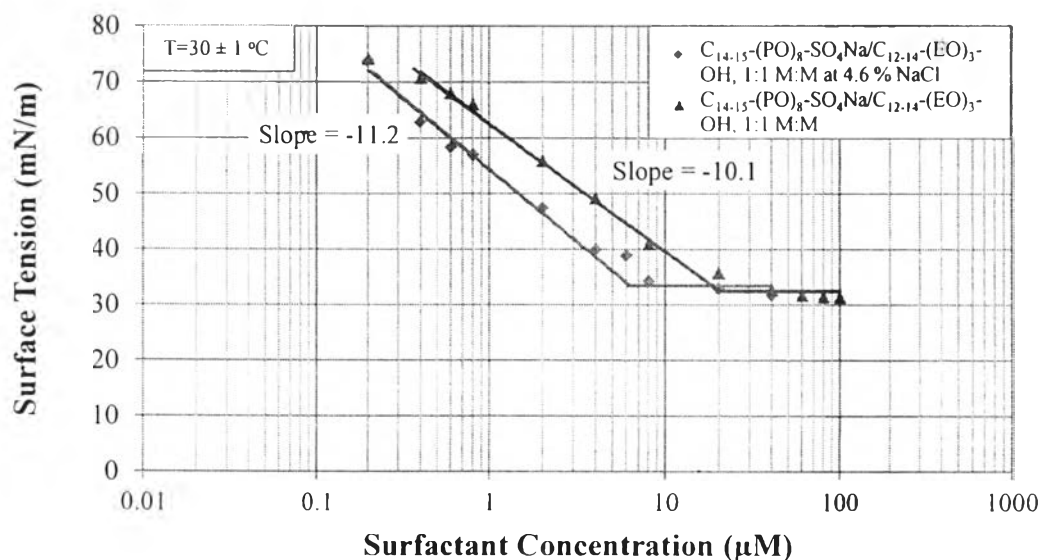


Figure 4.3 The CMC values of mixed surfactant system between $C_{14-15}H_{29-31}-(PO)_8-SO_4Na$ and $C_{12-14}H_{25-29}-(EO)_3-OH$, 1:1 by molar ratio with and without NaCl added.

4.1.2 The Effect of EO Group in Nonionic Surfactants

The CMC values of nonionic surfactants [$C_{12-14}H_{25-29}-(EO)_n-OH$] with different EO groups are presented in Figure 4.4. The result showed that the CMC values of $C_{12-14}H_{25-29}-(EO)_3-OH$, $C_{12-14}H_{25-29}-(EO)_5-OH$ and $C_{12-14}H_{25-29}-(EO)_9-OH$ were 20, 29, and 37 μM , respectively. It can be seen that the CMC values increased considerably as the number of EO groups increased. The reason for this due to the fact that the rise of EO groups in alcohol ethoxylated nonionic surfactant increase the HLB value from 8.0, 10.5 to 13.5 for 3, 5 and 9 EO groups, respectively as depicted in Table 4.1. The increase of EO group in surfactant molecule increase CMC value because of steric effect (Rosen, 2012).

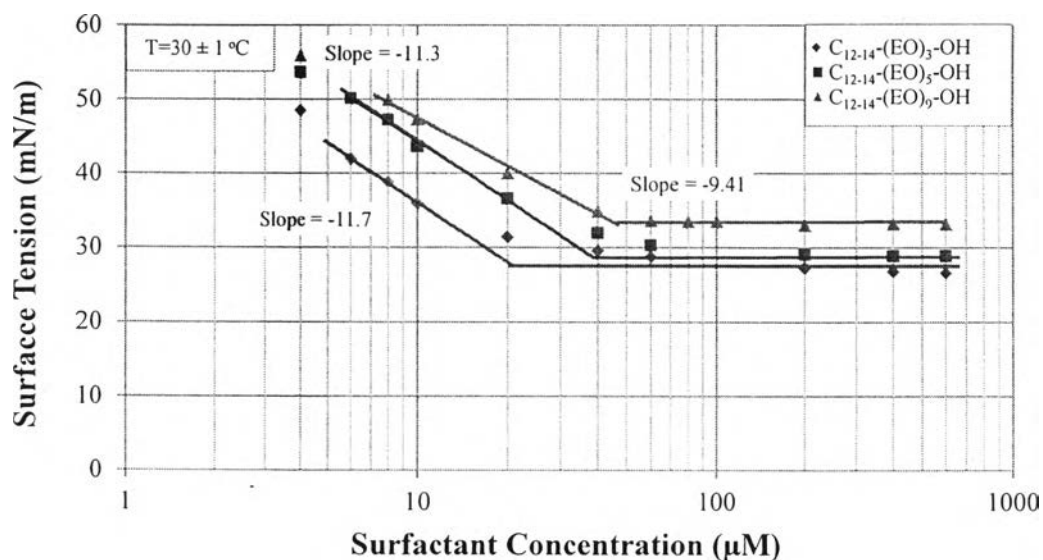


Figure 4.4 The CMC values of $C_{12-14}H_{25-29}-(EO)_n-OH$ with different EO groups.

4.1.3 The Synergism Effects on Mixed Surfactant Systems

The result from CMC measurement showed that there was a synergism effect in mixed surfactant systems for even both with NaCl and without NaCl addition. The CMC values of mixed surfactant systems without NaCl added were found between the CMC values of single anionic extended and nonionic surfactants as depicted in Figure 4.5. The CMC values of single anionic extended surfactant [$C_{14-15}H_{29-31}-(PO)_8-SO_4Na$] and nonionic surfactants [$C_{12-14}H_{25-29}-(EO)_3-OH$] and mixed anionic and nonionic surfactant system [$C_{14-15}H_{29-31}-(PO)_8-SO_4Na/C_{12-14}H_{25-29}-(EO)_3-OH$, 1:1 molar ratio] without NaCl added were almost similar about 20 μM . The synergism effect presented when NaCl added in surfactant systems, the CMC values of mixed anionic and nonionic systems by 1:0.1 molar ratio (8 μM), by 1:1 molar ratio (6.1 μM) decreased slightly from single anionic surfactant [$C_{14-15}H_{29-31}-(PO)_8-SO_4Na$] (10 μM) as illustrated in Figure 4.6. This can be implied that mixed system between anionic and nonionic surfactants had a synergism effect due to the reduction in CMC value (Kameyama, 1997; Zhang, 2004).

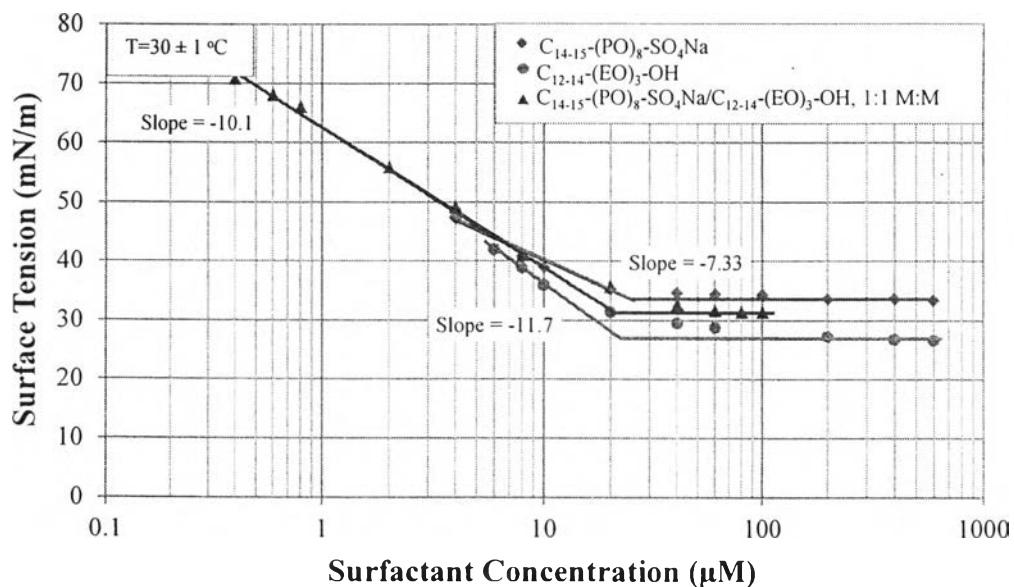


Figure 4.5 The CMC values of different surfactant systems without NaCl added.

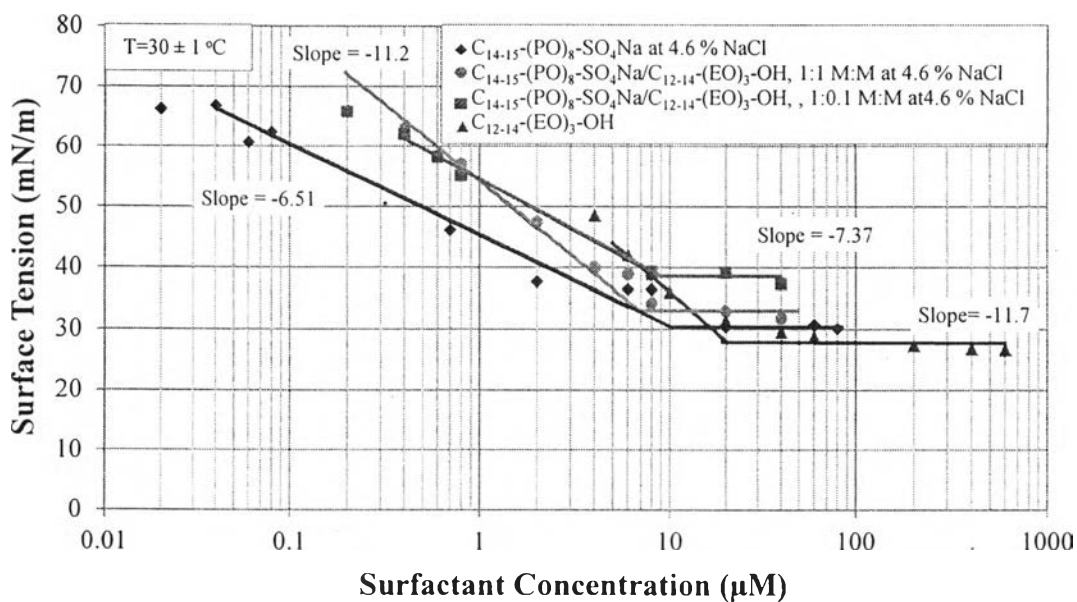


Figure 4.6 The CMC values of different surfactant systems with NaCl added.

4.2 Effective Area Per Molecule (A_s)

The effective area per molecule of surfactant is calculated from Gibb equation using the data from the plot between surface tension (mN/m) and surfactant concentration (M) (Rosen, 2012). The synergism effect (β) of mixed surfactant system was calculated from the regular solution theory (Rosen, 2012). Typically, the $CMC_{S_{ideal}}$ are different compared to $CMC_{S_{exp}}$ because of interaction between hydrophilic (electrostatic effect) and hydrophobic group (stearic effect) in surfactant molecule (Zhou, 2004).

The result from Table 4.1 showed that the addition of NaCl decreased effective area per molecule (A_s) for all surfactant systems. For example, $C_{14-15}H_{29-31}(PO)_8-SO_4Na$ without and with 4.6 %w/v NaCl added had the effective area per molecule of 262.96 and 148.04 $^{\circ}A^2$, respectively due to the fact that the addition of NaCl increases packing of micelle density. The number of EO groups in nonionic surfactants slightly increased with the A_s value of $C_{12-14}H_{25-29}(EO)_3-OH$ and $C_{12-14}H_{25-29}(EO)_9-OH$ from 82.37 to 102.24 $^{\circ}A^2$, respectively. It can be seen from Table 4.2 that the $CMC_{S_{exp}}$ were obviously lower than the $CMC_{S_{ideal}}$ of all mixed surfactant systems, $C_{14-15}H_{29-31}(PO)_8-SO_4Na/C_{12-14}H_{25-29}(EO)_3-OH$, 1:1 and 1:0.1 molar ratio. These mixed surfactant systems showed attractive synergism effect due to negative interaction parameter ($\beta =$ negative value). The greater negative values of β means the greater negative deviation of CMCs from the ideal mixture. The negative deviation of $CMC_{S_{exp}}$ from the ideal mixture ($CMC_{S_{ideal}}$) of $C_{14-15}H_{29-31}(PO)_8-SO_4Na/C_{12-14}H_{25-29}(EO)_3-OH$, 1:1 molar ratio at 4.6 % NaCl was higher than that in the mixed system at 1:0.1 molar ratio. Therefore, the mixed surfactant system of $C_{14-15}H_{29-31}(PO)_8-SO_4Na/C_{12-14}H_{25-29}(EO)_3-OH$, 1:1 molar ratio at 4.6 % NaCl had greater attractive synergism effect (-3.27) and led to the lowest effective area per molecule (A_s) value as shown in Table 4.1.

Table 4.1 The effective area per molecule as different surfactant systems

Surfactant System	NaCl Addition (4.6 %w/v)	HLB Value	CMC (μM)	($d\gamma/d\log C$) Slope	Effective Area Per Molecule ($^{\circ}\text{A}^2$)
Single System					
C ₁₄₋₁₅ H ₂₉₋₃₁ -(PO) ₈ -SO ₄ Na	None	37.6	21	-7.33	262.96
	Added		10	-6.51	148.04
C ₁₂₋₁₄ H ₂₅₋₂₉ -(EO) ₃ -OH	None	8.0	20	-11.7	82.37
C ₁₂₋₁₄ H ₂₅₋₂₉ -(EO) ₅ -OH	None	10.5	29	-11.3	85.29
C ₁₂₋₁₄ H ₂₅₋₂₉ -(EO) ₉ -OH	None	13.3	37	-9.41	102.42
Mixed System					
C ₁₄₋₁₅ H ₂₉₋₃₁ -(PO) ₈ -SO ₄ Na/ C ₁₂₋₁₄ H ₂₅₋₂₉ -(EO) ₃ -OH, 1:1	None		20	-10.1	190.84
	Added		6.1	-11.2	86.05
C ₁₄₋₁₅ H ₂₉₋₃₁ -(PO) ₈ -SO ₄ Na/ C ₁₂₋₁₄ H ₂₅₋₂₉ -(EO) ₃ -OH, 1:0.1	Added		8.4	-7.37	130.76

^aR²>0.95**Table 4.2** The interaction parameter (β) of mixed surfactant systems by molar ratio

Surfactant System	CMC _{exp} (mM)	CMC _{ideal} ^a (mM)	X ₁ ^b	β ^c
C ₁₄₋₁₅ H ₂₉₋₃₁ -(PO) ₈ -SO ₄ Na/4.6% NaCl	0.010	-	-	-
C ₁₂₋₁₄ H ₂₅₋₂₉ -(EO) ₃ -OH	0.020	-	-	-
C ₁₄₋₁₅ H ₂₉₋₃₁ -(PO) ₈ -SO ₄ Na/C ₁₂₋₁₄ H ₂₅₋₂₉ -(EO) ₃ -OH, 1:1 (M:M) at 4.6% NaCl	0.0061	0.013	0.57	-3.27
C ₁₄₋₁₅ H ₂₉₋₃₁ -(PO) ₈ -SO ₄ Na/C ₁₂₋₁₄ H ₂₅₋₂₉ -(EO) ₃ -OH, 1:0.1 (M:M) at 4.6% NaCl	0.0084	0.010	0.82	-2.29

$$a) \frac{1}{\text{CMC}_{\text{ideal}}} = \frac{\alpha_1}{\text{CMC}_1} + \frac{\alpha_2}{\text{CMC}_2}$$

$$b) I = \frac{X_1^2 \ln\left(\frac{\alpha_1 \text{CMC}_{\text{mix}}}{X_1 \text{CMC}_1}\right)}{(1-X_1)^2 \ln\left[(1-\alpha_1) \text{CMC}_{\text{mix}} / (1-X_1) \text{CMC}_2\right]}$$

$$c) \beta = \frac{\ln\left(\frac{\alpha_1 \text{CMC}_{\text{mix}}}{X_1 \text{CMC}_1}\right)}{(1-X_1)^2}$$

4.3 Phase Behavior and Microemulsion Formation Study

Winsor Type III microemulsion or middle phase microemulsion of water and oil phases at the IFT less than 10^{-3} mN/m have been presented remarkably oil solubilization capacity for oil and aqueous solutions (Tongcumpou, 2003). Therefore, the microemulsion phase behaviors are studied in this research in order to find optimum condition. The microemulsion formation study was conducted by palm olein to form a middle phase microemulsion (Winsor Type III microemulsion) at 30 ± 1 °C with varying surfactant concentrations (M), salinities (%w/v) and ratios of anionic and nonionic mixed surfactant systems. The phase behavior determination was conducted with a single anionic extended surfactant system [$C_{14-15}H_{29-31}-(PO)_8-SO_4Na$] and mixed surfactant systems of the anionic extended surfactant with varying nonionic surfactant types [sorbitan stearate (SS), sorbitan oleate (SO), and $C_{12-14}H_{25-29}-(EO)_n-OH$ ($n = 3, 5$ and 9)]

4.3.1 Microemulsion Phase Behavior and Optimum Salinity Determination

The optimum NaCl concentration was first studied using the single anionic extended surfactant [$C_{14-15}H_{29-31}-(PO)_8-SO_4Na$]. The result showed that the middle phase microemulsions were not observed visually after leaving the system to reach equilibrium and there were sponge formation appeared in all salinities as shown in Figure 4.7a. The optimum salinity observed before phase transition from Winsor Type I microemulsion (oil in water) to microemulsion Type II (water in oil) was then recorded.

4.3.2 Effect of Renewable-Based Nonionic Surfactants

The microemulsion formations of single bio-based surfactants (SS and SO) systems were conducted. The result indicates that both SS and SO were not able to form middle phase microemulsion, sponge phase were observed in all systems as single anionic extended surfactant with different NaCl concentrations as depicted in Figure 4.7c. Moreover, both the SS and SO participated at the bottom of flat test tube or on the only one side of the interface after leaving the systems, this observation is consistent with Acosta and coworker's work (Acosta, 2005). This

means that bio-based sorbitan nonionic surfactants (SS and SO) were not suitable in microemulsion formation with palm oil. As a result, both SS and SO were neglected in this research.

4.3.3 Effect of EO Group in Nonionic Surfactants

Since the sorbitan nonionic surfactants tend to precipitate in microemulsion formation with palm oil, alcohol ethoxylated surfactants [$C_{12-14}H_{25-29}-(EO)_n-OH$ ($n = 3, 5, \text{ and } 9$)] are conducted in this study. However, the microemulsion formation of alcohol ethoxylate with different EO groups [$C_{12-14}H_{25-29}-(EO)_n-OH$ ($n = 3, 5, \text{ and } 9$)] presented the same result as well. The middle phase microemulsions of nonionic surfactant alone and mixed anionic surfactant and nonionic surfactant system with palm olein were difficult to observe, and again there were sponge formations in all systems as shown in Figure 4.7b.

Apparently, there were no surfactant precipitations or phase separation with alcohol ethoxylated surfactant system. These nonionic surfactants were more practical and suitable for using in mixed surfactant systems to form microemulsions. Alcohol ethoxylated surfactants with different EO groups [$C_{12-14}H_{25-29}-(EO)_n-OH$ ($n = 3, 5, \text{ and } 9$)] will be selected for this study.

4.3.4 Effect of Mixed Surfactant Systems

The microemulsion behaviors of mixed surfactant systems between anionic extended surfactant [$C_{14-15}H_{29-31}-(PO)_8-SO_4Na$] and nonionic surfactants, alcohol ethoxylated surfactants with different EO groups [$C_{12-14}H_{25-29}-(EO)_n-OH$ ($n = 3, 5, \text{ and } 9$)] were performed using palm olein as an oil phase at 30 °C with different surfactant molar ratios and NaCl concentrations. The result also showed that middle phase microemulsion cannot be observed as shown in Figure 4.7d. The absence of middle phase microemulsion could be due to the fact that vegetable oils have very high hydrophobicity in tail structure and polarity in ester region, causing complicated system (Witthayapanyanon, 2006; Do, 2009). Although the middle phase microemulsion ($IFT < 0.001 \text{ mN/m}$) did not be observed from microemulsion phase scan study, this alcohol ethoxylated nonionic surfactant is selected to evaluate the

synergism interaction on oil solubilization for increasing the efficiency of semi-solid fat solubilization in mixed surfactant systems

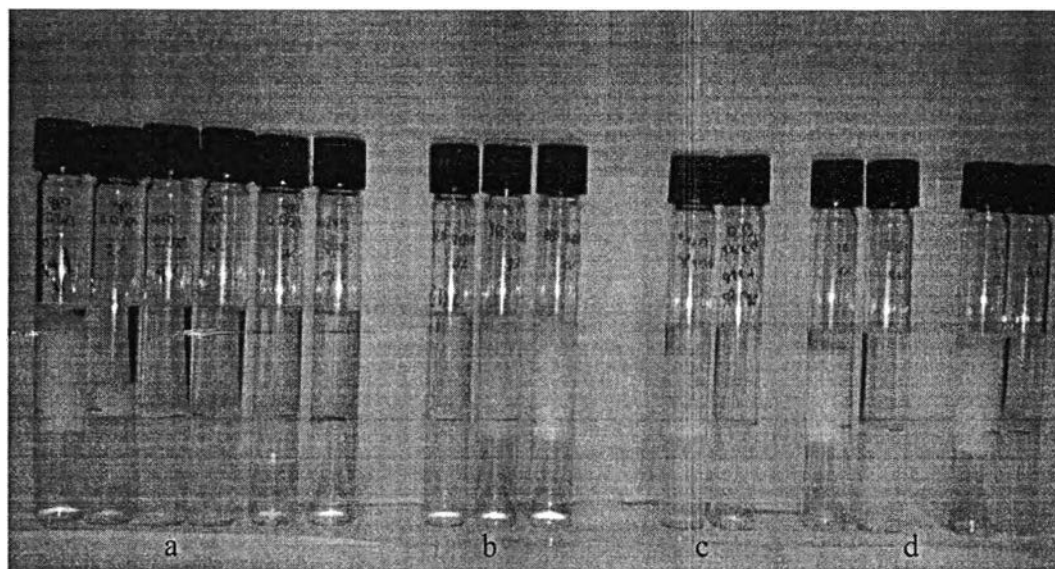


Figure 4.7 The microemulsion phase behavior of different surfactant formulation. a) $C_{14-15}H_{29-31}-(PO)_8-SO_4Na$ with different NaCl concentration, b) $[C_{12-14}H_{25-29}-(EO)_n-OH]$ ($n = 3, 5, \text{ and } 9$), c) SO and mixed surfactant systems [$C_{14-15}H_{29-31}-(PO)_8-SO_4Na$ and SO] and d.) mixed surfactant systems [$C_{14-15}H_{29-31}-(PO)_8-SO_4Na$ and $C_{12-14}H_{25-29}-(EO)_3-OH$] with different molar ratios. All systems were kept under the same condition at $30\text{ }^\circ\text{C}$.

4.4 Dynamic Interfacial Tension (IFT) Measurement

4.4.1 Effect of Salinity

Due to the fact that no middle phase microemulsion was observed in the phase scan experiment, this research had an effort to formulate the optimum microemulsion system providing the least IFT (less than 0.1 mN/m). In order to find the optimum salinity (S^*), the dynamic IFTs of the single anionic extended surfactant system with different NaCl concentrations and mixed surfactant systems between anionic extended surfactant [$C_{14-15}H_{29-31}-(PO)_8-SO_4Na$] and nonionic surfactant [C_{12-}

${}_{14}\text{H}_{25-29}-(\text{EO})_n-\text{OH}$ ($n = 3, 5, \text{ and } 9$)] were measured using spinning drop tensiometer (SVT 15, Dataphysics) at 30°C .

The result from IFT measurement showed that $0.0005\text{ M C}_{14-15}\text{H}_{29-31}-(\text{PO})_8-\text{SO}_4\text{Na}$ at different NaCl concentrations did not achieve ultralow IFT but the surfactant formulation was able to reach low IFT ($\text{IFT} < 0.1\text{ mN/m}$) (Acosta, 2005). This result is accordance with the microemulsion phase result. Figure 4.10 showed that NaCl concentration increased with decreasing the IFT value, until the system reached to a lowest IFT value at 4.6 \%w/v NaCl. When, NaCl concentration further increased, the dynamic IFT turned to increase significantly as depicted in Figure 4.8. This can be implied that phase of microemulsion changed from Winsor Type I to Type II microemulsion. Hence, the NaCl concentration of 4.6 \%w/v was selected as the optimum salinity (S^*) of anionic extended surfactant system for semi-solid fat (palm stearin) solubilization study.

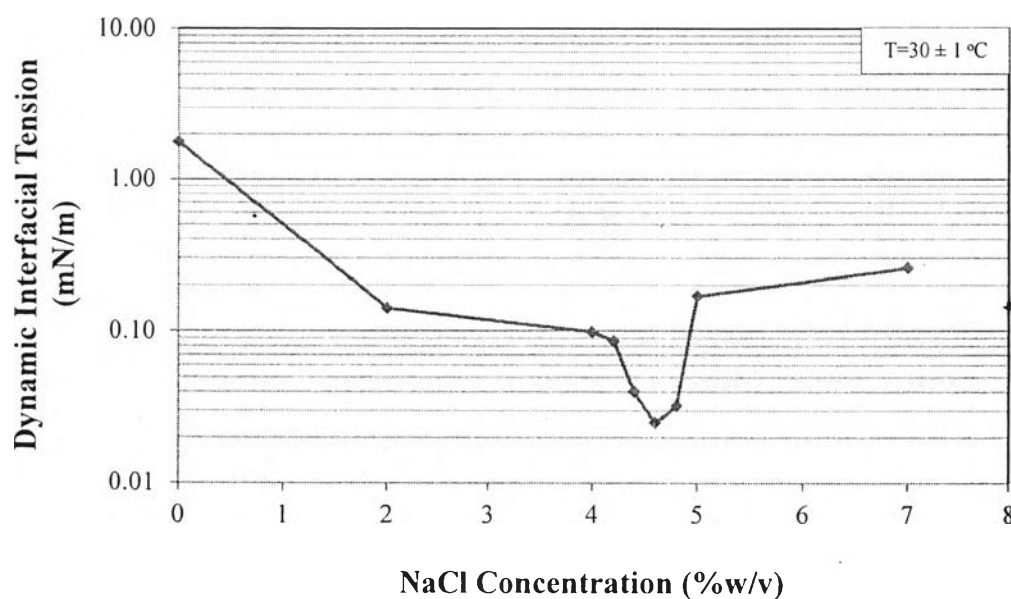


Figure 4.8 Dynamic interfacial tension as a function of NaCl concentration (salinity scan) using $0.0005\text{ M C}_{14-15}\text{H}_{29-31}-(\text{PO})_8-\text{SO}_4\text{Na}$ with palm olein after 20 min.

4.4.2 Effect of EO Group in Nonionic Surfactant

This work intends to study the effect of number of EO groups in nonionic surfactant molecule on dynamic IFT.

The result showed that the increase in number of EO group in alcohol ethoxylated surfactant reduced the IFT value. However, the IFT values of nonionic alcohol ethoxylated surfactant did not achieve an ultralow IFT (less than 10^{-3} mN/m) compared to that of anionic extended surfactant [$C_{14-15}H_{29-31}-(PO)_8-SO_4Na$] as shown in Figure 4.9.

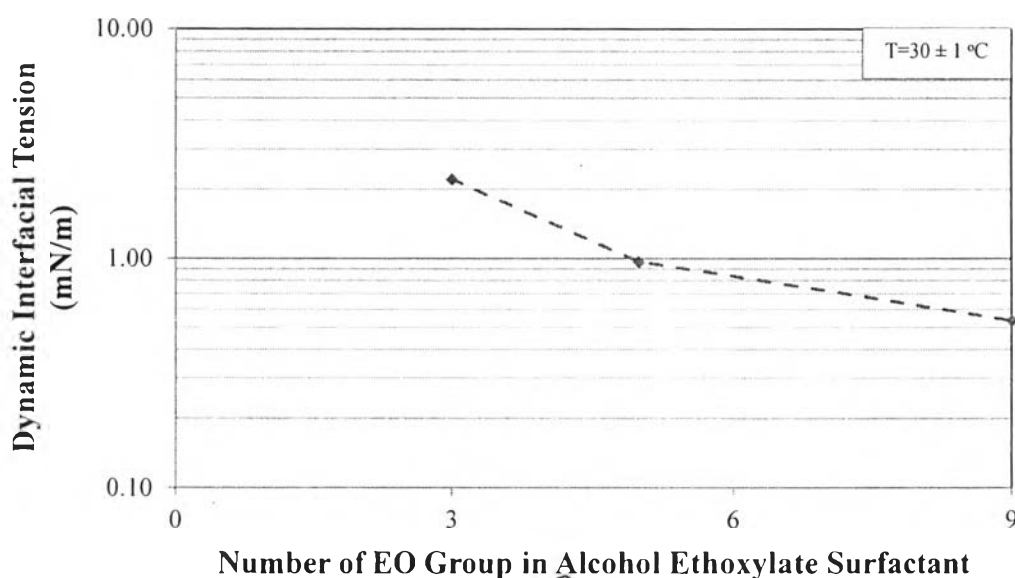


Figure 4.9 Dynamic interfacial tension as a function of number of EO group using 0.0005 M $C_{12-14}H_{25-29}-(EO)_n-OH$ ($n = 3, 5,$ and 9) with palm olein.

4.4.3 Effect of Mixed Surfactant System

The effect of IFT on mixed anionic and nonionic surfactant systems with different molar ratios was conducted at with 4.6 %w/v NaCl (optimum salinity) and without NaCl.

From Figure 4.10, the presence of NaCl in mixed anionic and nonionic extended surfactant system decreased IFT value. Both mixed surfactant systems of 1:1 and 1:0.1 by molar ratios had IFT approximately the same value as

anionic surfactant $[C_{14-15}H_{29-31}-(PO)_8-SO_4Na]$ alone. Therefore, the NaCl addition did not help the system reached ultralow IFT value.

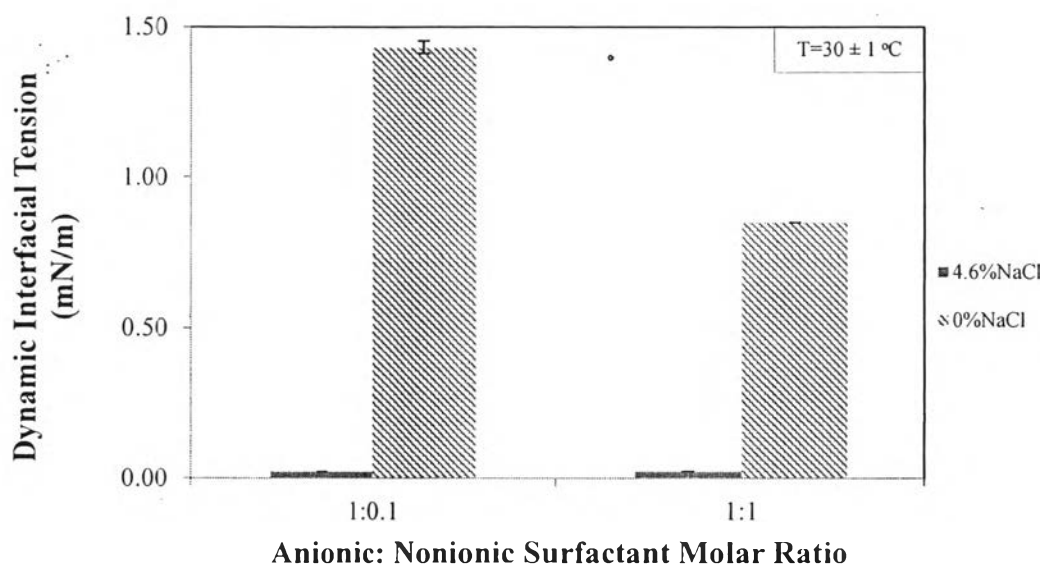


Figure 4.10 Dynamic interfacial tension as of 0.05 M $C_{14-15}H_{29-31}-(PO)_8-SO_4Na/C_{12-14}H_{25-29}-(EO)_3-OH$ with and without NaCl added with palm olein after 20 min.

4.5 Optimum Condition of Palm Stearin (Semi-Solid Fat) Solubilization Study

To investigate semi-solid fat (palm stearin) solubilization at below its melting temperature which liquid vegetable oil turns to be a solid fraction, both single anionic extended surfactant and mixed anionic and nonionic surfactant systems were used in this study. There are two factors that should be sought to provide optimum solubilization condition; the optimum time and followed by NaCl concentration. These two parameters are examined in the single anionic extended surfactant because the anionic extended surfactant is used as a dominant surfactant in mixed surfactant systems due to the fact that it is insensitive to temperature. Meanwhile, nonionic surfactants play a minor role in mixed surfactant systems to enhance solubilization and may decrease NaCl addition in the mixed surfactant

systems. The effect of EO groups of nonionic surfactant in single and mixed systems on solubilization capacity is investigated between surfactant and semi-solid fat.

4.5.1 Effect of Time

• A plateau region providing maximum semi-solid fat solubilization in surfactant solution (aqueous phase) was determined by varying period of time for shaking from 6 hr to 96 hr. This experiment used single anionic extended surfactant under fixed concentration [0.05 M $C_{14-15}H_{29-31}-(PO)_8-SO_4Na$] at 4.6 %w/v NaCl. The operated conditions were shaken at 120 rpm at 30 ± 1 °C.

For semi-solid fat removal determination, the result showed that at the beginning, semi-solid fat solubilization capacity increased significantly and then remained constant after 72 hr as shown in Figure.4.11. Therefore, 72 hr was selected as the optimum time in the palm stearin (semi-solid fat) solubilization study.

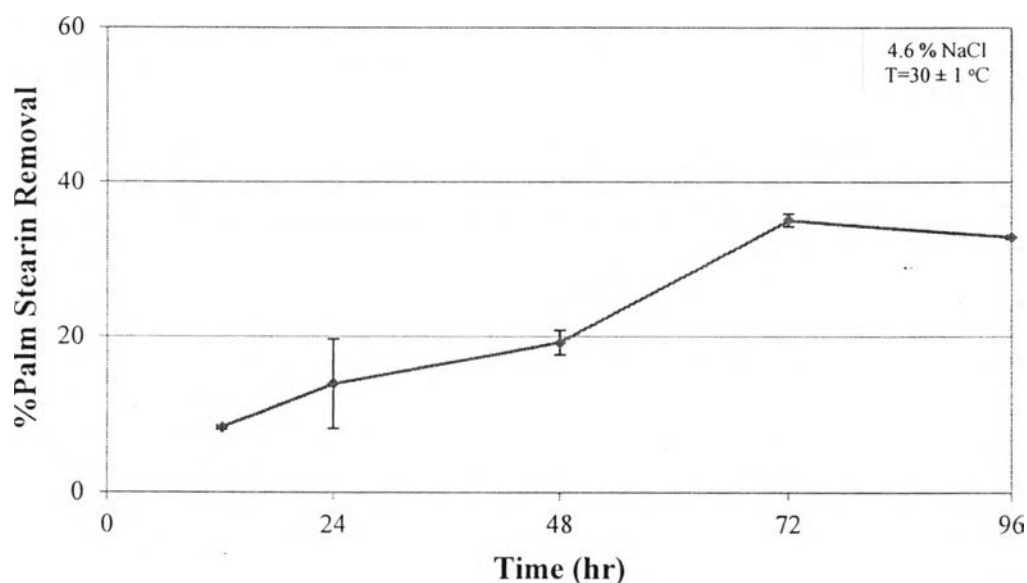


Figure 4.11 The percentage of fat removal as a function of time at 0.05 M $C_{14-15}H_{29-31}-(PO)_8-SO_4Na$.

4.5.2 Effect of Salinity

To ensure the optimum NaCl concentration for solubilization study conducted at 0.05 M $C_{14-15}H_{29-31}-(PO)_8-SO_4Na$ by varying NaCl concentrations from 0 to 7 %w/v as in the IFT experiment.

In Figure 4.12, NaCl concentration increased (5 %w/v or more) with semi-solid fat removal efficiency but semi-solid fat did not be solubilized in surfactant solution or emulsion as the excess layer was observed on the top of the supernatant. These NaCl concentrations would not suitable in solubilization test requiring solubilized oil in the micelle. Therefore, solubilization study was conducted at 4.6 %w/v NaCl concentration as similar to the optimum salinity that was found in IFT measurement, which provides high oil solubilization in surfactant micelle.

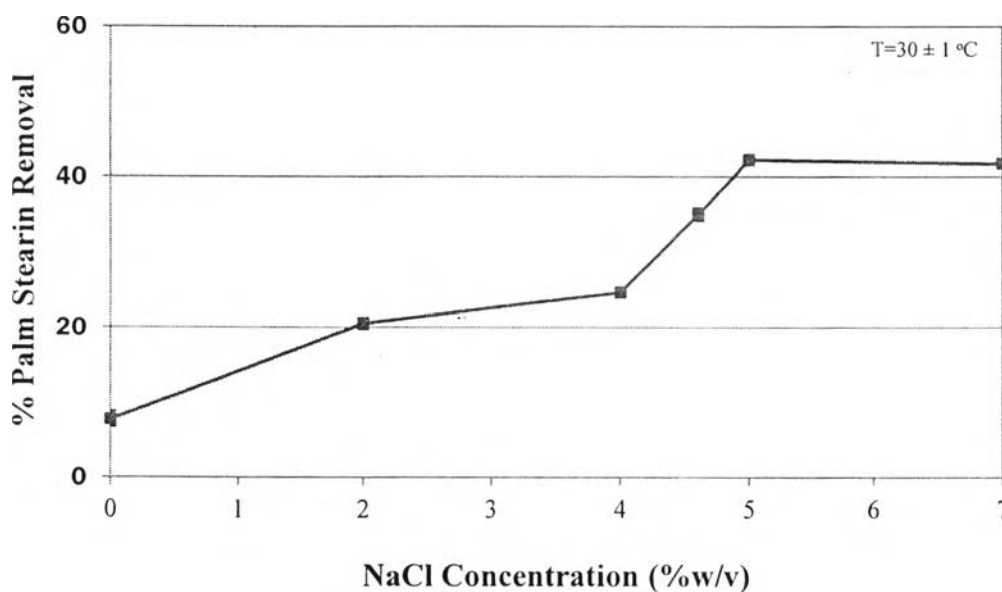


Figure 4.12 The percentage of oil removal at different NaCl concentrations with 0.05 M $C_{14-15}H_{29-31}-(PO)_8-SO_4Na$.

4.5.3 Effect of EO Group

To find the appropriate EO group of nonionic surfactant in mixed anionic surfactant and nonionic surfactant systems, single alcohol ethoxylated surfactants with different EO groups [$C_{12-14}H_{25-29}-(EO)_n-OH$ ($n=3, 5, \text{ and } 9$)] were evaluated to find the optimum EO group for semi-solid solubilization study. This study used 0.05 M for all nonionic surfactant systems.

As can be seen in Figure 4.13, the efficiency of oil removal decreased significantly when the number of EO groups increased. The alcohol ethoxylated surfactant with 3EO groups showed the highest semi-solid fat removal (59.59 %). The lower number of EO group in nonionic surfactants had less CMC and HLB values than those of the higher EO group as shown in Table 3.1. This means that lower EO groups in ethoxylated surfactant have more efficiency to solubilize the organic solute (palm stearin). This could be implied that the nonionic surfactant with less CMC and HLB values had more efficiency for semi-solid fat removal. This result agreed with previous works (Lim, 2005; Dillan, 1979). Therefore, $C_{12-14}H_{25-29}-(EO)_3-OH$ was used in mixed surfactant systems to obtain the maximum solubility.

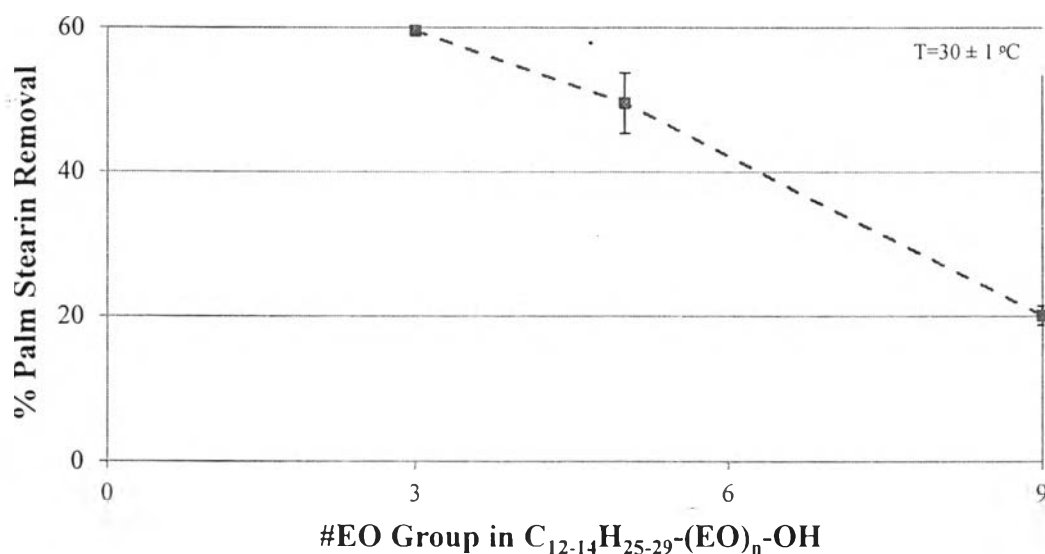


Figure 4.13 The percentage of palm stearin removal with different EO groups in nonionic surfactants.

4.5.4 Effect of NaCl in Mixed Surfactant Systems

To study the effect of NaCl concentration on semi-solid fat removal efficiency of mixed surfactant systems,

Figure 4.14 showed that the mixed surfactant systems without NaCl substantially decreased the efficiency of semi-solid fat removal in both mixed surfactant systems (1:1 and 1:0.1 by molar ratios). Therefore, NaCl addition was necessarily required to enhance semi-solid fat solubilization.

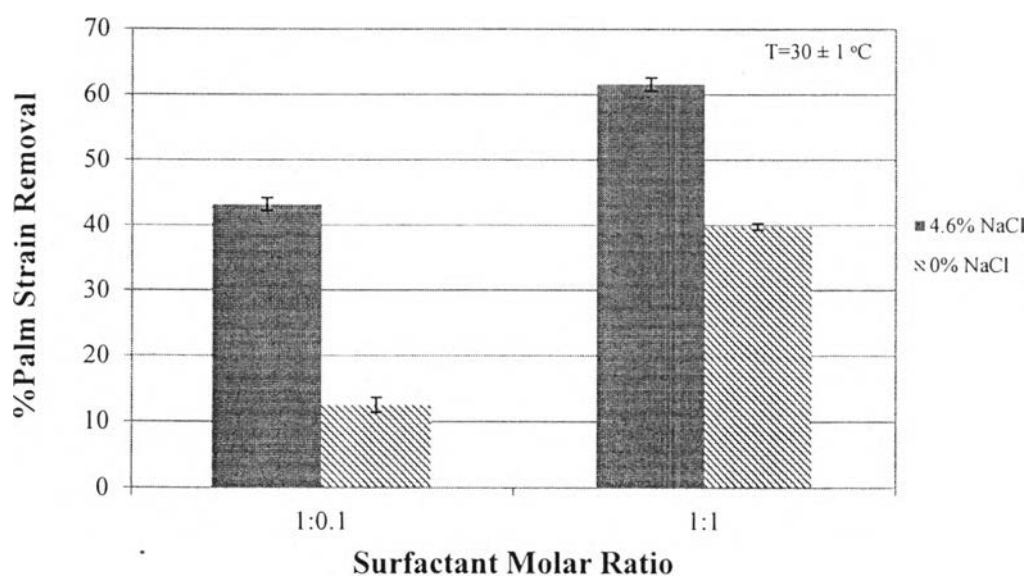


Figure 4.14 The percentage of palm stearin removal with different surfactant ratios and NaCl concentrations.

4.5.5 Effect of Different Surfactant Concentrations

The result showed that at below the transition point, the solubility of palm stearin (semi-solid fat) was very slight. At above the transition point, the semi-solid fat solubility significantly increased with different levels as depicted in Figure 4.15.

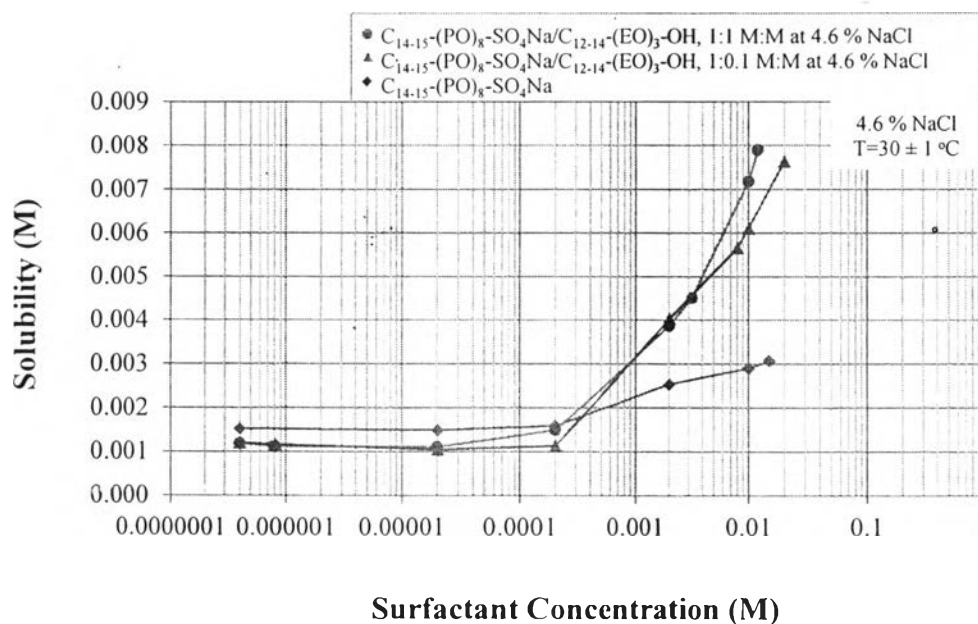


Figure 4.15 The surfactant concentration (M) versus palm stearin (semi-solid fat) solubility (M).

4.6 Semi-Solid Vegetable Fat (Palm Stearin) Solubility Study

Palm stearin consists of palmitic acid (64.4 ± 0.1 %), oleic acid (23.8 ± 0.1 %), linoleic acid (4.9 ± 0.0 %) and stearic acid (4.5 ± 0.1 %) (Soares, 2009). This various mixtures of fatty acids lead to the complication of palm stearin. Palmitic acid is the majority of fatty acid in palm stearin leading to a solid fraction at low temperature (below its melting point). Molar solubilization ratio (MSR), and K_{mic} ($\log K_{mic}$) have been used to quantify solubilization capacity of the micelles solutions by plotting between solubility (M) of organic solute (palm stearin) as a function of surfactant concentration (M). MSR is calculated from slope of the linear plot above the transition point. As MSR value is defined to explain as the number of mole of solute solubilized (palm stearin) by each mole of surfactant. Due to improper unit of solubility, the concentration of oil is changed to be molar unit as surfactant concentration unit by its molecular weight (or 834 g/mole) (Chetpattananondh, 2008). Therefore, K_{mic} represents the distribution of organic compound (solubilize) between surfactant micelles and the aqueous phase derived from X_a and X_{mic} .

The result from Figure 4.16 showed the MSR of single anionic extended surfactant [$C_{14-15}H_{29-31}-(PO)_8-SO_4Na$] with 4.6 %w/v NaCl was 0.050. This means that 0.050 mole of palm stearin solubilized per mole of surfactant micelle. However, the mixed surfactant systems between mixed anionic and nonionic surfactant [$C_{14-15}H_{29-31}-(PO)_8-SO_4Na$ and $C_{12-14}H_{25-29}-(EO)_3-OH$] system by 1:1 and 1:0.1 molar ratio had higher MSR value, with 0.399 and 0.195, respectively. Moreover, the mole fraction of solubilize (palm stearin) in the micelle (X_{mic}) was correlated to MSR. All surfactant systems had greater X_{mic} than X_a as depicted in Table 4.3. It can be noted that palm stearin favored partition into the core of micelle (Lim, 2005) because X_m is more than X_a . We found that the mixed surfactant system of $C_{14-15}H_{29-31}-(PO)_8-SO_4Na/C_{12-14}H_{25-29}-(EO)_3-OH$. 1:1 molar ratio at 4.6 % NaCl had the greatest solute partitioning in surfactant micelle according to the highest K_{mic} ($\log K_{mic}$), of 6.30. Palm stearin (semi-solid fat) thus is greater preferentially solubilized in micelle environment than that in water phase. It is interesting to note that the greater negative β value provides greater solubility of hydrophobic compounds (Zhou, 2004). Moreover, the surfactant systems having lower HLB tend to have greater micelle core volume compared to surfactant having a higher HLB value (Evans, 1999; Rosen, 2012).

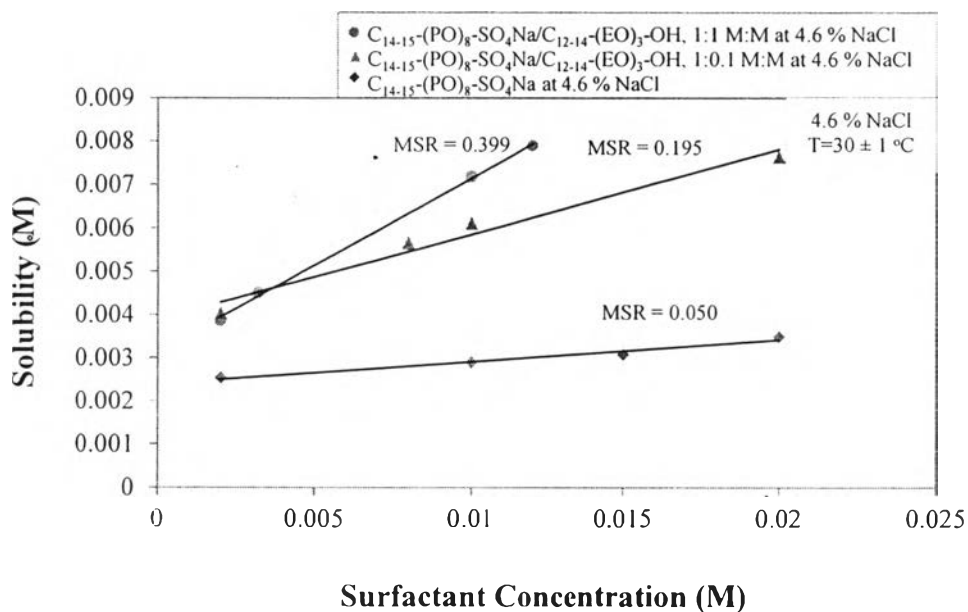


Figure 4.16 The solubility versus surfactant concentration. All experiments were performed at 30 ± 1 °C.

Table 4.3 The correlation between β , MSR, and K_{mic}

Surfactant System	CMC (μ M)	β	MSR	X_a	X_{mic}	K_{mic}	$\log K_{mic}$
Single Anionic System [$C_{14-15}H_{29-31}-(PO)_8-SO_4Na$ at 4.6 % NaCl]							
1:0 at 4.6 % NaCl	10	-	0.050	0.045	0.05	1.05	0.02
Mixed Systems [$C_{14-15}H_{29-31}-(PO)_8-SO_4Na$ and $C_{12-14}H_{25-29}-(EO)_3-OH$]							
1:0.1(M:M) at 4.6 % NaCl	8.4	-2.29	0.195	0.045	0.16	3.61	0.56
1:1 (M:M) at 4.6 % NaCl	6.1	-3.27	0.399	0.045	0.29	6.30	0.80

^a $R^2 > 0.95$

This research aimed to enhance the palm stearin (semi-solid fat) solubilization at 30 ± 1 °C using vegetable oil based microemulsion to select the appropriate surfactant formulation. The optimum salinity for the selected surfactant formulation was obtained from dynamic IFT measurement since the middle phase microemulsion with palm olein cannot be visually observed for all surfactant systems. The dynamic IFT measurement showed that $C_{14-15}H_{29-31}-(PO)_8-SO_4Na$ with 4.6 %w/v NaCl exhibited the lowest IFT value and their mixed surfactant systems also required 4.6 %w/v NaCl added to reach the minimum IFT. These surfactant conditions were conducted for palm stearin (semi-solid fat) solubilization study. The solubilization study was operated at 72 hr to ensure the maximum solubilization as indicated by plateau region. To confirm the lowest IFT value providing highest semi-solid fat removal, the palm stearin solubilization was investigated with different NaCl concentrations. The result showed that higher semi-solid fat solubilization in the surfactant solution was obtained at 4.6 %w/v NaCl, this concentration also similar with the optimum salinity from IFT measurement. To select appropriate nonionic surfactants for formulating with mixed anionic and nonionic surfactants, the solubilization capacity was determined for each single surfactant system. The result showed that $C_{12-14}H_{25-29}-(EO)_3-OH$ witnessed the highest palm stearin removal. For the solubilization study, the MSR and K_{mic} values of mixed surfactant systems [$C_{14-15}H_{29-31}-(PO)_8-SO_4Na/C_{12-14}H_{25-29}-(EO)_3-OH$] at 4.6 %w/v NaCl increased significantly in comparison with single anionic surfactant [$C_{14-15}H_{29-31}-(PO)_8-SO_4Na$ alone] at 4.6 %w/v NaCl. According to synergism of mixed surfactant system, it is interesting to note that the mixed surfactant systems had attractive interaction (negative value of β) between the head group of surfactant molecule. The higher nonionic proportion in mixed surfactant system (1:1 molar ratio) provided greater attractive interaction (more negative value of β), with -3.27 leading to greater MRS (0.399), X_{mic} (0.29) and K_{mic} (6.30) values. To come to the point, this study obtained valuable information for guiding the selection of appropriate surfactant system for semi-solid fat which can be applied for the cold water detergency applications.