



CHAPTER IV RESULTS AND DISCUSSION

4.1 Critical Micelle Concentration (CMC) Results

The critical micelle concentration (CMC), one of the main properties for surfactants, is the concentration at which surfactant molecule in solutions start to form micelle. Surface tensions of the surfactant solution at different concentrations were measured and plotted versus logarithmic concentrations. The point at which the surface tension levels off when surfactant concentration increased was taken as the CMC. The surface tension of the surfactant at CMC, γ_{CMC} , indicates the ability of surfactant's lowering surface tensions, and accordingly CMC indicates the efficiency.

The CMC of the fatty alcohol ethoxylates and nonylphenol ethoxylates are shown in Figure 4.1 and 4.2, respectively. In comparisons of the number of the EO group, the approximately CMC values of $\text{C}_{12-14}\text{EO}_3$, $\text{C}_{12-14}\text{EO}_5$, $\text{C}_{12-14}\text{EO}_7$, and $\text{C}_{12-14}\text{EO}_9$ were 0.0251, 0.0297, 0.0302, and 0.0345 mM, respectively whereas NPE-6, and NPE-9 were 0.0308, and 0.0607 mM, respectively. The CMC of fatty alcohol ethoxylates slightly increased with increasing the number of the EO group. The CMC of nonylphenol ethoxylates also slightly increased with increase in the number of the EO group. An increase in the EO content will increase water solubility by increasing the interaction between the EO group and water molecules, resulting in an increase the amount of energy required to dehydrate the molecule during it form micelles. Increasing EO content also increases molecular size, resulting in difficulty for the head group (hydrophilic part) to pack at the water-air interface. Therefore, the ability to lower surface tension is decreased. However the change of the CMC per EO unit in hydrophilic chain is much smaller than hydrophobic effect (Rosen, 2004). Table 4.1 shows the measured values of the CMC.

These CMC values of fatty alcohol ethoxylates were higher than reported CMC of single surfactant system (synthetic-based), which were in the range 0.052 to 0.1 mM (Rosen, 2004). The possible reason for this is explained in that the presence of small amounts of organic materials may change the CMC in aqueous solution. Some of organic materials may be act as impurity or by products from the

manufacturing of surfactants. Their presence may cause significant differences, which normally are found in commercial surfactants. The possible organic materials for this are, for example, short-chain alcohols, water-soluble esters, and ethylene glycol. These impurities may increase the CMC because they increase the water solubility by increasing hydration and resulting to an increase CMC.

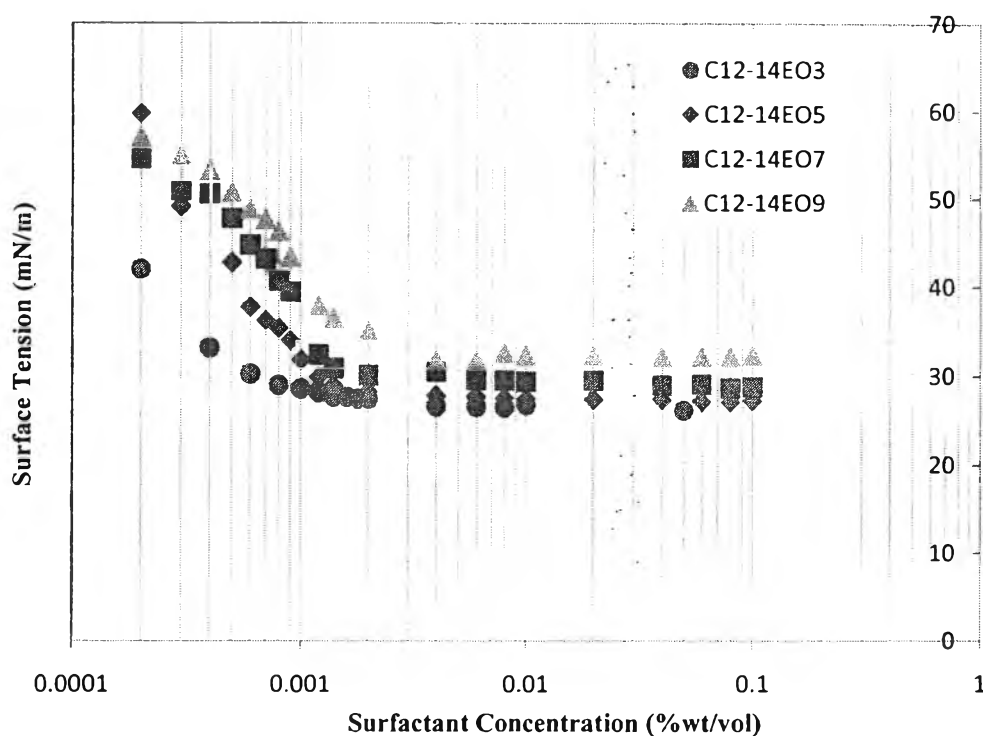


Figure 4.1 Critical micelle concentration (CMC) of single fatty alcohol ethoxylates surfactant system at 25°C.

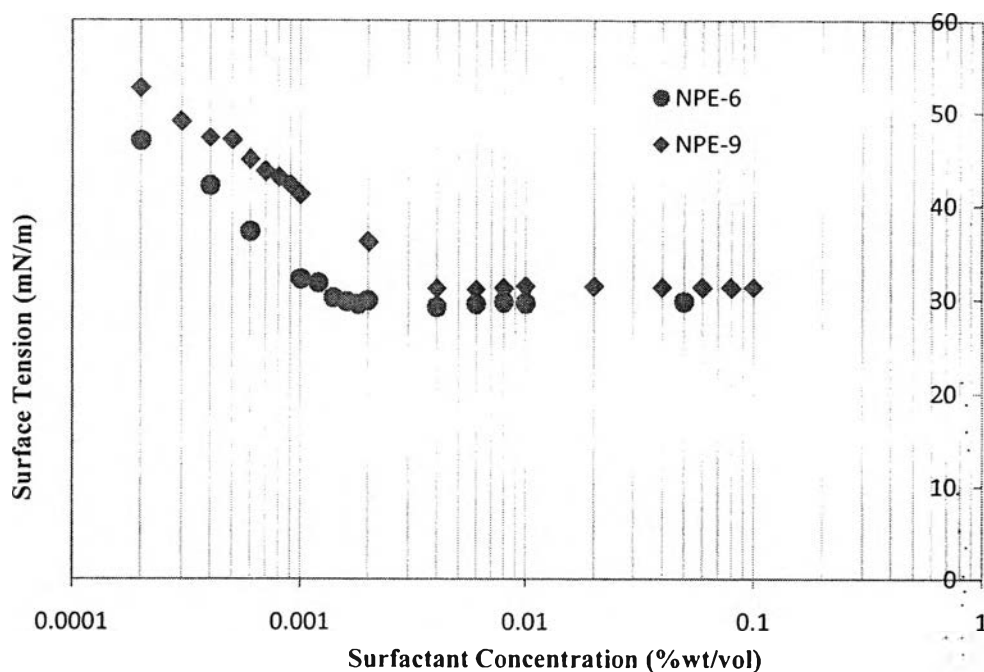


Figure 4.2 Critical micelle concentration (CMC) of single nonylphenol ethoxylates surfactant system at 25°C.

Table 4.1 Critical micelle concentration (CMC) of single alcohol ethoxylate and nonylphenol ethoxylates surfactant system at 25°C

Surfactant	CMC (% wt/vol)	CMC(mg/L,mM)
C ₁₂₋₁₄ EO ₃	0.0008	8,0.0251
C ₁₂₋₁₄ EO ₅	0.0012	12,0.0297
C ₁₂₋₁₄ EO ₇	0.0015	15,0.0302
C ₁₂₋₁₄ EO ₉	0.0020	20,0.0345
NPE-6	0.0015	15,0.0308
NPE-9	0.0020	40,0.0607

4.2 Cloud Point Results

A cloud point is the temperature that makes the surfactant solutions are cloudy and divide in two phases. The cloud point temperature was investigated by

wt% surfactant. This test method finds the cloud point or the solubility inversion temperature on nonionic surfactant. The accuracy of the cloud point temperature was $\pm 0.5^\circ\text{C}$.

The effect of the number of the EO group on cloud point temperature is shown in Figure 4.3. The cloud point of fatty alcohol ethoxylates— $\text{C}_{12-14}\text{EO}_3$, $\text{C}_{12-14}\text{EO}_5$, $\text{C}_{12-14}\text{EO}_7$, and $\text{C}_{12-14}\text{EO}_9$ —were ~ 0 , 18.5, 54, and 81°C , respectively. For the nonylphenol ethoxylates—NPE-6 and NPE-9—were ~ 0 , and 53.3°C , respectively as shown in Table 4.2. From the results, Increasing EO content increases water solubility, resulting in an increase in cloud point temperature. Mostly, a nonionic surfactant is less soluble in water at higher temperatures than at a lower temperature because the interaction of hydrogen bond between water and EO chain of surfactant is reduced. If a temperature is high enough, most nonionic surfactant molecules tends to form a separate phase. The transition point from a single phase to two separate phases can be simply justified when the solution becomes cloudy.

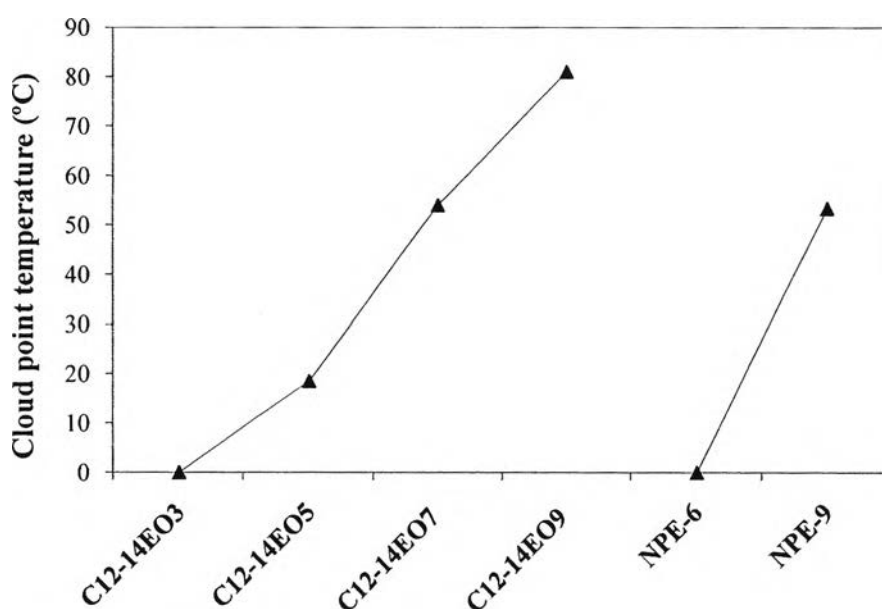


Figure 4.3 Cloud point of 1 wt% surfactant of fatty alcohol ethoxylates and nonylphenol ethoxylates as a function of the number of the EO group.

In the case of $C_{12-14}EO_3$ and NPE-6 were both definitely cloudy at room temperature, which was above their cloud point temperature. So, they were difficult to find the exact cloud point temperature unless there were additives. The cloud point can be increased by addition of long chain nonpolar material, anions that are water structure breakers and certain cation (Huibers, 1997). For the surfactant $C_{12-14}EO_5$, it was slightly cloudy at room temperature. It was found its cloud point by cooling in cool water.

Table 4.2 The cloud point of 1 wt% surfactant of fatty alcohol ethoxylates, nonylphenol ethoxylates and reference surfactants

Surfactant	Cloud point temperature (°C)	Surfactant	Cloud point temperature (°C)
$C_{12-14}EO_3$	~0	$C_{14}EO_{3.5}^a$	Cloudy at T_{room}
$C_{12-14}EO_5$	18.5	$C_{14}EO_{5.2}^a$	Cloudy at T_{room}
$C_{12-14}EO_7$	54	$C_{12}EO_7(b)^c$	~53
$C_{12-14}EO_9$	81	$C_{12}EO_9(b)^c$	~78
NPE-6	~0	$C_{12}EO_7(n)^c$	~70
NPE-9	53.3	$C_{12}EO_9(n)^c$	~87
Chl- EO_{10}^b	50	^a Data from Reference (Michael F. C.,1989) ^b Data from Reference (Piispanen P. S.,2003) ^c Data from Reference (Hama I.,1997)	
Chl- EO_{13}^b	84		
Chl- EO_{35}^b	130		

The effect of the number of the EO group on cloud point temperature was also found in synthetic-based surfactant as shown in Table 4.2. The cloud point of the alcohol ethoxylates which has the EO lower than 5 units was found cloudy at room temperature (Michael F.C., 1989). The cloud point increased with the head group chain length was not only found in alcohol ethoxylates but commonly found for other ethoxylated surfactant, for example, polyoxyethylene cholesteryl ethers, Chl- EO_n (Piispanen et al., 2003 & Michael F. C., 1989). In comparison the cloud

point of this study with previous study (synthetic-based), the cloud point temperature of $C_{12-14}EO_7$, and $C_{12-14}EO_9$ were similar to alcohol ethoxylates with broad (b) EO adduct distribution. The effect of EO distribution was also found that the cloud point of alcohol ethoxylates, which has a narrow (n) EO adduct distribution is higher than that of broad distribution (Hama I., 1997).

4.3 Contact Angle Results

In these screening tests, the contact angle (Θ) was measured on the sessile drop technique by using the contact angle measuring instrument (Krüss, DSA10). A 10 μ L drop of surfactant solution was placed onto the nonpolar parafilm, HDPE (High Density Polyethylene), and Nylon6, 6 and measured after 1 minute in order to allow equilibrium.

The values of contact angles of water on three surfaces used in this work are shown in Table 4.3. The contact angle of pure water on nonpolar parafilm surface was the highest and follows by HDPE, and Nylon6, 6, respectively. From this result, it shown that the degree of hydrophobicity of surfaces increases in order:

$$\text{nonpolar parafilm} > \text{HDPE} > \text{Nylon6, 6}$$

The evaluation of hydrophobicity can be made through water contact angle measurements.

The contact angle of surfactant solutions at concentration of 1 wt% of fatty alcohol ethoxylates— $C_{12-14}EO_3$, $C_{12-14}EO_5$, $C_{12-14}EO_7$, and $C_{12-14}EO_9$ —are shown in Figure 4.6. The contact angles on the nonpolar parafilm and HDPE surfaces were in the range 38 to 53° and 20 to 34°, respectively which gradually increased with increasing the number of the EO unit. The lower EO has better wetting abilities because it may be better packing of the hydrophobe on the surface. The lower EO group has the smaller head group (hydrophilic part), which can be adsorbed on surface with higher density. So, the interfacial tension of liquid and surface will be

decreased, resulting in the lower contact angle, as suggested by the Young's equation, showing in Equation's (4):

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \quad (4)$$

Where γ_{SV} , γ_{SL} , γ_{LV} are solid/vapor, solid/liquid and liquid/vapor interfacial tensions, respectively, and θ is the equilibrium contact angle.

Therefore, the number of the EO group has effect to the contact angle resulting in the wettability. Moreover, the Nylon6, 6 surface, the drop shape analysis instrument were not detected the contact angle because it might be much lower contact angle.

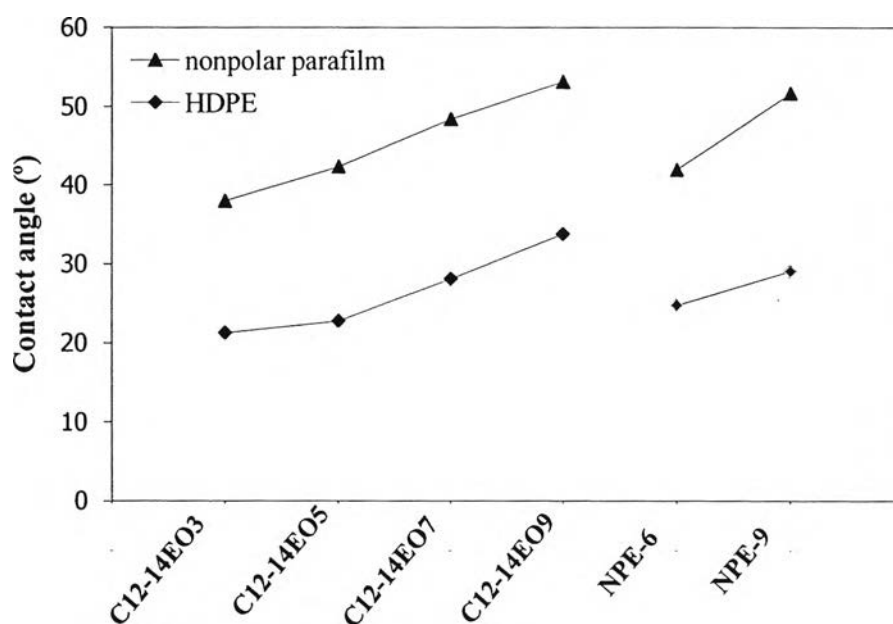


Figure 4.4 Wettability (Contact angle, degrees) of fatty alcohol ethoxylates and nonylphenol ethoxylates at 1 wt% after 1 minute on nonpolar parafilm, and HDPE surface at 30°C.

The contact angle of the solution of fatty alcohol ethoxylates and nonylphenol ethoxylates on nonpolar parafilm, HDPE, and Nylon6, 6 are shown in

Table 4.3. For any surfactant system, the contact angle at concentration of 1 wt% increased in the following order:

$$\text{nonpolar parafilm} > \text{HDPE} > \text{Nylon6, 6.}$$

These results were related to the order of the degree of hydrophobicity, as shown the contact angle of water in Table 4.3. Moreover, nonpolar parafilm surface has a strong driving force for the surfactants to adsorb and diminish the unfavorable surface–water contact (Piispanen, 2004).

The wetting properties of alcohol ethoxylates were also determined by comparison with nonylphenol ethoxylates and water as references. The wetting scale of 0–6 was used (6 represents the best wettability) which was modified from Piispanen et al., 2004). From the contact angle, the references were defined 5, 3, and 0 for NPE-6, NPE-9, and water, respectively. The wetting ability of fatty alcohol ethoxylates were compared with the references as shown in Table 4.3.

Table 4.3 The contact angle of fatty alcohol ethoxylates and nonylphenol ethoxylates at 1 wt% after 1 minute on nonpolar parafilm, HPDE, and Nylon6, 6 surface

Surfactant	Contact angle (°)			Wetting ability scale
	Parafilm	HDPE	Nylon6, 6	
C ₁₂₋₁₄ EO ₃	38.0	21.3	~0	5
C ₁₂₋₁₄ EO ₅	42.4	22.8	~0	5
C ₁₂₋₁₄ EO ₇	48.4	28.2	~0	3
C ₁₂₋₁₄ EO ₉	53.2	34.0	~0	3
NPE-6	42	24.8	~0	5
NPE-9	51.4	29.1	~0	3
Water	95.6	80.9	51.4	0

4.4 Foaming Test Results

The objective of this study was to study the foam performance properties. Fatty alcohol ethoxylates— $C_{12-14}EO_3$, $C_{12-14}EO_5$, $C_{12-14}EO_7$, and $C_{12-14}EO_9$ and nonylphenol ethoxylates—NPE-6, and NPE-9 were used to investigate foamability and foam stability by the standardized Ross-Miles test. In the foam properties, the effects of number of ethylene oxide groups and surfactant concentration were studied. Moreover, pneumatic foam, and simple shaking foam test were studied.

4.4.1 Ross-Miles foam test

Foamability and foam stability were investigated by using Ross-Miles test which modified from the standard test method D1173-53. During the measurement, the heat jacket was kept at 49°C. Foaming experiments were studied at surfactant concentration of 0.01, 0.1, and 1 wt% for those surfactants. The foam height was measured as a function of time.

4.4.1.1 *Effect of ethylene oxide content on foam properties*

Foam characteristics in terms of foamability and foam stability of single surfactant systems at concentration nearly CMC (Critical Micelle Concentration) of 0.01 wt% are shown in Figure 4.5. In comparison of the ethylene oxide group, the foamability of fatty alcohol ethoxylates increased with increasing of the number of the EO group. This can be explained in that increasing number of the EO group increases its water solubility, resulting in a high density of the monomers in the liquid. Therefore, it is a higher repulsion force between the two adsorbed surfaces of the foam lamellae with increasing number of the EO group. As shown in Figure 4.5, the foamability and foam stability of the studied AEs increase with increasing number of the EO group until it reaches the maximum at the EO equal 7-9 units.

The foamability of $C_{12-14}EO_7$, and $C_{12-14}EO_9$ were higher than that can be explained by the water solubility and the lower surface tension. The surface tension of the surfactant at CMC, γ_{CMC} , indicates the ability of surfactant's lowering surface tensions, and accordingly CMC indicates the efficiency. The lower surface tension leads to form foam easily resulting in the high foamability. As seen from Figure 4.1,

the lower surface tension of $C_{12-14}EO_7$, and $C_{12-14}EO_9$ showed lower than the others of fatty alcohol ethoxylates. This behavior has been found in nonylphenol ethoxylates. The NPE-6 system has the lowest foamability and foam stability than NPE-9. The foamability is also explained by the lowering of the dynamic surface tension. The increasing of foamability is parallel to the lowering of the dynamic surface tension illustrated more description in the next part.

Figure 4.6 and 4.7 show the foam characteristics in term of foamability and foam stability at concentration of 0.1 and 1 wt%, respectively. The foamability and foam stability increased with increasing number of the EO group both the fatty alcohol ethoxylates and nonylphenol ethoxylates. The foamability and foam stability of the studied fatty alcohol ethoxylates increased until it reaches the maximum at the EO equal 7-9 units, which were apparently similar characteristic with concentration of 0.01 wt%. As shown in the Figure 4.7, the maximum foam is passed initially when the number of the EO group reach to 7 units. The results of the present study are in good agreement with previous work. For a dodecyl hydrophobe, the maximum foam volume was passed when the EO chain reaches to 7 units (Garrett et al., 1995). Hence, the foamability and foam stability increase with increasing the number of the EO group until their reach to high sufficiently.

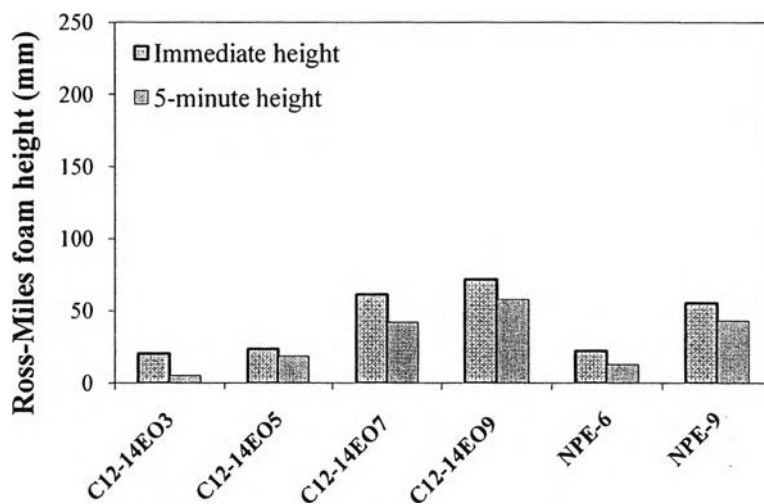


Figure 4.5 Foam characteristics of fatty alcohol ethoxylates and nonylphenol ethoxylates as a function of the number of the EO group at 0.01 wt%, surfactant, and temperature of 49°C using the Ross–Miles foam test.

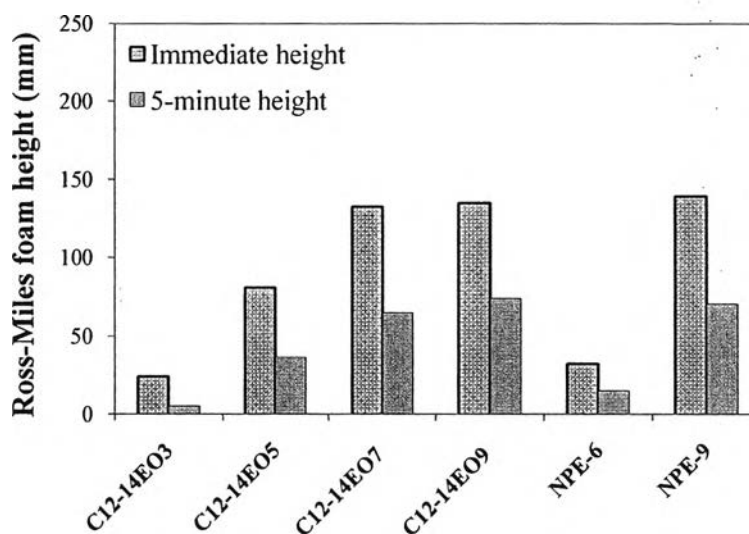


Figure 4.6 Foam characteristics of fatty alcohol ethoxylates and nonylphenol ethoxylates as a function of the number of the EO group at 0.1 wt% surfactant and temperature of 49°C using the Ross–Miles foam test.

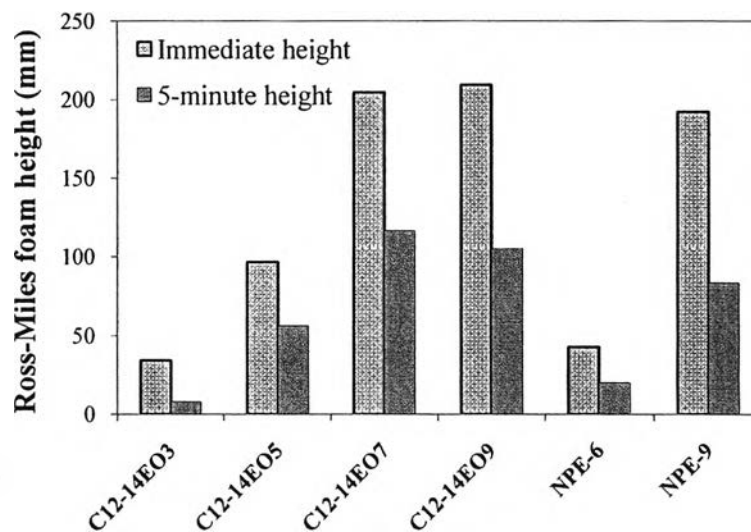


Figure 4.7 Foam characteristics of fatty alcohol ethoxylates and nonylphenol ethoxylates as a function of the number of the EO group at 1 wt% surfactant and temperature of 49°C using the Ross–Miles foam test.

4.1.1.2 Effect of surfactant concentration

Figure 4.3 shows the foam characteristics in term of foamability and foam stability of fatty alcohol ethoxylate $C_{12-14}EO_3$ at concentration of 0.01, 0.1 and 1 wt%. In comparison of concentration, the foamability and foam volume after 5 minutes increase with increasing surfactant concentration. It can be explained by the drainage in the liquid film, which is occurred because of gravitational force, the pressure different between the film lamellae, and the plateau boarder. The different in the drainage rate indicates different foam stability. The foamability increased with increasing surfactant concentration but foam stability tended to reach a maximum at around 0.01 wt% (nearly the CMC). It can be explained in that the drainage of the liquid film by the gravitational force increases with increasing foam production rate and the Gibbs/Maragoni effect is found to be maximum around the CMC.

Moreover, in the case of $C_{12-14}EO_5$, $C_{12-14}EO_7$, and $C_{12-14}EO_9$ found that foamability and foam stability increase with increasing surfactant concentration similar with the previous result and also found in nonylphenol ethoxylates—NPE-6,

and NPE-9. From this phenomenon, it shows that the foam properties depend on the size of the EO and surfactant concentration.

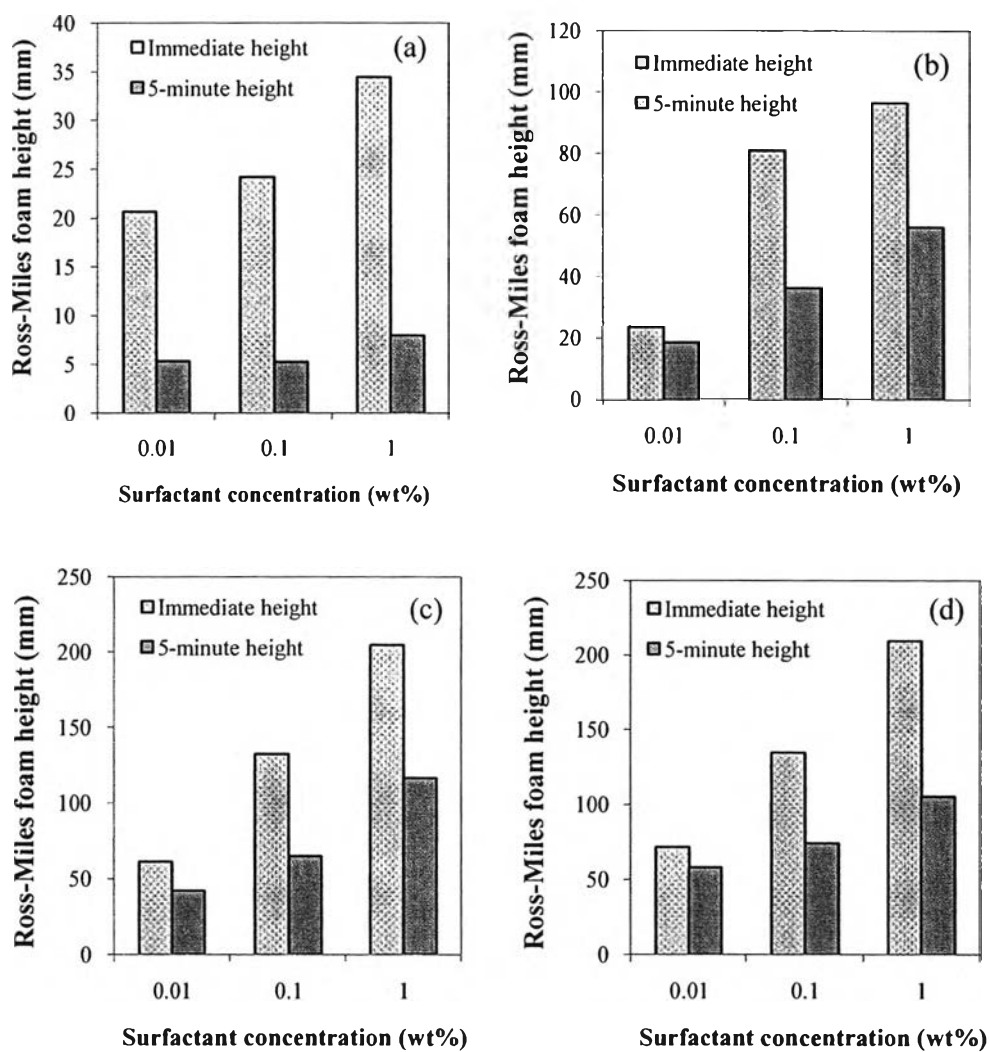


Figure 4.8 Foam characteristics of fatty alcohol ethoxylates as a function of the surfactant concentration of 0.01, 0.1, and 1 wt% and temperature of 49°C using the Ross–Miles foam test; (a) $C_{12-14}EO_3$, (b) $C_{12-14}EO_5$, (c) $C_{12-14}EO_7$, and (d) $C_{12-14}EO_9$.

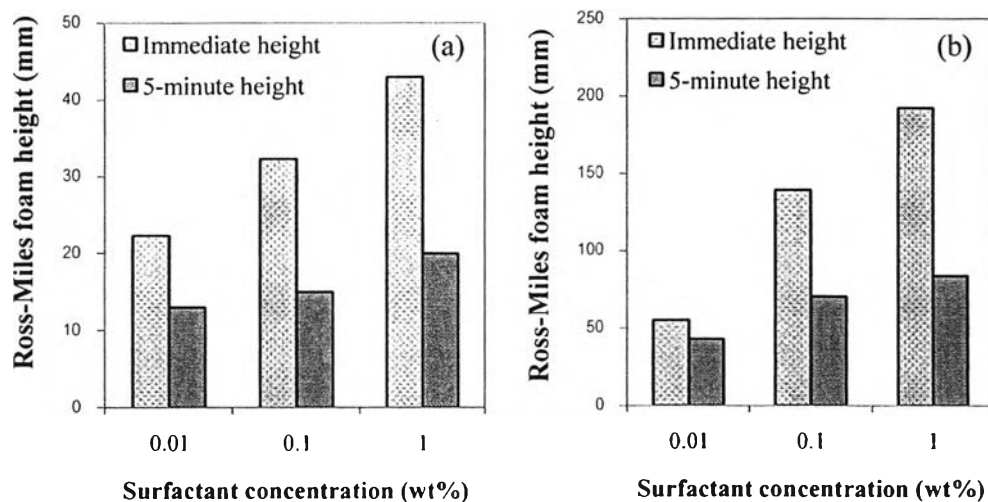


Figure 4.9 Foam characteristics of nonylphenol ethoxylates as a function of the surfactant concentration of 0.01, 0.1, and 1 wt%, and temperature of 49°C using the Ross–Miles foam test; (a) NPE-6, and (b) NPE-9.

4.4.2 The Pneumatic foam test

Foamability and foam stability were investigated by using pneumatic foam test method, which was tested at room temperature. Foaming experiments were studied at surfactant concentration of 0.01, 0.1, and 1 wt%. Foamability is defined as the ratio of the maximum foam height to the initial surfactant solution height and foam stability is defined as the time that required for maximum foam collapse to half of foam volume.

4.4.2.1 *Effect of ethylene oxide content on foam properties*

Figure 4.10 show foam characteristics in terms of foamability (a) and foam stability (b) at concentration nearly CMC of 0.01 wt%. In comparison of the ethylene oxide group, the $C_{12-14}EO_3$ showed low foamability and foam stability. The $C_{12-14}EO_5$, $C_{12-14}EO_7$, and $C_{12-14}EO_9$ were shown high foamability but foam stability of the $C_{12-14}EO_5$ was lower than the $C_{12-14}EO_7$, and $C_{12-14}EO_9$. In the case of nonylphenol ethoxylates, NPE-6 showed higher foamability than NPE-9 slightly but the foam stability of NPE-9 is significantly higher than NPE-6. So, an increase the

number of the EO group will increase foam stability but have slightly effect to the foamability.

Foam characteristics of single surfactant systems at concentration of 0.1 wt% is shown in Figure 4.11. The $C_{12-14}EO_3$ showed lower foamability and foam stability than the $C_{12-14}EO_5$, $C_{12-14}EO_7$, and $C_{12-14}EO_9$ which were shown high foamability and foam stability. For nonylphenol ethoxylates, the foamability slightly increases with increasing the number of the EO group. Both fatty alcohol ethoxylates and nonylphenol ethoxylates, foam stability increased with increasing the number of the EO group but not much different in $C_{12-14}EO_7$, and $C_{12-14}EO_9$.

Figure 4.12 shows foam characteristics of single surfactant systems at concentration of 1 wt%. In the group of fatty alcohol ethoxylates except $C_{12-14}EO_3$, the $C_{12-14}EO_7$ was shown high foamability and foam stability than the $C_{12-14}EO_9$, $C_{12-14}EO_5$, respectively. For nonylphenol ethoxylates, NPE-6 was shown higher foamability than NPE-9 slightly but the foam stability of NPE-9 showed higher than NPE-6. In the case of $C_{12-14}EO_3$ at concentration of 1 wt% found that foamability and foam stability much higher than others system. A possible explanation for this is shown in next part.

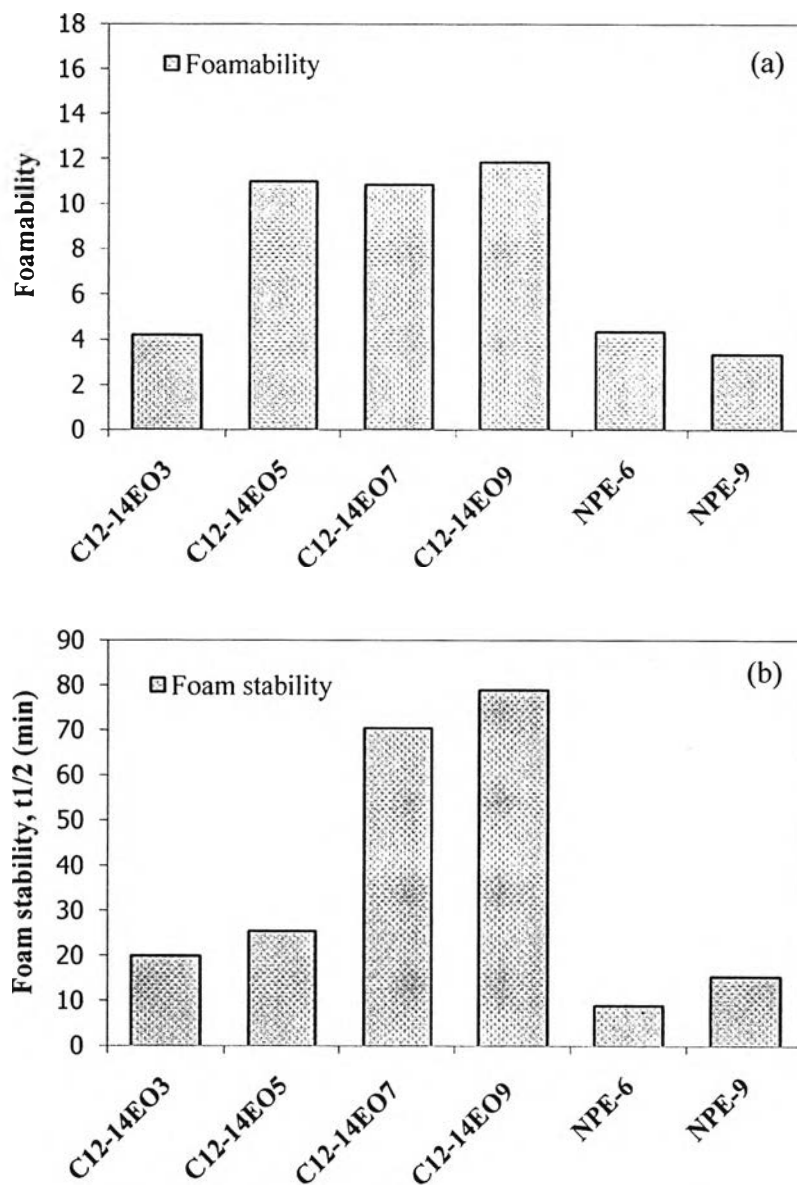


Figure 4.10 Foam characteristics of fatty alcohol ethoxylates and nonylphenol ethoxylates as a function of the number of the EO group at 0.01 wt% surfactant using the pneumatic foam test, air flow rate = 20 ml/min, and room temperature; (a) Foamability, and (b) Foam stability.

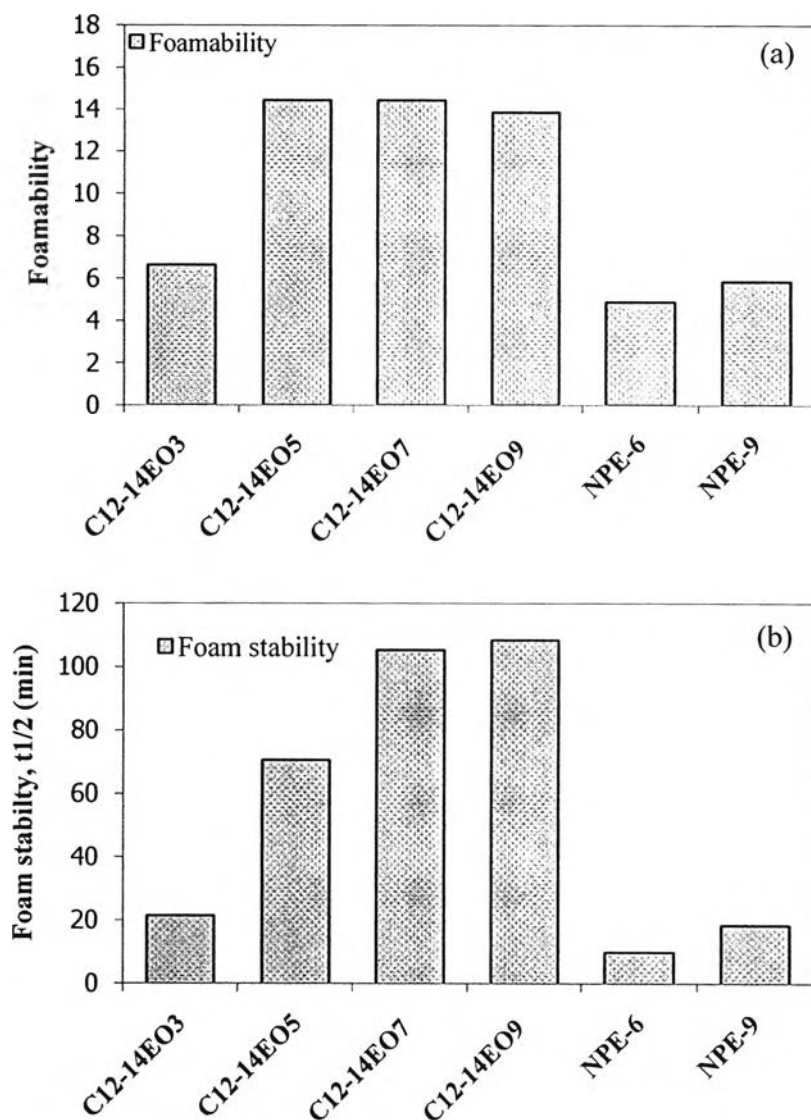


Figure 4.11 Foam characteristics of fatty alcohol ethoxylates and nonylphenol ethoxylates as a function of the number of the EO group at 0.1 wt% surfactant using the pneumatic foam test, air flow rate = 20 ml/min, and room temperature; (a) Foamability, and (b) Foam stability.

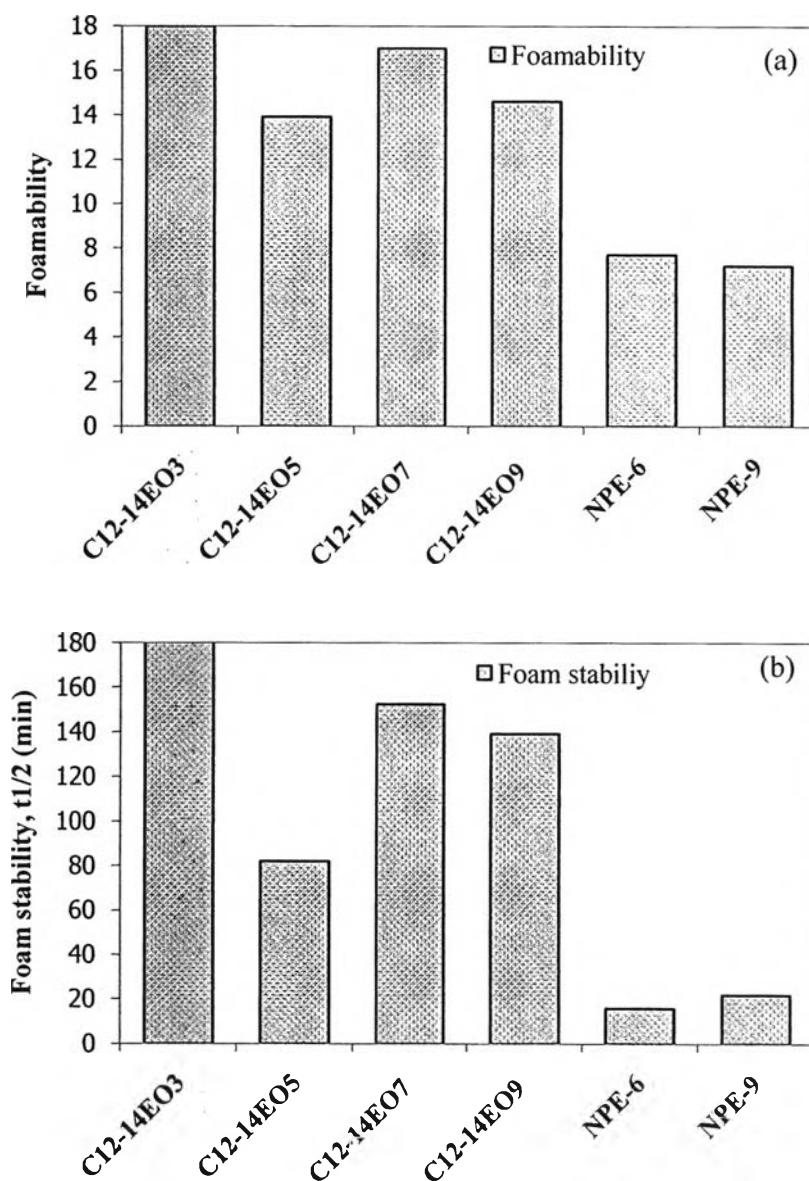


Figure 4.12 Foam characteristics of fatty alcohol ethoxylates and nonylphenol ethoxylates as a function of the number of the EO group at 1 wt% surfactant using the pneumatic foam test, air flow rate = 20 ml/min, and room temperature; (a) Foamability, and (b) Foam stability.

4.4.2.2 Effect of surfactant concentration

Figure 4.13-4.18 show the foam characteristics in term of foamability and foam stability of fatty alcohol ethoxylates and nonylphenol ethoxylates at concentration of 0.01, 0.1 and 1 wt%. In comparison of concentration, the foamability and foam stability of $C_{12-14}EO_3$, $C_{12-14}EO_5$, $C_{12-14}EO_7$, and $C_{12-14}EO_9$ slightly increase with increasing surfactant concentration. It can be explained in that the formation of foam in this test is due to the creation and expansion of the surface area by aerating to generate air bubbles at the bottom of column. At higher surfactant concentrations, a high amount of surfactant molecules can adsorb at the new interface to form foam and act as barriers repulsion force between the two surfaces of lamellae to prevent the coalescence of foam. The surfactant adsorption is required for foam formation, reducing the surface tension of the expanded surface area.

Moreover, in the case of $C_{12-14}EO_3$ at a high concentration of 1 wt%, foamability and foam stability were much higher than those at lower concentrations. The possible reasons are the effect of cloud point temperature of $C_{12-14}EO_3$ solution ($\sim 0^\circ$) and less water solubility. In this test, the solution in the column was aerated continuously until the foam height in the column was constant and maximum. It took a long time for measurement thus the solution might tend to separate phase by effect of lower cloud point and less water solubility showing that one was diluted phase and another was high concentration phase. Hence, the introduced air might be aerated through the later phase for high foamability and spend amount of time for foam volume to collapse by half.

For nonylphenol ethoxylates, NPE-6, and NPE-9 were apparently similar characteristic with fatty alcohol ethoxylates. NPE-6 at concentration of 0.01 and 0.1 wt% foamability and foam stability slightly increase with increasing concentration and shows high foamability and foam stability at concentration of 1 wt% as similar in the case of $C_{12-14}EO_3$ at concentration of 1 wt%. From this phenomenon, it shows that the foam stability depend on surfactant concentration.

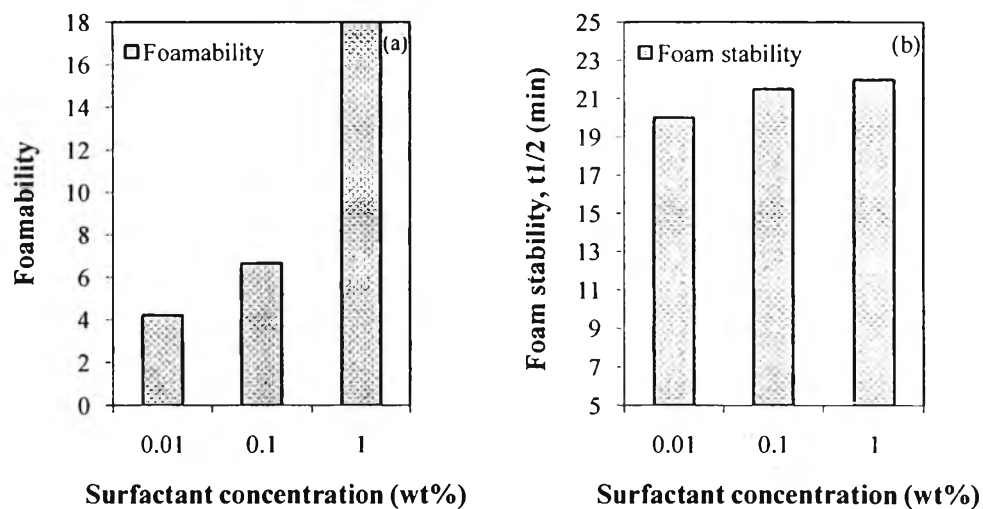


Figure 4.13 Foam characteristics of $C_{12-14}EO_3$ as a function of the surfactant concentration of 0.01, 0.1, and 1 wt% using the pneumatic foam test, air flow rate = 20 ml/min, and room temperature; (a) Foamability, and (b) Foam stability.

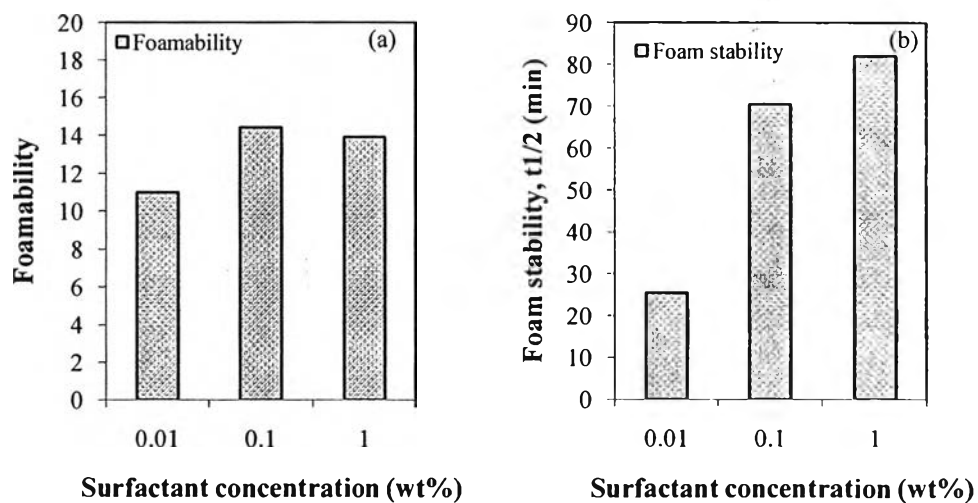


Figure 4.14 Foam characteristics of $C_{12-14}EO_5$ as a function of the surfactant concentration of 0.01, 0.1, and 1 wt% using the pneumatic foam test, air flow rate = 20 ml/min, and room temperature; (a) Foamability, and (b) Foam stability.

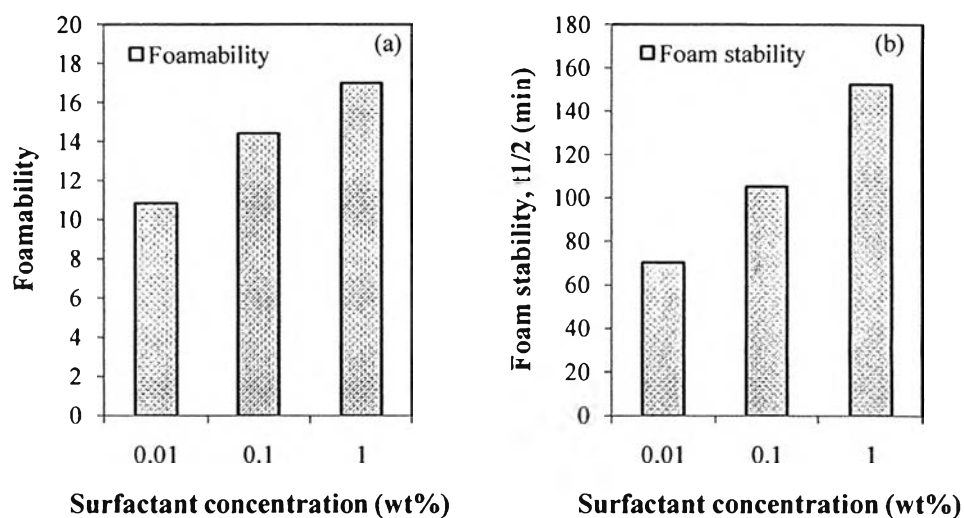


Figure 4.15 Foam characteristics of $C_{12-14}EO_7$ as a function of the surfactant concentration of 0.01, 0.1, and 1 wt% using the pneumatic foam test, air flow rate = 20 ml/min, and room temperature; (a) Foamability, and (b) Foam stability.

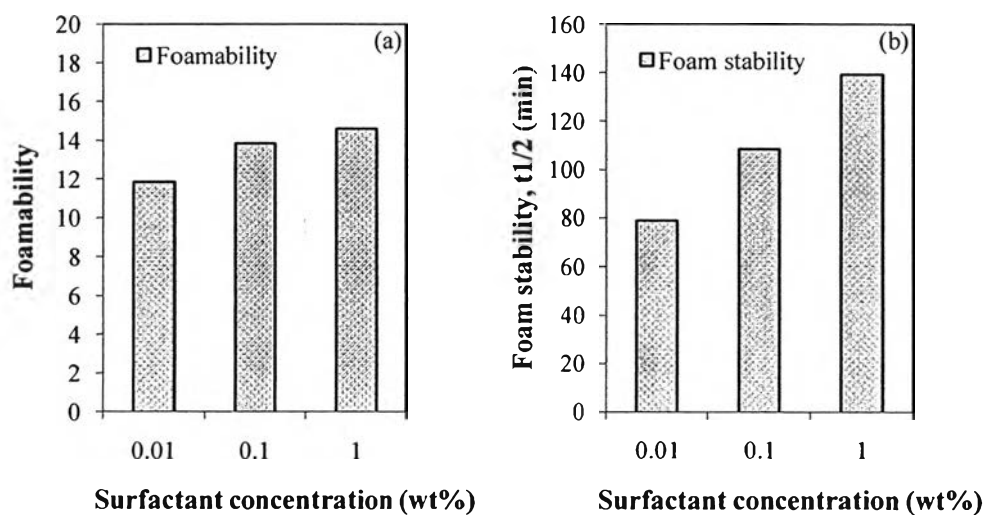


Figure 4.16 Foam characteristics of $C_{12-14}EO_9$ as a function of the surfactant concentration of 0.01, 0.1, and 1 wt% using the pneumatic foam test, air flow rate = 20 ml/min, and room temperature; (a) Foamability, and (b) Foam stability.

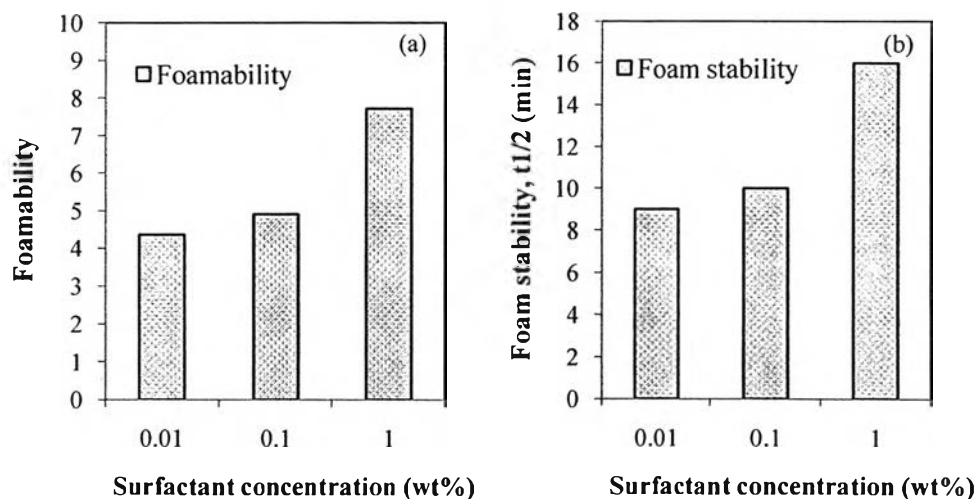


Figure 4.17 Foam characteristics of NPE-6 as a function of the surfactant concentration of 0.01, 0.1, and 1 wt% using the pneumatic foam test, air flow rate = 20 ml/min, and room temperature; (a) Foamability, and (b) Foam stability.

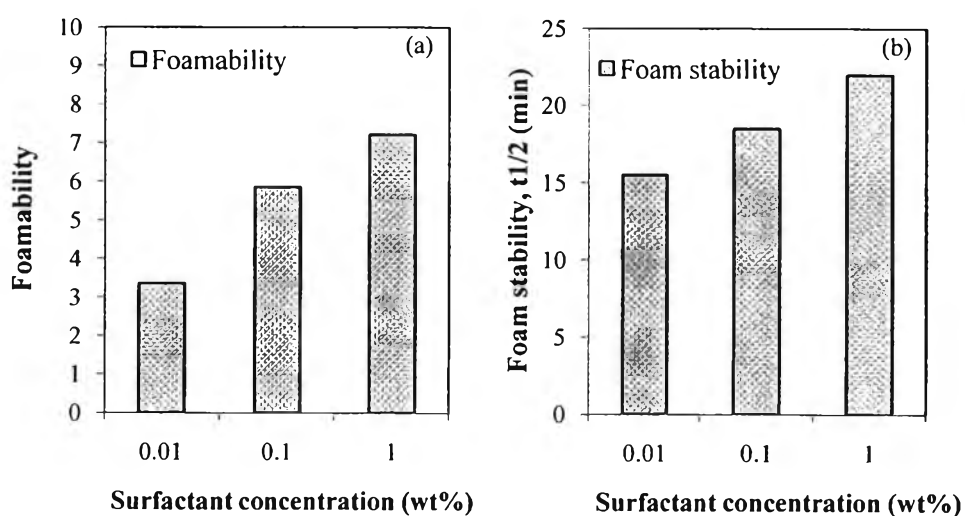


Figure 4.18 Foam characteristics of NPE-9 as a function of the surfactant concentration of 0.01, 0.1, and 1 wt% using the pneumatic foam test, air flow rate = 20 ml/min, and room temperature; (a) Foamability, and (b) Foam stability.

4.4.3 The Simple Shaking foam test results

Foamability and foam stability were investigated by using shaking method. This method is similar to the washing step action in our daily life. Foaming experiments were studied at surfactant concentration of 0.01, 0.1, and 1 wt% for those surfactants at room temperature.

Figures 4.19-4.22 show the foam characteristics of $C_{12-14}EO_3$, $C_{12-14}EO_5$, $C_{12-14}EO_7$, and $C_{12-14}EO_9$, respectively. In the system of $C_{12-14}EO_3$, the increase concentration 0.01 to 0.1 wt% slightly affect the behavior of foam stability but the foam height of 1 wt% was higher than 0.01 and 0.1 wt%. For this system, the first zone, the foam heights gradually decreased from initial time to about 30 min and then the foam heights slightly decreased from 30 to 60 minutes as shown in Figures 4.19.

The foam characteristics of $C_{12-14}EO_5$ at concentration of 0.01, 0.1, and 1 wt% are shown in Figure 4.20. The increase concentration increased foamability and foam stability but not much difference for concentration of 0.1, and 1 wt%. For this system, the foam heights decreased in first zone from initial time to 10 minutes and then the foam heights slightly decreased until 60 minutes.

In the system of $C_{12-14}EO_7$, the increase concentration affects the behavior of foamability and foam stability definitely as shown in Figure 4.21. The increase concentration increased foamability and foam stability. At concentration of 0.01 wt%, the foam height was slightly decreased from initial time to 60 minutes. Moreover, the foam heights of the testing solution of 0.1 and 1 wt% gradually decreased from initial time to 40 minutes and finally the foam of 1 wt% decreased to equal as foam height of 0.1 wt%.

Figure 4.22 is shown the foam characteristics of $C_{12-14}EO_9$ at concentration of 0.01, 0.1, and 1 wt%. Generally, at concentration of test solution of 0.01 and 0.1 wt%, the foam heights gradually decreased from initial time to 60 minutes. Moreover, at the concentration of 1 wt%, the foam height significantly decreased from initial time to about 30 minutes, and finally, the foam height gradually decreased from $t = 30$ minutes to 60 minutes, which the foam height was not much different to 0.1 wt% of concentration.

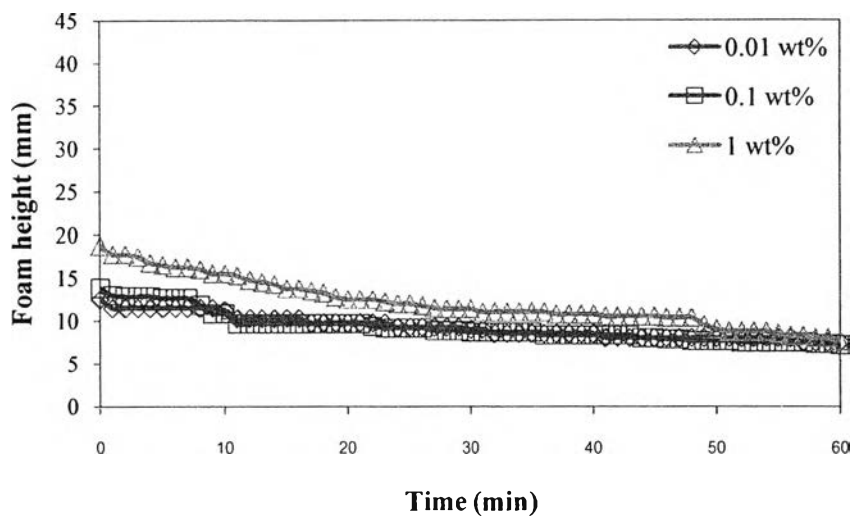


Figure 4.19 Foam characteristics of $C_{12-14}EO_3$ as a function of the surfactant concentration of 0.01, 0.1, and 1 wt% using the simple shaking foam test at room temperature.

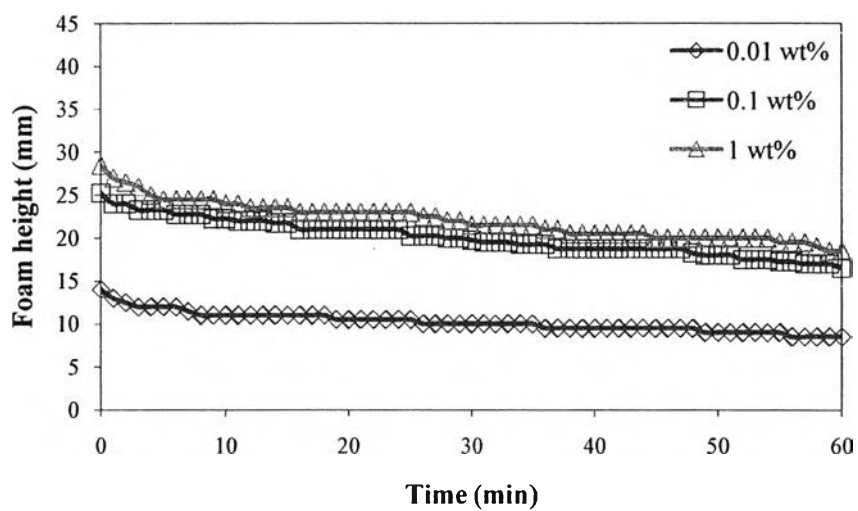


Figure 4.20 Foam characteristics of $C_{12-14}EO_5$ as a function of the surfactant concentration of 0.01, 0.1, and 1 wt% using the simple shaking foam test at room temperature.

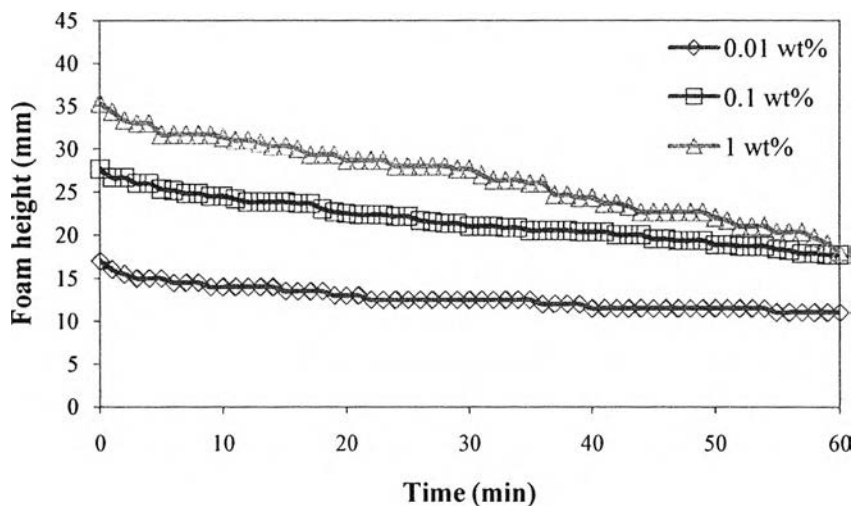


Figure 4.21 Foam characteristics of $C_{12-14}EO_7$ as a function of the surfactant concentration of 0.01, 0.1, and 1 wt% using the simple shaking foam test at room temperature.

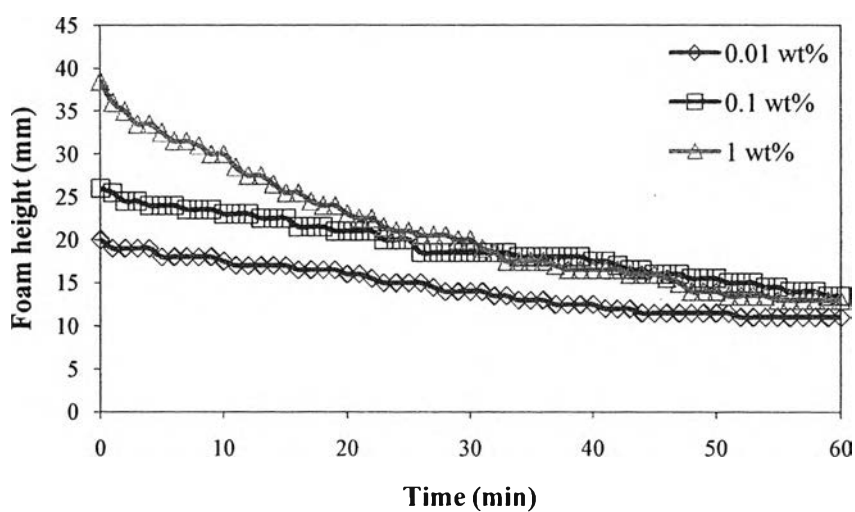


Figure 4.22 Foam characteristics of $C_{12-14}EO_9$ as a function of the surfactant concentration of 0.01, 0.1, and 1 wt% using the simple shaking foam test at room temperature.

The foam characteristics of NPE-6 at concentration of 0.01, 0.1, and 1 wt% are shown in Figure 4.23. For this system, the foam stability at concentration of 0.01 and 0.1 wt% slightly decreased. Moreover, the foam height of test solution of 1 wt% significantly decreased at the first zone, finally, the foam height gradually decreases from about $t = 40$ minutes to 60 minutes, which the foam height did not much difference from 0.1 wt%.

Figure 4.24 is shown the foam characteristics of NPE-9 at concentration of 0.01, 0.1, and 1 wt%. At concentration of 0.01 and 0.1 wt%, the foam heights slightly decreases. Moreover, at the first zone of the foam height of test solution of 1 wt% significantly decreased from initial time to about 35 minutes, and finally, the foam height slight decreased from about $t = 35$ minutes to 60 minutes, which the foam height did not much difference from 0.1 wt%.

From these results, it can be observed in that the foamability, the increase of the number of the EO content or concentration of surfactant increases the foamability which is the ability of foam generation as shown in Figure 4.25. Also, the foam stability was affected by both the concentration and the number of the EO group of fatty alcohol ethoxylates and nonylphenol ethoxylates as shown in the behavior of foam height in Figure 4.19-4.22.

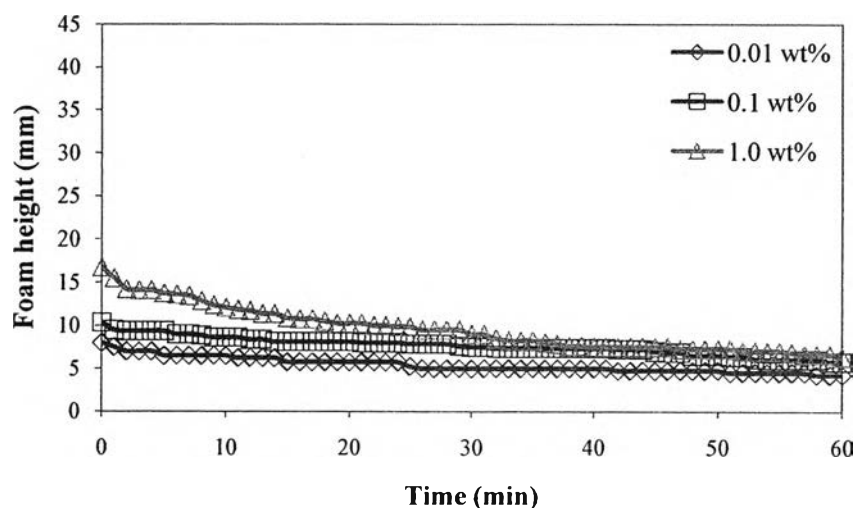


Figure 4.23 Foam characteristics of NPE-6 as a function of the surfactant concentration of 0.01, 0.1, and 1 wt% using the simple shaking foam test at room temperature.

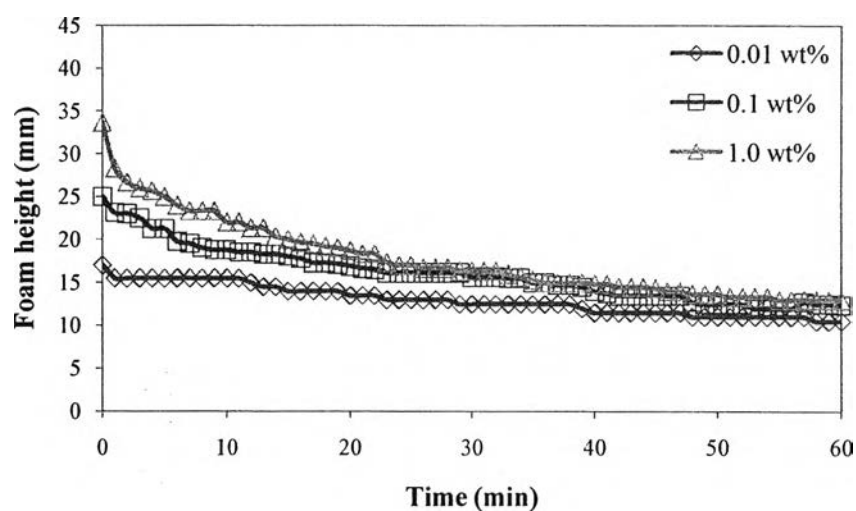


Figure 4.24 Foam characteristics of NPE-9 as a function of the surfactant concentration of 0.01, 0.1, and 1 wt% using the simple shaking foam test at room temperature.

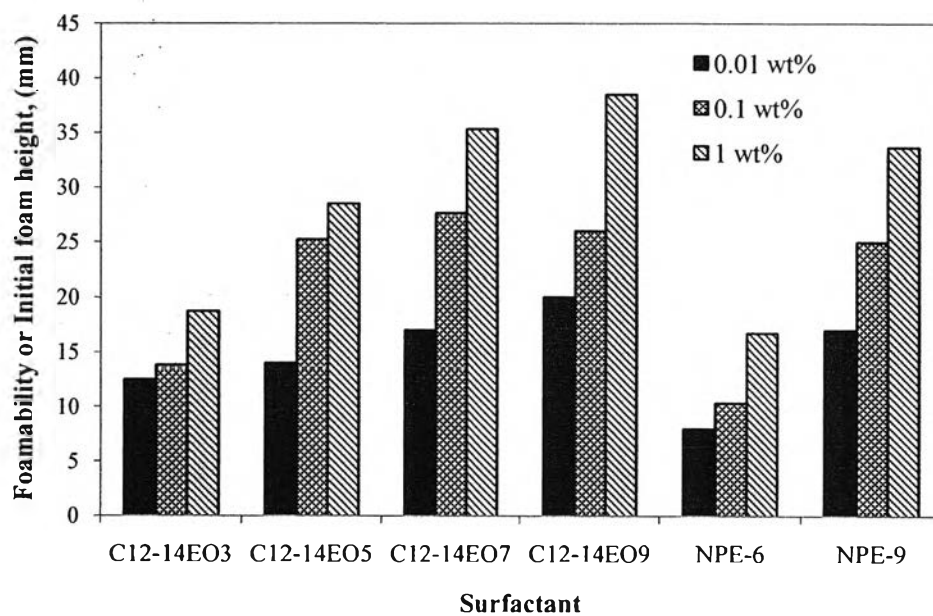


Figure 4.25 Foamability of $C_{12-14}EO_3$, $C_{12-14}EO_5$, $C_{12-14}EO_7$, $C_{12-14}EO_9$, NPE-6, and NPE-9 as a function of the surfactant concentration of 0.01, 0.1, and 1 wt% using the simple shaking foam test at room temperature.

4.5 Dynamic Surface Tension Results

Dynamic surface tension was determined for each alcohol ethoxylates by using bubble pressure tensiometer (Krüss, BP2), which was tested at temperature of 30°C. The dynamic surface tension was tested at concentration of 0.01, 0.1, 1 wt%. The dynamic surface tension, especially at short periods, corresponding to the surface of the air bubbles is found an important property for the foamability.

4.5.1 Effect of ethylene oxide content

Figure 4.26 shows the dynamic surface tension of fatty alcohol ethoxylates and nonylphenol ethoxylates as a function of the number of the EO group at concentration of 0.01 wt%. The number of the EO group influenced the dynamic surface tension in the studied range time at fixed surfactant concentration. It is seen that both the fatty alcohol ethoxylates and nonylphenol ethoxylates, the lower number of the EO group shows higher surface tension than that of higher number of the EO group with in the time range, which is very short in comparison to time required to reach meso–equilibrium of surface tension. In general, foamability of the aqueous surfactant solution is related to the dynamic surface tension. The higher EO group such as C₁₂₋₁₄EO₇, C₁₂₋₁₄EO₉, and NPE-9 had a tendency to show high foamability at fixed surfactant concentration. From this result, it is agree with foam test results. The fatty alcohol ethoxylates especially at high EO group (7 and 9) showed better foaming properties.

Figure 4.27 illustrates the dynamic surface tension of fatty alcohol ethoxylates and nonylphenol ethoxylates as a function of the number of the EO group at concentration of 0.1 wt%. The number of the EO group also influenced the dynamic surface tension in the studied range time at fixed surfactant concentration. It is seen clearly that both the fatty alcohol ethoxylates and nonylphenol ethoxylates, the lower EO group needed the longer time to establish the meso–equilibrium of surface tension. As a result it is expected to have low foamability than that of the higher EO group because the dynamic surface tension can tell how fast of surfactant molecule adsorption at the lamellae interface during foam formation.

Figure 4.28 shows the dynamic surface tension of fatty alcohol ethoxylates and nonylphenol ethoxylates as a function of the number of the EO group at concentration of 1 wt%. The number of the EO group also influenced the dynamic surface tension in the studied range time, which the same characteristic as concentration of 0.1, and 1 wt%. From Figure 4.28, both the fatty alcohol ethoxylates and nonylphenol ethoxylates, the higher EO group showed the rapid fall of the dynamic surface tension especially $C_{12-14}EO_7$, and $C_{12-14}EO_9$. The dynamic surface tension trends are important because faster reduction of surface tension has been correlated with faster surfactant adsorption and faster foam forming too. Hence, the foamability tended to increase with increase in the number of the EO group.

In comparison between $C_{12-14}EO_9$ and NPE-9, that both are the same number of the EO groups. From the result, the reduction rate of surface tension of $C_{12-14}EO_9$ was faster than that of NPE-9. The possible reason for this is the different of molecular size. The molecular weight of NPE-9 (~616) is higher than $C_{12-14}EO_9$ (578.35). The higher molecular weight represented large molecular size resulting in difficult for monomer of surfactant diffusion to adsorb at the interface. Hence, the time required reaching to meso-equilibrium of $C_{12-14}EO_9$ shifted to shorter time than that of NPE-9.

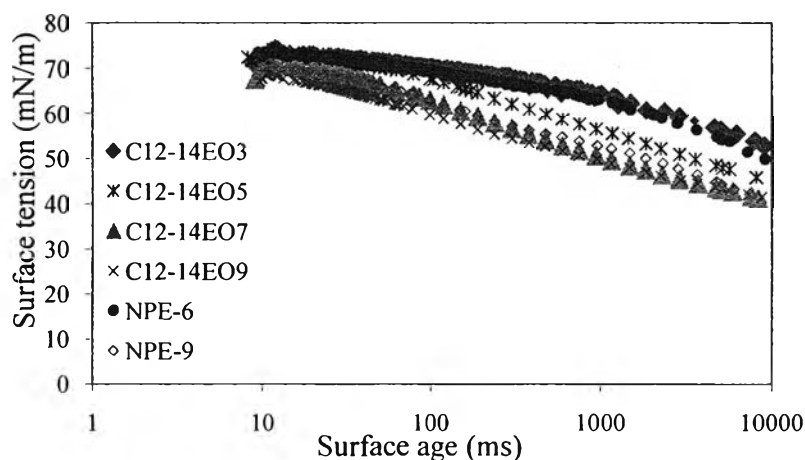


Figure 4.26 Dynamic surface tension of fatty alcohol ethoxylates and nonylphenol ethoxylates as a function of the number of the EO group at 0.01 wt%.

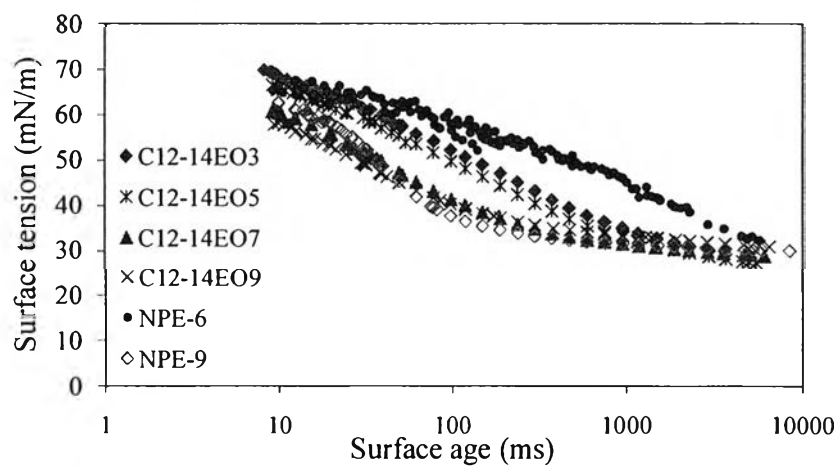


Figure 4.27 Dynamic surface tension of fatty alcohol ethoxylates and nonylphenol ethoxylates as a function of the number of the EO group at 0.1 wt%.

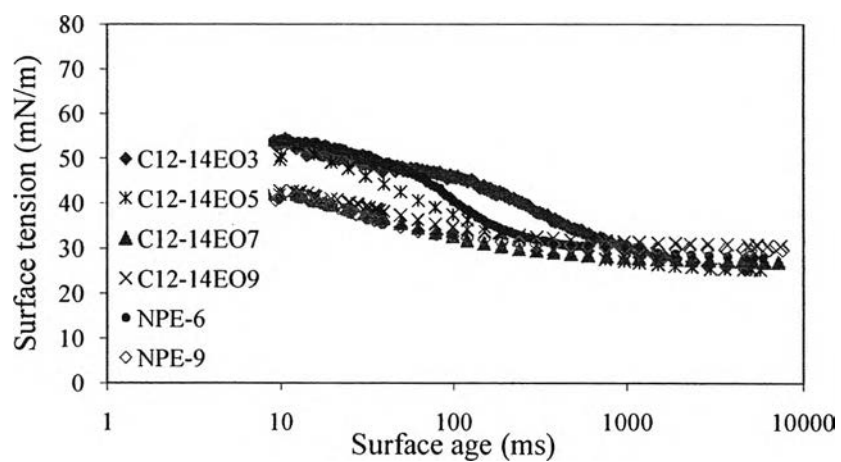


Figure 4.28 Dynamic surface tension of fatty alcohol ethoxylates and nonylphenol ethoxylates as a function of the number of the EO group at 1 wt%.

4.5.2 Effect of surfactant concentration

Figure 4.29 shows the dynamic surface tension of fatty alcohol ethoxylates as a function of the surfactant concentration of 0.01, 0.1, and 1 wt%. The surfactant concentration influenced the dynamic surface tension in the studied range time and surfactant concentration. It is clearly seen that the lower surfactant concentration shows higher surface tension than that of higher surfactant concentration within the time range. The low surfactant concentration, 0.01 wt% required longer time to reach meso-equilibrium of surface tension whereas the higher surfactant concentration showed the rapid fall of dynamic surface tension shift to a shorter time. The reduction rate of surface tension became faster as the surfactant concentration increases because the systems were above CMC, the micelles acted as a reservoir to supply monomers of surfactant for adsorption on the interface (Shama et al., 2007). In general, foamability of the aqueous surfactant solution is related to the dynamic surface tension. Hence, the time required tended to decrease with the increase in surfactant concentration. It is expected that the higher surfactant concentration have better foambility than the lower concentration which it is agree with foam test results. This behavior was also found in the case of nonyphenol ethoxylates as shown in Figure 4.30.

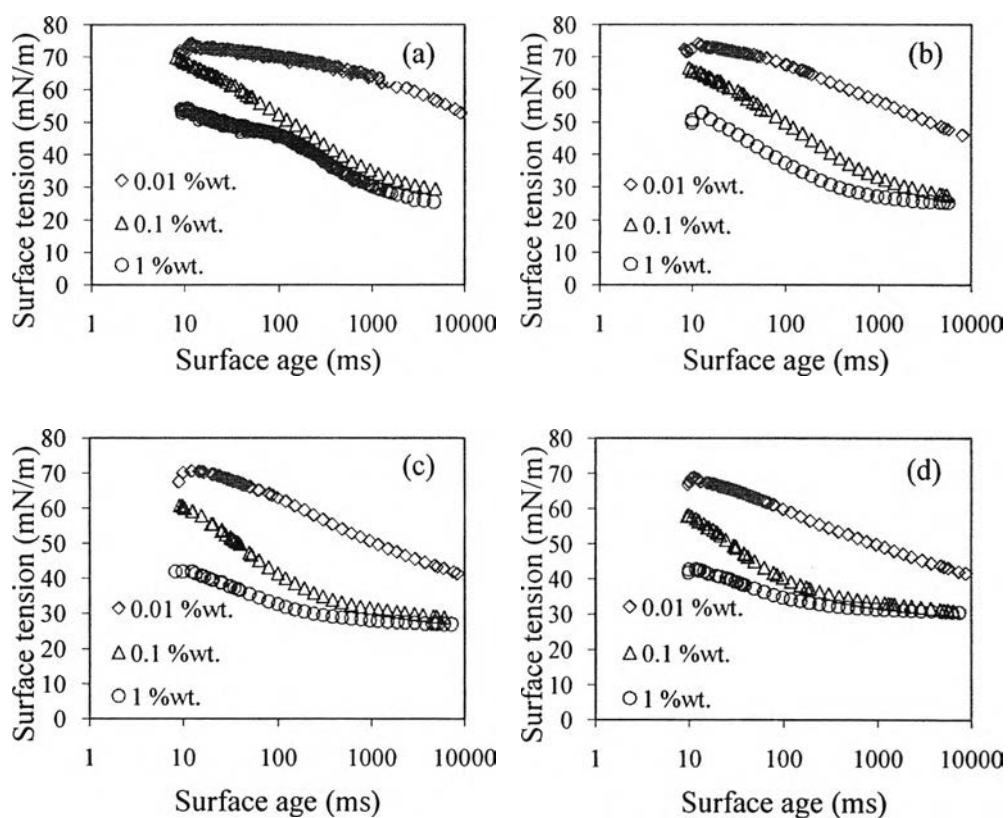


Figure 4.29 Dynamic surface tension of fatty alcohol ethoxylates as a function of the surfactant concentration of 0.01, 0.1, and 1 wt% at temperature of 30°C; (a) $C_{12-14}EO_3$, (b) $C_{12-14}EO_5$, (c) $C_{12-14}EO_7$, and (d) $C_{12-14}EO_9$.

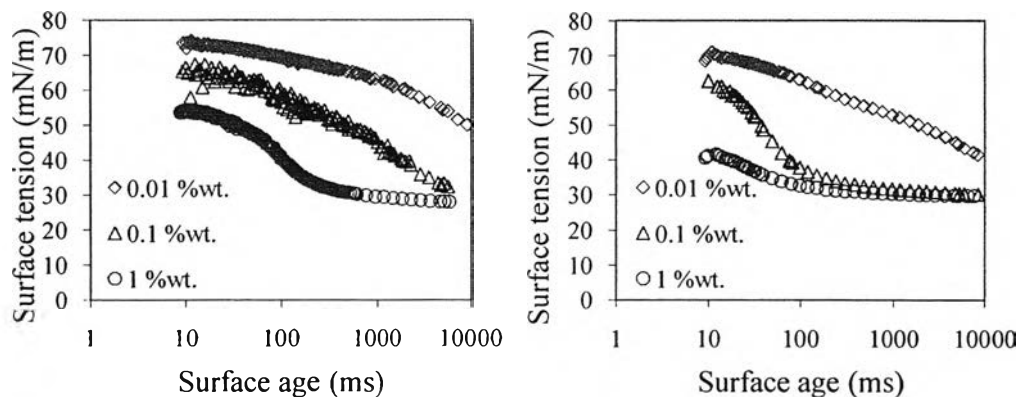


Figure 4.30 Dynamic surface tension of nonylphenol ethoxylates as a function of the surfactant concentration of 0.01, 0.1, and 1 wt% at temperature of 30°C; (a) NPE-6, (b) NPE-9.

4.6 Gel Range

The general phase behavior of surfactants is helpful to understand and desire parameter in the right way because many formulations and products consist of blend of surfactant and water. The type of phase structure depends on parameters such as molecular structure, surfactant concentration, and temperature. The influences of concentration and aggregation form in this study were observed by the viscosity. Fatty alcohol ethoxylates also tend to form gel in the preparation of aqueous solutions. Figure 4.31–4.34 show the influence of concentration and aggregation form on the viscosity behavior of fatty alcohol ethoxylates— $C_{12-14}EO_3$, $C_{12-14}EO_5$, $C_{12-14}EO_7$, and $C_{12-14}EO_9$, respectively. Also, the viscosity behavior of nonylphenol ethoxylates—NPE-6, and NPE-9—are shown in Figure 4.35 and 4.36, respectively. Above their critical micelle concentration (CMC) of each surfactant, the ethoxylates solution formed globular micelles, denoted as L_1 which did not influence the flow properties as seen the behavior of viscosity in the first zone of each surfactant. When the concentration of surfactant increased, the aggregation form changed from globular micelle to rod-like micelles which the flow of this phase was influenced. Because, aggregation phase appeared anisotropic shape and tended to form complex

at a sufficiently high surfactant concentration. As increased surfactant concentration, the hexagonal phase (H) tended to form which this phase the stiff gel was occurred and inhibited the flow property almost completely. This caused the viscosity was increased dramatically. The gel readily form as ethoxylate concentration, average ethylene oxide content were increased as obviously seen in figure 4.33, and 4.34 for $C_{12-14}EO_7$, and $C_{12-14}EO_9$, respectively. This behavior was also found in NPE-6 and NPE-9 as shown in figure 4.35, and 4.36, respectively, high average ethylene oxide resulting in broader gel range. Surprisingly, when surfactant concentrations increasing go on hexagonal phase, the viscosity dramatic decreased despite the concentration increasing. The possible reason for this is the packing of surfactants change to lamellar (L_2). The planar lamellar are capable of sliding and react more flexibly to external pressure. Therefore, the phase of these ethoxylates were observed at increasing concentration of surfactant solution which occurred the phase in order following.

L_1 (micellar solution) \rightarrow H (hexagonal phase) \rightarrow L_2 Lamellar phase

Figure 4.37 show Gel boundary diagram of fatty alcohol ethoxylates and nonylphenol ethoxylates as a function of the surfactant concentration at 25°C, as illustrated gels shown in black c. In comparison with $C_{12-15}EO_7$ based on modified from Oxo-type alcohol at temperature of 25°C, gel phase are in the range of 40–80 wt% of concentration which is also board gel range (Michael F. C., 2007)

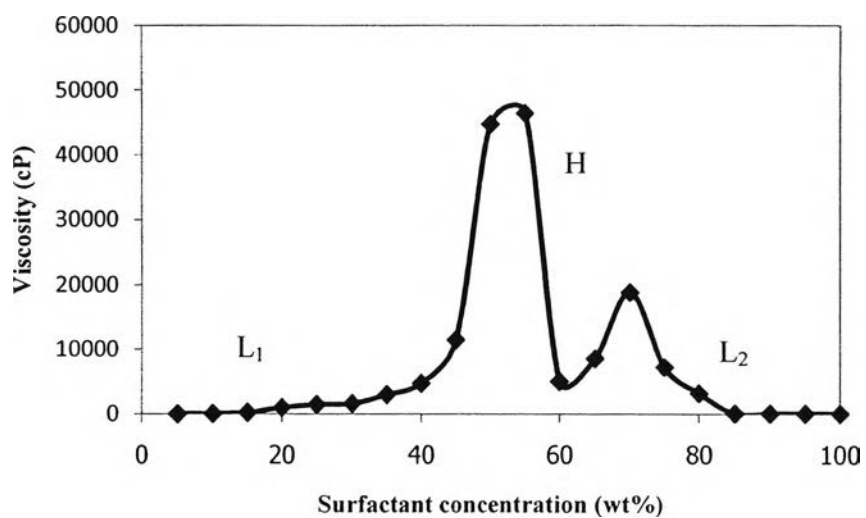


Figure 4.31 Viscosity behavior of $C_{12-14}EO_3$ as a function of the surfactant concentration at 25°C.

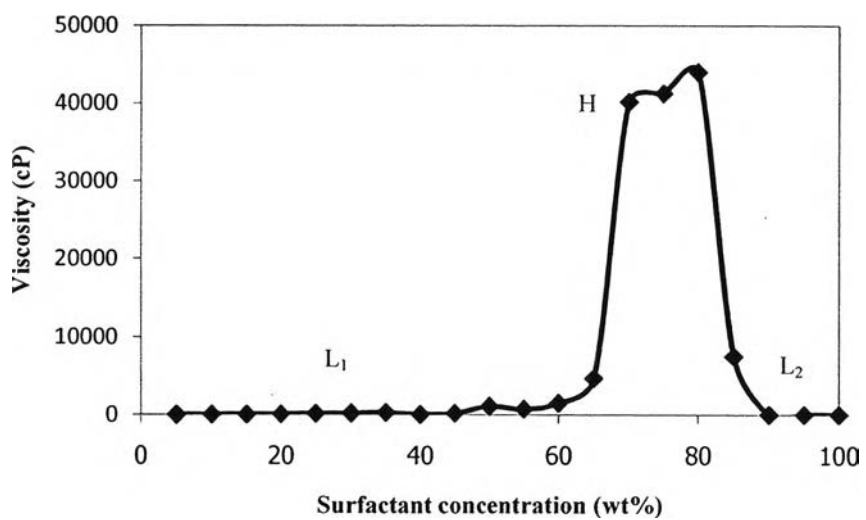


Figure 4.32 Viscosity behavior of $C_{12-14}EO_5$ as a function of the surfactant concentration at 25°C.

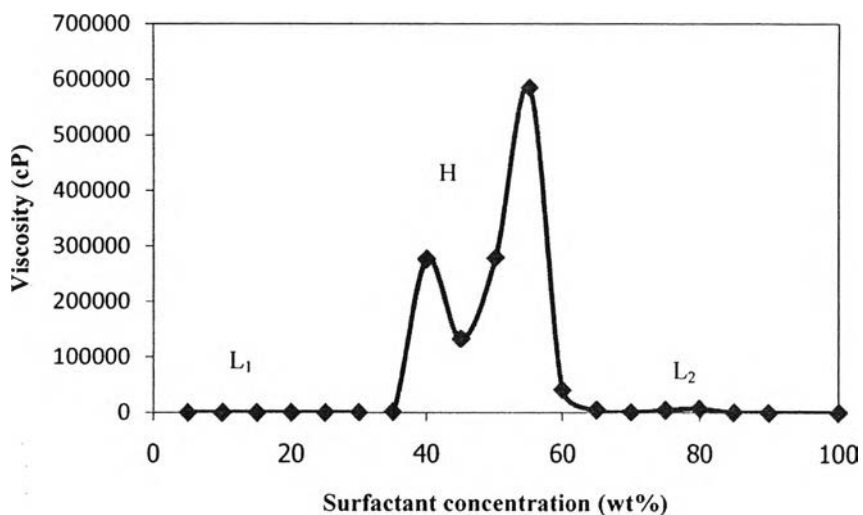


Figure 4.33 Viscosity behavior of $C_{12-14}EO_7$ as a function of the surfactant concentration at 25°C.

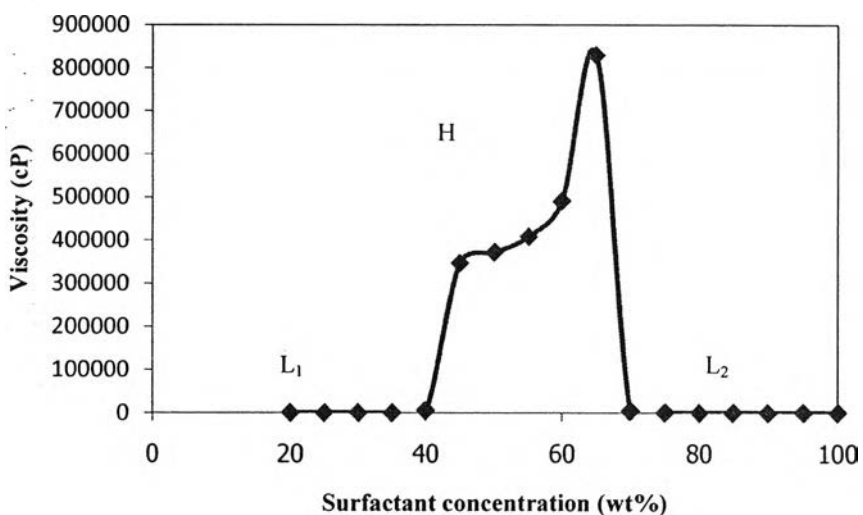


Figure 4.34 Viscosity behavior of $C_{12-14}EO_9$ as a function of the surfactant concentration at 25°C.

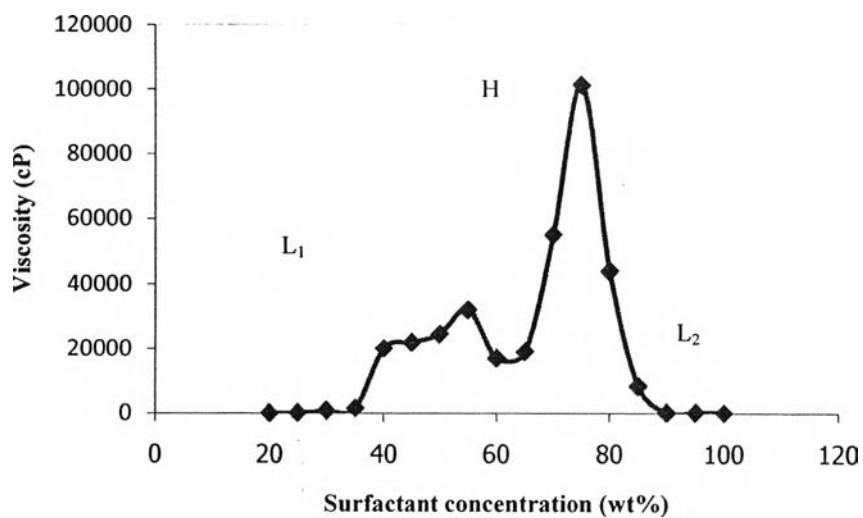


Figure 4.35 Viscosity behavior of NPE-6 as a function of the surfactant concentration at 25°C.

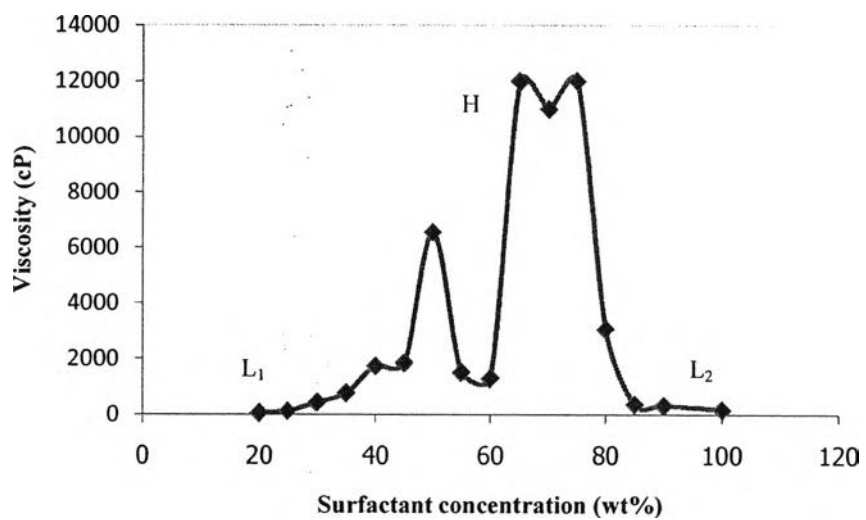


Figure 4.36 Viscosity behavior of NPE-9 as a function of the surfactant concentration at 25°C.

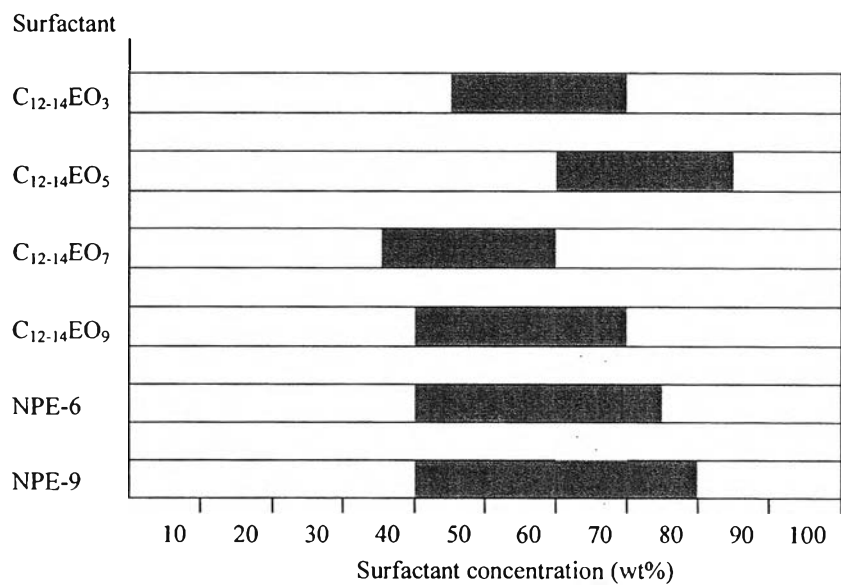


Figure 4.37 Gel boundary diagram of fatty alcohol ethoxylates and nonylphenol ethoxylates as a function of the surfactant concentration at 25°C. (□ = low viscosity liquid; ■ = gel.)