

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Phase Behavior Study

The pseudo-ternary phase diagram was used to determine the microemulsion region, which consists of three vertices of three phase. Two vertices at the bottom of triangle represent surfactant and co-surfactant mixture at a constant ratio and mixture of castor oil and sunflower oil at the left side and the right side, respectively, while the upper vertex represents the amount of water. The composition at each point in a ternary phase diagram demonstrates the volume percent of the three components.

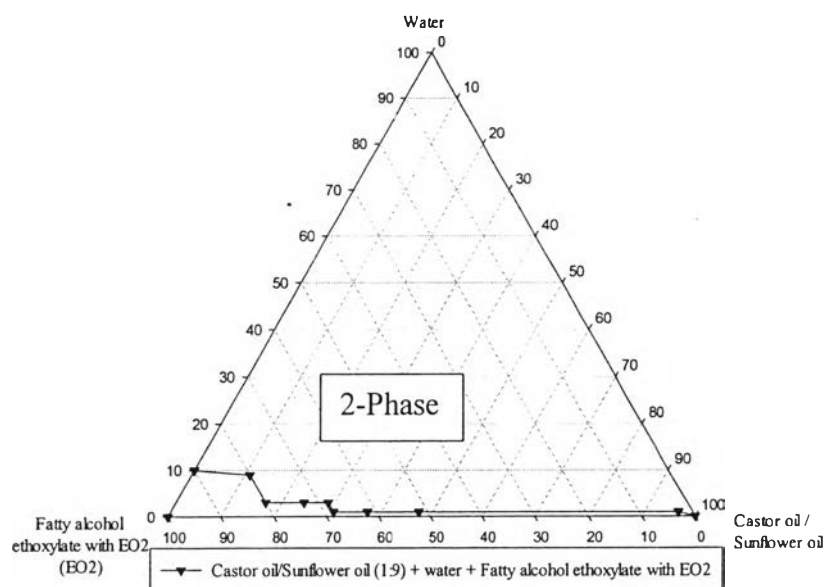
4.1.1 Effect of Surfactants Types

The water solubilization capacity was affected by surfactant types. The surfactant played an important role in microemulsion formation by reducing the interfacial tension and essential for emulsion stability. The stability was judged on the basis of changes in appearance, especially macroscopic separation. Moreover, the chain length hydrocarbon of nonionic surfactant, configuration of the polar head group, and type of oil are a strong factor in a formation of microemulsion so that the chemical structure of surfactant should be considered.

Pseudo-ternary phase diagram was constructed by selecting castor oil and sunflower oil in volume ratio of 1:9 as oil phase, sorbitan monooleate (Span 80) and alcohol ethoxylate with 2 ethylene oxide group (EO2) as a surfactant and water as an aqueous phase for observing the single phase region. The microemulsion system which uses 2 EO groups as a surfactant is observed towards surfactant rich apex, when surfactant/oil ratio is more than 1 as shown in Figure 4.1a. On the other hand, the single phase region of microemulsion is observed when using Span 80 as a surfactant as shown in Figure 4.1b. In addition it was found that the appearance of w/o microemulsion using the alcohol ethoxylate with 2 EO group was more transparent than Span80. These phenomena was due to the number of carbon chain

length of the surfactant molecule. The alcohol ethoxylate with 2 EO group was shorter carbon chain length (C12-14) than Span80 (C18), may influence their ability to form small droplet size and present more transparent. Moreover, the alcohol ethoxylate with 2 EO group has more hydrophilicity than the others, and therefore, led to the more compatibility with water. These results suggested that the single phase solution of the emulsion was controlled by both the molecular size and hydrophilicity of the surfactant.

Figure 4.2 shows the comparison of the number of EO groups in surfactant series (EO2, EO5 and EO7) with a surfactant-to-oil ratio of 2:3 is the relation with the water content. The result was found that the degree of the polarity of surfactant affects the water solubilization in the microemulsion system. As the higher degree of polarity, the more water soluble in the water in oil (w/o) microemulsion system.



(a)

Figure 4.1 Pseudo-ternary phase diagrams of a) oil-alcohol ethoxylate with 2 ethylene oxide (2EO)-water system b) oil-polysorbate 80 -water system at ambient temperature, below the line curve of microemulsion zone.

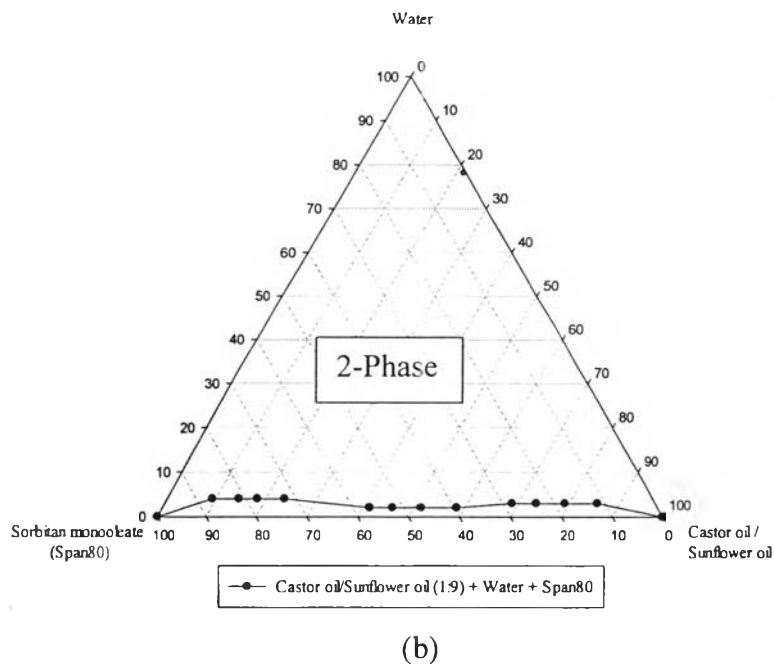


Figure 4.1 Pseudo-ternary phase diagrams of a) oil-alcohol ethoxylate with 2 ethylene oxide (2EO)-water system b) oil-polysorbate 80 -water system at ambient temperature, below the line curve of microemulsion zone (Con't.).

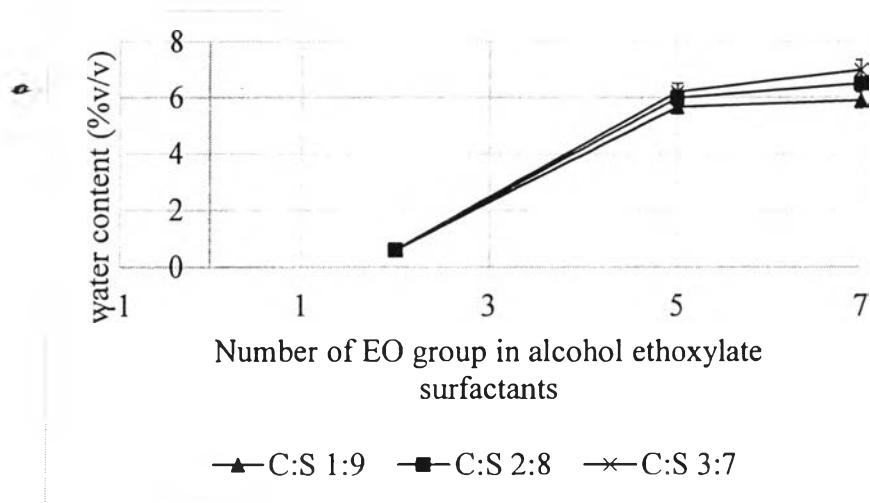


Figure 4.2 Study of water content of various ratio of castor oil and sunflower oil (C:S = 1:9, 2:8, and 3:7) in alcohol ethoxylate with different ethylene oxide (EO2, EO5 and EO7).

4.1.2 Effect of Co-surfactants Types

The effect of co-surfactant type on water solubilization capacity in microemulsion system was displayed in Figure 4.3. When ethanol was used as a co-surfactant, transparent emulsion was observed when concentration of co-surfactant was increased from 0.1M to 0.9M.

The solubilization mechanism of reverse micellar is explained in Figure 4.4. The highly polar moiety solute is solubilized in to a hydrophilic core (Figure 4.5a), whereas slightly polar moiety is located in the palisade boundary region (Figure 4.5b). The others polar solute might be found entirely in the palisades region (Figure 4.5c) or near the surface of the micelles (Figure 4.5d) (Wang *et al.*, 2014).

The observation of clear solution was due to the fact that ethanol molecules are slightly polar materials, which could efficiently pack themselves between the larger bio-surfactant chains. Because of the steric repulsion of Span80, which are not easy to associate into micelles. After adding a co-surfactant, the alcohol molecules could be inserted between the Span80 molecules. The distance between the hydrophilic groups was increased, while the steric repulsion was reduced (Figure 4.6). As a result, the reverse micelles were formed.

When a co-surfactant was change from ethanol to propylene glycol and glycerol, all of the samples were unstable and seperated into two phases (the single-phase area was not shown). This may be due to the differences size of their molecular of co-surfactant will change their droplet size formations with the oil, water, and surfactant molecules. In addition, more hydrophilic co-surfactant such as glycerol and propylene glycol tended to dissolve in the water phase instead of being inserted into the interface layer. Hence, it occupied a smaller mole fraction at the interfacial layer and not enough to allow the solubilization of a high amount of water. Moreover, the increment of co-surfactant's viscosity makes the water more difficult to diffuse across the water-oil interface. It was suggested that the microemulsion formed spontaneously with ethanol.

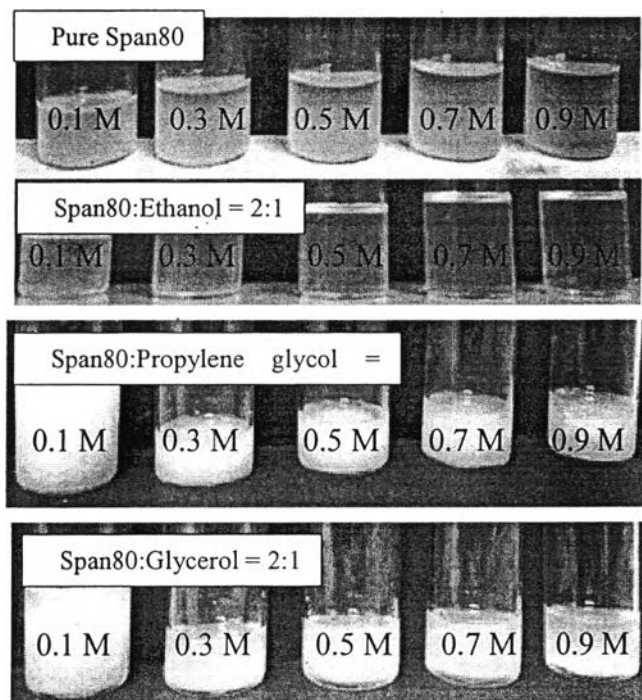


Figure 4.3 Picture of the oil-span80/ethanol (propylene glycol or glycerol) mixture–water system with/without co-surfactant at ambient temperature.

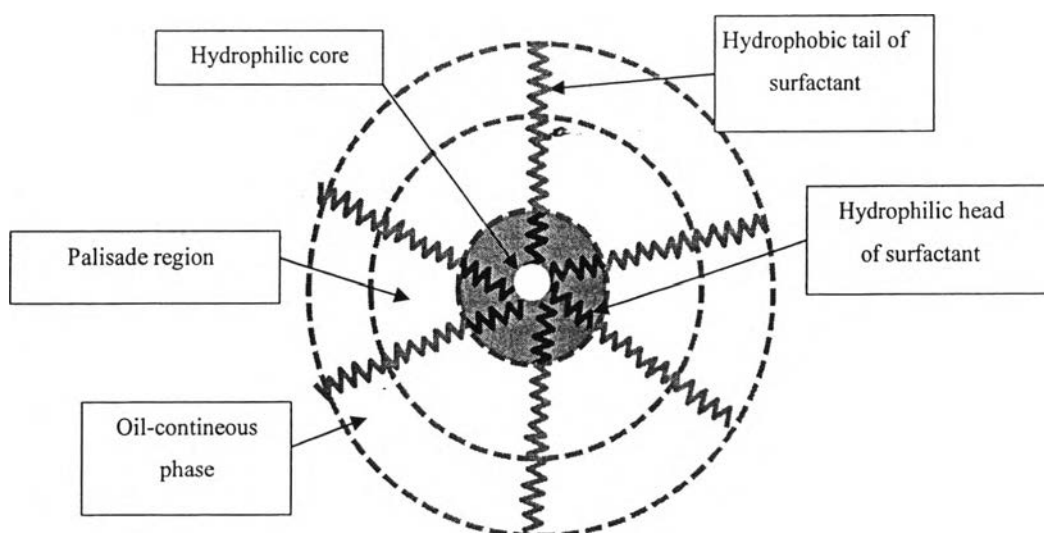


Figure 4.4 Mechanism of the soluble moiety in the w/o reverse micelles system was divided into three sections, an oil-continuous phase, a palisade layer, and a hydrophilic core.

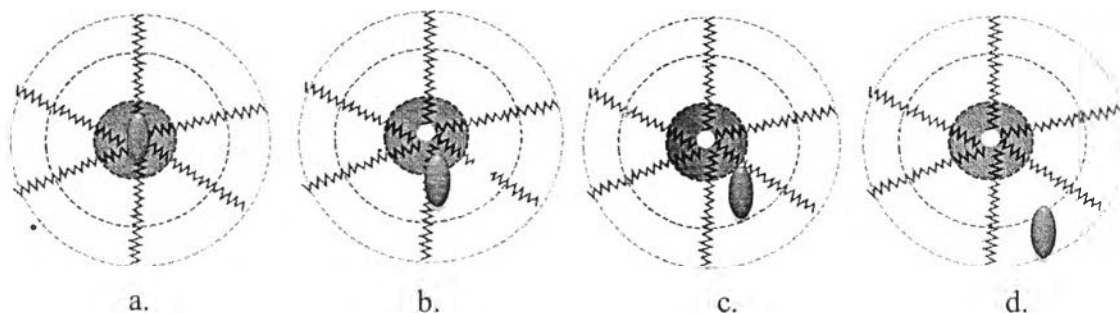


Figure 4.5 Location for the solubilization of additives in the reverse micelles: (a) all of the solubilization of moieties exists in the hydrophilic core, (b) some the solubilization of moieties exist in the hydrophilic core and some exist in the palisades layer, (c) all of the solubilization of moieties exists in the palisades layer, and (d) all of the solubilization of moieties exist in the oil-continuous phase.

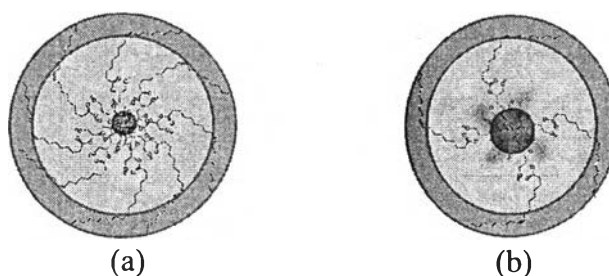


Figure 4.6 Arrangement of castor oil and co-surfactant (ethanol) in reverse micellar (a) the steric repulsion of Span80 which are not easy to associate into micelles, and (b) the steric repulsion was reduced by adding co-surfactant (ethanol).

4.1.3 Effect of Surfactant/Co-surfactants Ratios (S:Co Ratios)

To study the effect of surfactant to co-surfactant ratios (S:Co ratios), Span80 and alcohol ethoxylate with 2 EO groups were used as a surfactant and ethanol was used as a co-surfactant at different molar ratios (Figure 4.3). The appearance of the microemulsions after using the co-surfactant was transparent liquid solution.

This result is consistent with the three pseudo ternary phases (Figure 4.7) which were prepared using the surfactant and co-surfactant of molar

ratios of 1:4, 1:8, and 1:16. It was implied that the co-surfactant could decrease the interfacial free energy under isothermal conditions, while causing an uptake of water into the microemulsion. From the phase diagram, the increasing of S:Co ratios from 1:4 to 1:16, the lower single phase regions were observed. In addition, when increasing S:Co ratios to 1:32, all of the microemulsions tend to be separated into two phases. The reason for this could be attributed to the fact that the excess ethanol penetrate to the aqueous phase, thus the interfacial film becomes saturated leading to a broken balance of interfacial film and a decreased in microemulsion single region phase (Figure 4.8) (Zhu *et al.*, 2014). However, the microemulsion of castor oil system with 40 %v/v of Alcohol ethoxylate with 5 EO groups and 7 EO groups (Figure 4.9) show that the microemulsion could form successfully without a co-surfactant, and water content in microemulsion system become higher in the absence of ethanol (7.0 %v/v). This may be due to the molecular structure of main fatty acid esters among castor oil and property of surfactant. Since the hydroxyl of ricinoleic molecular, castor oil is soluble with Alcohol ethoxylate with 5 EO groups and 7 EO groups resulted in a single phase formation.

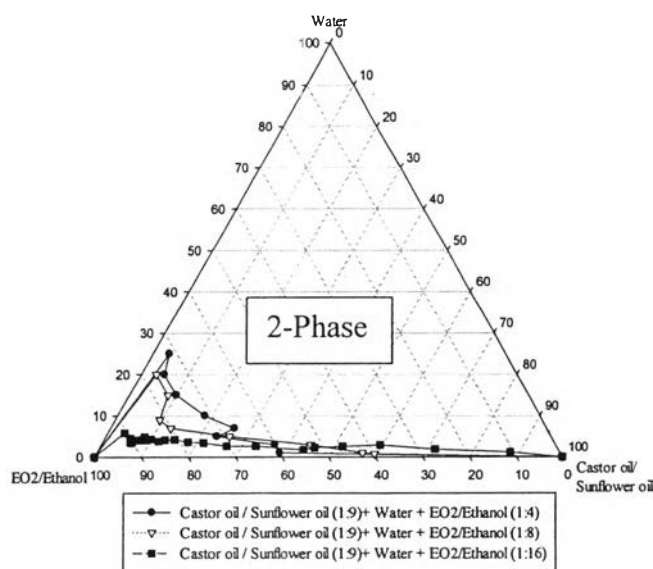


Figure 4.7 Pseudo-ternary phase diagrams of the vegetable oils-water with surfactant/co-surfactant mixture-water system at the 1:4, 1:8, and 1:16 molar ratio of Alcohol ethoxylate with 2 EO groups /ethanol at ambient temperature (25 ± 2 °C), below the curve line shown the single phase microemulsion zone.

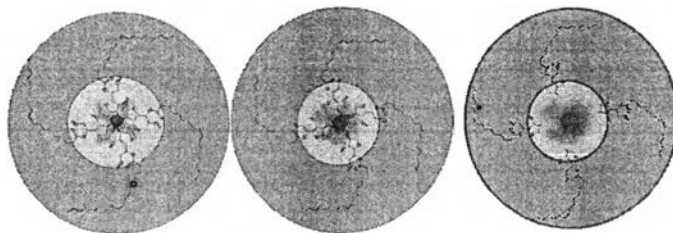


Figure 4.8 Destruction of reverse micelles by the excess co-surfactant at 1:8 and 1:16 molar ratio.

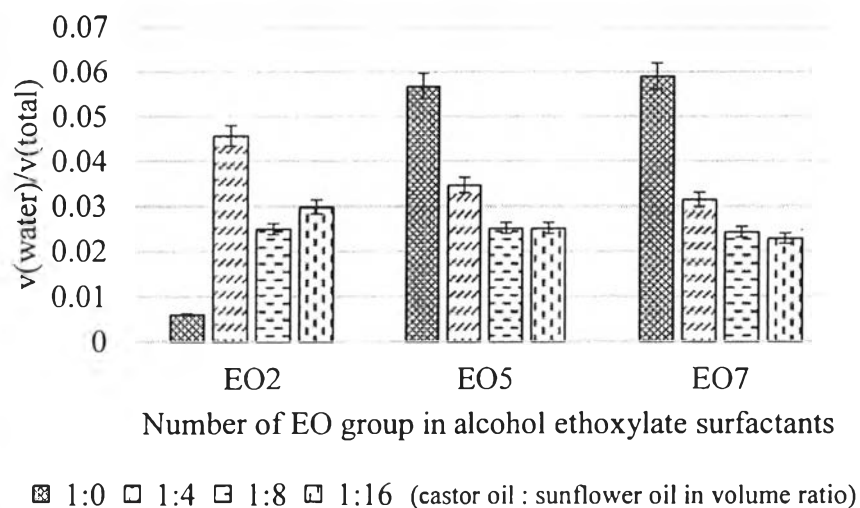


Figure 4.9 Water content in castor oil and sunflower oil in volume ratio at 1:9 by alcohol ethoxylate with 2 EO groups, 5 EO groups and 7 EO groups surfactant system with/without co-surfactant.

4.1.4 Effect of Castor Oil/Sunflower Oil Ratios (C:S Ratios)

From previous results, the ratio of castor oil to sunflower oil (C:S ratios) was fixed at 1:9. In this section, we attempted to investigate the effect of polarity of castor oil on the microemulsion system by varying C:S ratios at 1:9, 2:8 and 3:7 (v/v).

Figure 4.10 illustrates the experimental paths of the phase diagram which compose of water, using EO5 as a surfactant with the C:S ratio at 1:9. For a faster screening of the countless possibilities of mixing three components, The appropriate formulation depicted from the pseudo-ternary phase diagram was fixed at a constant surfactant-to-oil ratio (S/O ratio) hence this system enable for further used as an emulsion formulation. The value of b^* is the dilution line with a 2:3 S/O ratio and a^* is the path within the microemulsion area (Klossek *et al.*, 2014). From the phase diagram, the critical percentage of water was obtained at 7 %v/v (Table 4.1).

Result from Figure 4.11 was observed that the higher water content were obtained at 2:8 and 3:7 of C:S ratios than those from the others. It can be concluded that the higher degree of oil polarity led to increase water content in microemulsion system. While in the system at 4:6 and 5:5 of C:S ratios apparently showed undesirable behaviors with the observed water content being lower than that predicted, then the higher C:S ratio condition was not appropriate in this system. The undesirable behavior was due to the fact that the excessive amounts of castor oil could dissolved in the aqueous phase or the palisades layer, the surfactant molecules would be separated too far by excessive castor oil molecules. The palisades layer would become less stable and a decreased in water solubilization capacity (Figure 4.12). Consequently, the results of the different C:S ratios in Table 4.2 led to conclusion that the condition which gave the highest water soluble (7 %v/v) was C:S ratio of 3:7.

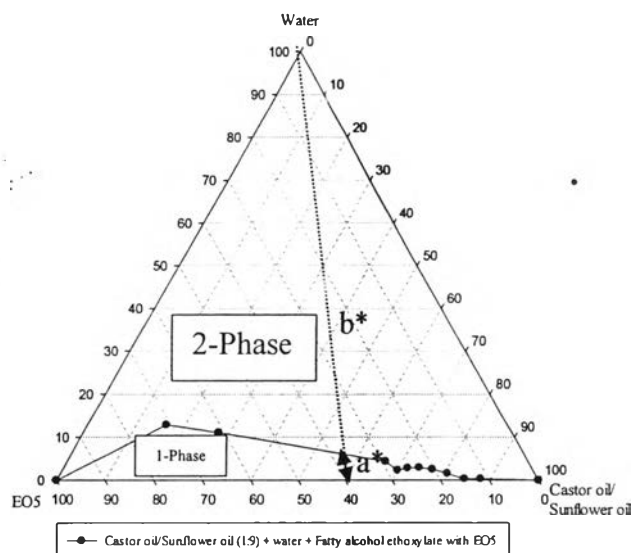


Figure 4.10 Illustration of a representative pseudo-ternary phase diagram with water/surfactant/oil. The yellow area represents the microemulsion region. Additionally, two experimental paths are shown. b^* is the dilution line with a surfactant-to-oil ratio of 2:3. Path a^* is the part of b^* within the microemulsion area.

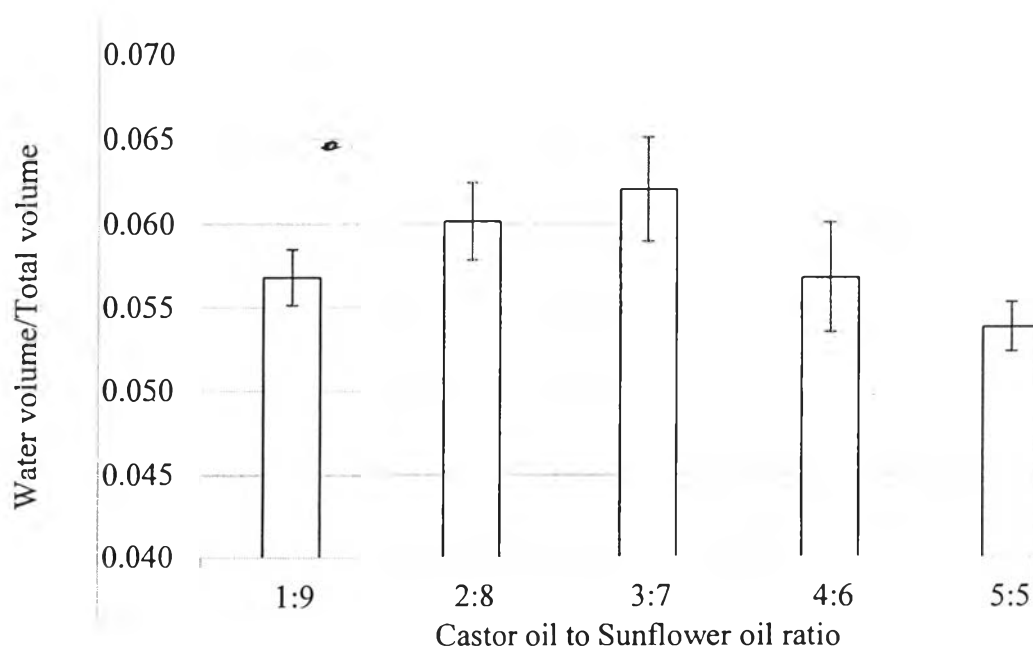


Figure 4.11 Water content in various ratio of castor oil and sunflower oil (C:S volume ratio) microemulsion by Alcohol ethoxylate with EO5 as a surfactant.



Figure 4.12 Decreasing of micelle boundary stability from excessive amounts of castor oil. The castor oil molecule (green line) make the palisades layer become less stable by separate surfactant molecule (red line) leading to decrease water solubilization capacity.

4.2 Study of Oil Make Up Remover Characterization

Table 4.1 Characteristics of oil make up remover

Physical Parameters	Alcohol Ethoxylate with	2 EO Groups (HLB= 6.1)			5 EO Groups (HLB= 10.3)			7 EO Groups (HLB= 12.1)		
	C:S (%v/v)	1:9	2:8	3:7	1:9	2:8	3:7	1:9	2:8	3:7
Droplet size (nm)		416	1521	2445	14	13	11	27	28	21
Zeta potential (mV)		-0.115	-0.167	-0.265	-0.109	-0.219	-0.445	-0.090	-0.265	-0.493
Viscosity (cst)		34.70	39.30	44.50	73.30	77.30	84.13	84.30	95.60	106.20
Water content (%v/v)		0.60	0.60	0.60	5.68	6.00	6.21	5.90	6.51	7.00

4.2.1 Study of Viscosity

Castor oil is a viscous oil (990 centipoises), the high viscosity is due to the fact that it has three hydroxyl groups in the ricinoleic acid molecule. Microemulsion was formed by adding the oil with another low viscosity oil

(sunflower oil), surfactant and water. Viscosity of the emulsion was decrease and would be useful for cleansing application and non-greasy.

The viscosity of microemulsion increased from 44.50 to 106.2 cst with decreasing droplet size from 2445 nm to 21 nm by using alcohol ethoxylate with 7 EO. When decreased droplet size of microemulsion, contact surface area increased leading to increase resistance movement of droplet (Figure 4.13). Thus, viscosity in small droplet emulsion is higher than a big droplet emulsion.

Study of the water content in microemulsions at the same number of EO groups was shown in Table 4.1. The increase in viscosity of microemulsion could be related to increment of water content. It is due to the fact that the increase of hydrogen bonds, leading to decrease in the molecular distances of the emulsion system as well as an increase of resistance to flow and lead to an increase in the viscosity as well.

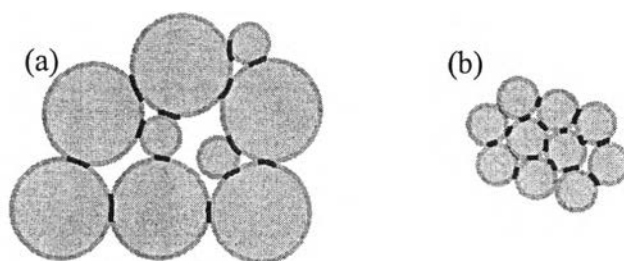


Figure 4.13 Contact surface area of small droplets and big droplets.

4.2.2 Study of Water Content

The hydrophobic and lipophilic balance of the surfactant molecule is described in terms of HLB value. HLB value was correlated with water content in the microemulsion system because the surfactant's head group had higher polarity (i.e EO9) and increased the polar region in the system. As a results, water content (v/v %) in microemulsions was increased from 0.6 to 7.0. when HLB value was changed to 12.1.

The increment of surfactant polarity could increase the hydrophilic moiety of the reverse micellar system, therefore water were more solubilized in reverse micelle and the diameter of microemulsion droplet size would increase

(Table 4.1). Slightly polar moiety such as castor oil was not favor to associate into the hydrophilic core because of the steric repulsion or coiling effect between the hydrophilic groups of the EO group inserted between head and tail of the alcohol ethoxylate surfactant. Therefore the solute might exist in palisade layer. In the case of the EO2 system, the trend was not follow as we expected. Even though, the system with 2EO had the lowest water content in hydrophilic core (0.6 %v/v), it had the largest droplet size (2445 nm). However, it was hypothesized that both water and castor oil could exist in the hydrophilic core and accumulate at palisade layer between the EO chains, which had the lowest hydrophilic groups than the others.

4.2.3 Study of Stability

ζ -Potential is a parameter commonly used for the evaluation of microemulsion stability. High absolute zeta-potential values correspond to very stable dispersions due to mutual electrostatic repulsion. When the ζ -potential is close to zero, flocculation (formation of larger assemblies of particles) is very fast causing fast sedimentation. From this result, ζ -Potential was significantly affected by both the type of the surfactant and the ratio of castor oil in the mixture. High negative values of ζ -potential showed the alcohol ethoxylate with 7 EO groups surfactant is the highest stability while 2 EO groups surfactant resulted in the lowest moreover, values ζ -potential indicating instability (Figure 4.14).

Moreover, Table 4.2 show the droplet size distribution at 1 month storage time. The trend of droplets size in 2EO groups systems is larger droplet size with increasing of castor oil ratio and has bimodal distribution while the 5 and 7 EO groups system has opposite tend. In addition, in case of 7 EO groups, it shown a mono distribution with more narrow distribution. Hence, the 7 EO groups system has a uniform of droplet size leading to highest stability system.

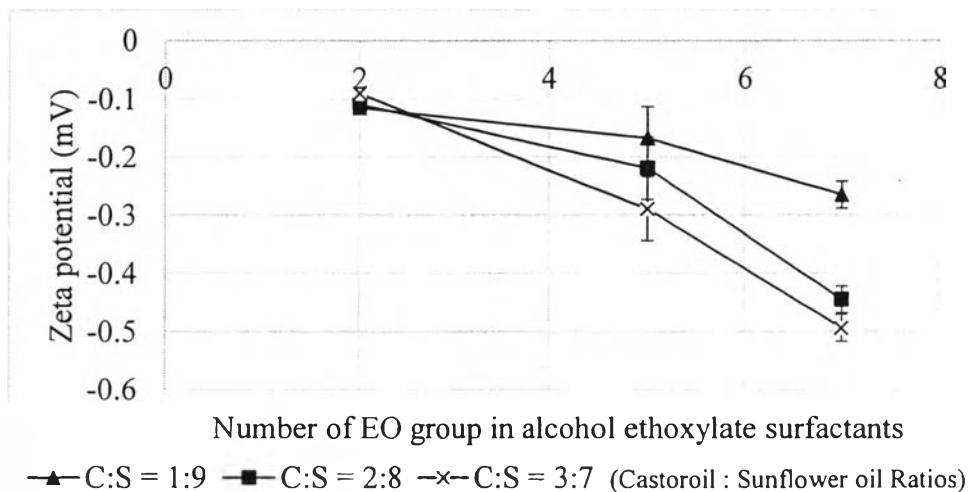


Figure 4.14 ζ -Potential values of 1:9, 2:8 and 3:7 castor oil and sunflower oil ratio (C:S ratio) with different ethylene oxide (EO) groups.

Table 4.2 Droplet size distribution of microemulsion at castor oil to sunflower oil ratio of 1:9, 2:8, and 3:7 by using alcohol ethoxylate with 2, 5, and 7 EO groups

The Group Number of Ethylene Oxide (EO) with Alcohol Ethoxylate	C:S Ratios		
	1:9	2:8	3:7
2 EO			
5 EO			
7 EO			

4.2.4 Study of Cleansing Efficiency

In this experiment, the rubbing times and amount of water were used as indicators to investigate the cleansing efficiency. The water was used as controlled variable. The control condition was observed at 40 times of rubbing and 3.8 ml of amount of water. When compared results of commercial cleansing oil with prepared microemulsion, it showed that when increase the ratio of castor oil in prepared microemulsion, the cleansing efficiency was higher than the commercial cleansing oil by the decreasing of the number of rubbing and the volume of used water. The number of rubbing times and water used of prepared microemulsion decreased from 40 times to 12 times and 3.8 ml to 1.1 ml, respectively (Figure 4.15 to 4.16). It suggested that the cleansing efficiency of prepared microemulsion which has C:S equal to 3:7 with alcohol ethoxylate with 7 EO group is better than that of using only water and commercial cleansing oil.

When the ratios of the polarity of Castor oil and the number of EO increased, the cleansing efficiency increased as well. It was hypothesized that the sample with higher polarity had higher ability to dissolve into the red lipstick and the water. Consequently, the proper condition in cleansing application was microemulsion formulated with C:S equal to 3:7 with alcohol ethoxylate with 7 EO group.

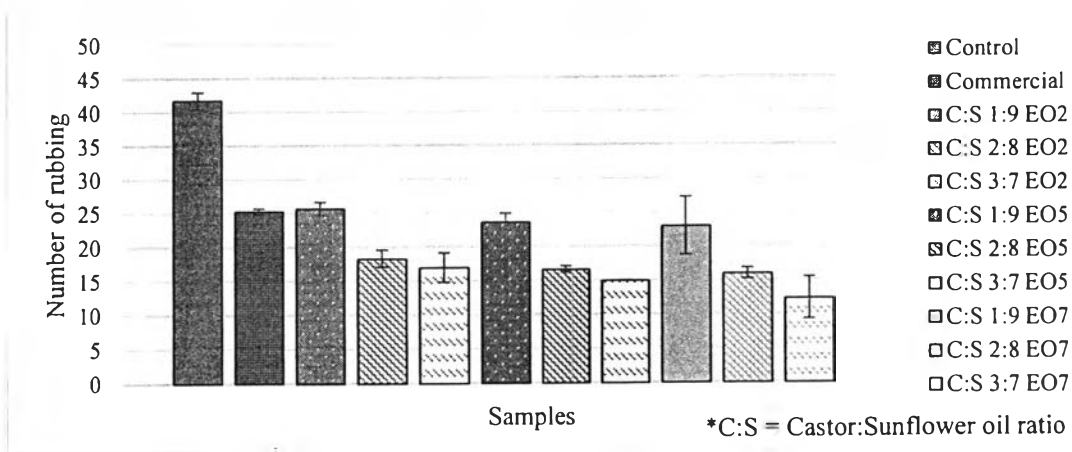


Figure 4.15 Number of rubbing for cleansing red lipstick in each samples.

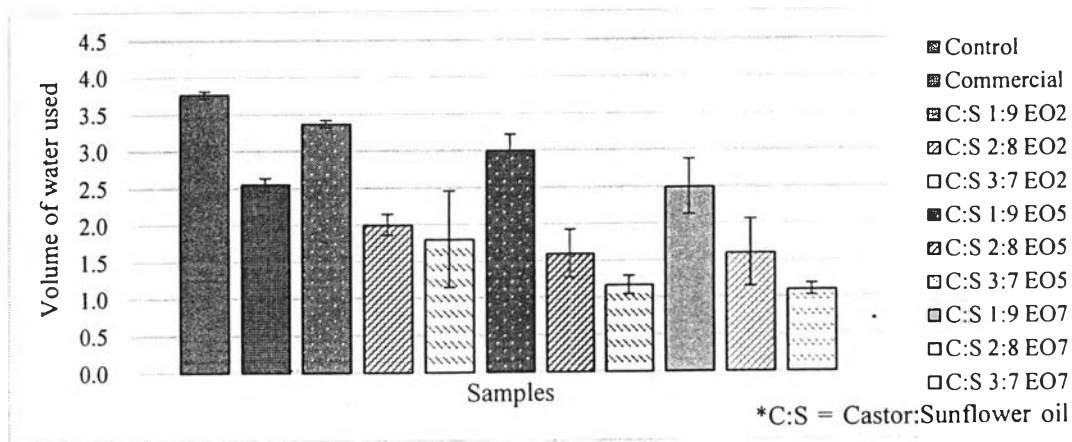


Figure 4.16 Volume of water used for cleansing cosmetic in each samples.