

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Single Surfactant Systems

##### 4.1.1 Basic Properties of Surfactants

First of all, basic properties of surfactants have to be concerned to gain a better understanding of interesting surfactant and understand the behavior of surfactant in uses and application. In this presence work, main basic properties used to explain behavior of surfactant for detergency application consist of water solubility, solubilization, surface tension and critical micelle concentration (CMC).

##### 4.1.1.1 Solubility

Solubility is the one of important factors, which involves in the detergency performance. Various studies have been reported that the detergency performance usually increases with the increasing of hydrophobic chain length. (Rosen, 2012). In this study, the solubility of two main groups of surfactant— (1) anionic and (2) nonionic—was study as shown in Table 4.1. The first group, anionic surfactant, methyl ester sulfonate (MES) with different alkyl chain lengths (MES 14C, MES 16C and MES 18C) was selected as the representative of this group because it was well known that longer hydrophobic chain length is, higher detergency performance becomes. However, very long hydrophobic chain length inhibits the water soluble of surfactant. The results are clearly seen that the highest solubility value of 35%wt/v was found from MES-C14, while MES-C16 and MES-C18 gave the solubility value less than 1%wt/v. Therefore, MES-14C was selected as the representative of anionic surfactant for further investigation. The second group, nonionic surfactants, consisting of two group; (1) gemini surfactants (oleic acid based) with 20 and 30 polyoxyethylene head groups (FE-1020E, FE-1030E) and (2) methyl ester ethoxylates nonionic (MEE) with different amount of ethylene oxide groups (MEE-8EO, MEE-14EO and MEE-18EO). The results showed that all of these nonionic surfactants had the solubility value more than 50%wt/v. Hence, all of them were selected for further study.

**Table 4.1** Water solubility and inverse cloud points (°C) of Surfactants

Type of Surfactant	Solubility(%wt/v)	Inverse Cloud Point (°C)
MES-14C	35.2750	-
MES-16C	0.5206	-
MES-18C	0.0428	-
FE-1020E	>50	40.0
FE-1030E	>50	59.0
MEE-8EO	>50	42.0
MEE-14EO	>50	79.5
MEE-18EO	>50	88.5

Moreover, the inverse cloud point of nonionic surfactant was also measured by heating a 1%wt/v aqueous solution of these nonionic surfactants, and determining the temperature at which the solution start to be turbid (the “cloud point”). Water solubility of nonionic surfactant is directly related to the interaction between the EO chain in surfactant molecule and water molecules. As temperature is increased, hydration of the EO chain decreases. Eventually, the extent of dehydration becomes sufficient for the surfactant to become insoluble, as measured by the appearance of cloudy solution. Hence, a higher inverse cloud point would show the greater water solubility (Cox *et al.*, 1997). As shown in Table 4.1, the inverse cloud point increased with increase in the number of OE units in the polyoxyethylene chain in both gemini and MEE surfactants. It suggested that FE-1030E and MEE-18EO could have higher solubility than the other in gemini and MEE surfactant respectively. Conversely, although gemini surfactants were composed of OE units more than MEE surfactants, cloud point measurements for gemini surfactants were lower than MEE surfactants. It was due to gemini surfactants consisted of more the number of carbon atoms than MEE surfactants making it difficult to be soluble in the water.

#### 4.1.1.2 Critical Micelle Concentration and Surface Tension

In order to obtain a better understanding on the solubilization and detergency mechanism, CMC determination experiments were conducted. The CMC value of all surfactants used in this experiment is shown in Table 4.2. Micelle formation is an important phenomenon because a number of important interfacial

phenomena depend on the existence of micelles in solution. The minimum concentration at which this phenomenon occurs is called CMC. That means surfactant which has lower CMC will give easier micelle formation at lower concentration affecting to the use of lower surfactant concentration in detergency. From the result, the CMC value of gemini is the lowest and much less than the others. While, the CMC value of MES is highest. The result is not surprising because, in general, nonionic surfactants have lower CMC than ionic surfactants containing equivalent hydrophobic groups. For MEE (MEE-8EO, MEE-14EO and MEE-18EO), the result indicates that the CMC increased with increase in the number of OE units in the polyoxyethylene chain. It may be due to the bulky nature of the hydrophilic group have a strong effect for inhibiting micelle formation, leading to higher CMC (Cox et al., 1997). And the reasonable explanation that why gemini had the lowest CMC is that the larger total numbers of carbon atoms in the hydrophobic chains, the greater the distortion of the water structure of the aqueous phase and the greater the tendency to form micelles in the aqueous phase. In addition, the results showed that FE-1030E gave lower CMC than FE-1020E. The result here may be due to the bulky nature of the hydrophobic group in these molecules, which produces an almost parallel arrangement of the surfactant molecules in the micelle, similar to that at the planar liquid-air interface. At that interface, the introduction of an EO group causes a slight increase in the hydrophobic nature of the molecule leading to lower CMC (Rosen, 2012).

**Table 4.2** CMC value of surfactants used in this experiment

Type of Surfactant	CMC (%wt/v)
FE-1020E	0.000482
FE-1030E	0.000356
MEE-8EO	0.009
MEE-14EO	0.011
MEE-18EO	0.023
MES-14C	0.072

#### 4.1.2 Microemulsion Formation and Detergency Performance Results

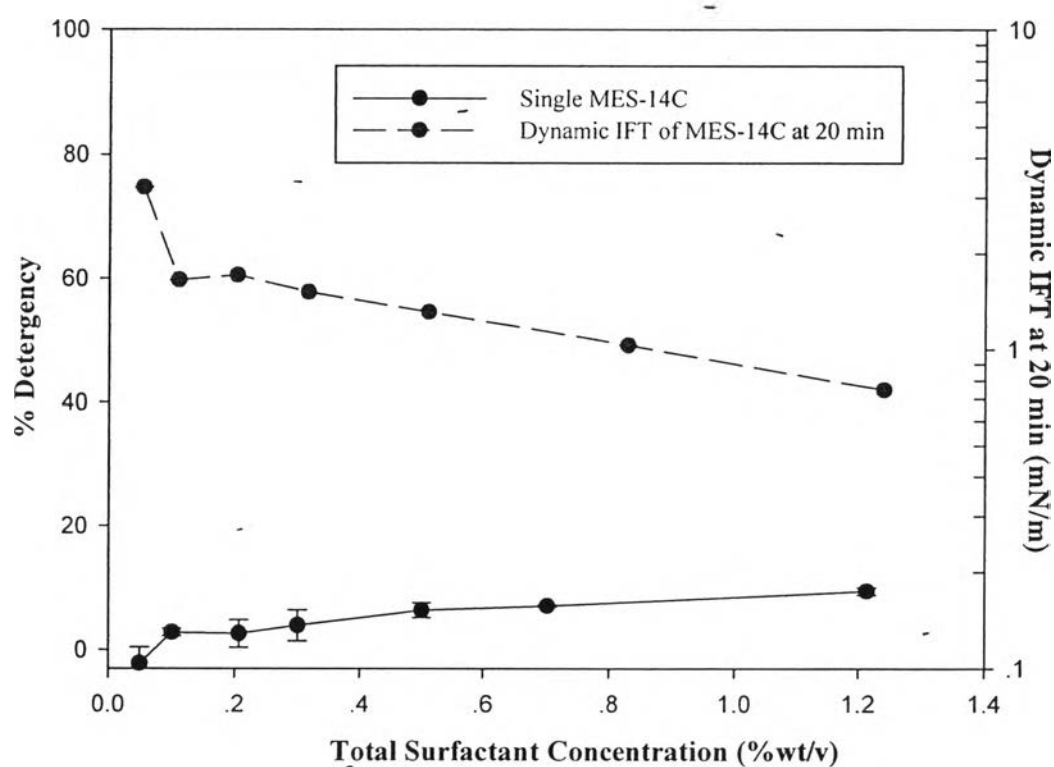
A low or ultralow oil/water IFT, which corresponds to the presence of a Winsor Type III microemulsion, can greatly enhance the detergency performance, as mentioned in our previous (Acosta *et al.*, 2003, Tongcumpou *et al.*, 2003, Tongcumpou *et al.*, 2003, Tanthakit *et al.*, 2010). Hence, MES-14C, MEE with different the number of EO groups (8EO, 14EO and 18EO), and gemini with different the number of EO groups (20EO and 30EO) were selected to form microemulsions with palm oil in the present study. It is interesting to know a minimum surfactant concentration required to provide low or ultralow IFT and used to explain the relation between IFT and detergency performance. In this present work, surfactant concentration was varied from 0.05 to 1.2 %wt/v. And all experiments were carried out under constant washing temperature of 30 °C and agitation speed of 120 rpm.

##### 4.1.2.1 *Effect of MES Concentration*

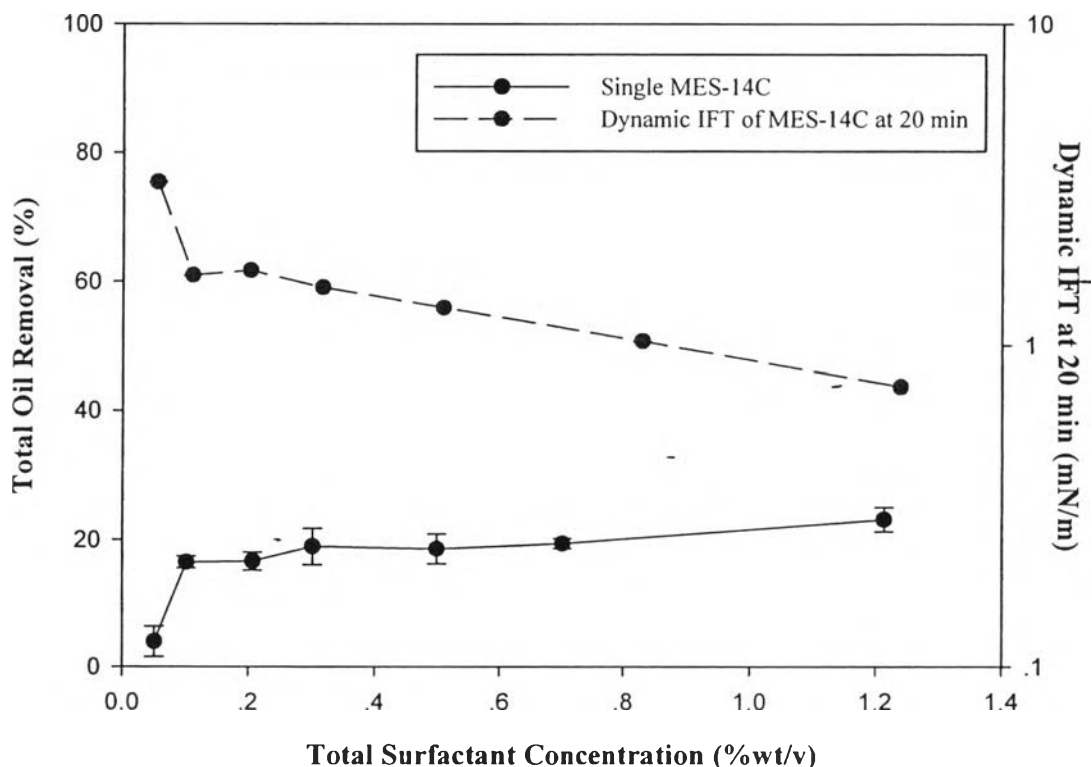
Figure 4.1 shows the percentage of detergency and dynamic interfacial tension (IFT) at 20 min between MES-14C solution and palm oil as a function of total surfactant concentration. The result revealed that when surfactant concentration increased, detergency performance tended to be increased, while the IFT decreased. It suggested that the adsorption of surfactants at the interfaces increase with an increasing of surfactant concentration leading to a reduction of IFT. This result is corresponding to the cleaning efficiency of palm oil, which was determined from the amount of attached palm oil residue on the fabric in order to calculate the amount of palm oil removal in terms of the percentage of palm oil removal as shown in Figure 4.2. It can be described that the increase in surfactant concentration caused the increasing in micelle concentration, resulting in higher oil solubilization.

In general, IFT is constant when at the interface is completely adsorbed resulting in the reaching to a maximum oily soil removal. However, the precipitation or the formation of liquid crystal could cause the loss of surfactant molecules in the system, resulting in the increasing of IFT. Unfortunately, the precipitation with a very small size could not be visual observation. However, it still could be seen by the increasing of IFT: Beyond the surfactant concentration of

1.2 %wt/v, IFT and detergency performance might be continuously changed, but further experiment with increasing surfactant concentration is not required. It is because surfactant concentration used in microemulsion-based detergency is not more than 0.3%wt/v (Tongcumpou *et al.*, 2006, Phan *et al.*, 2010, Tanthakit *et al.*, 2010).

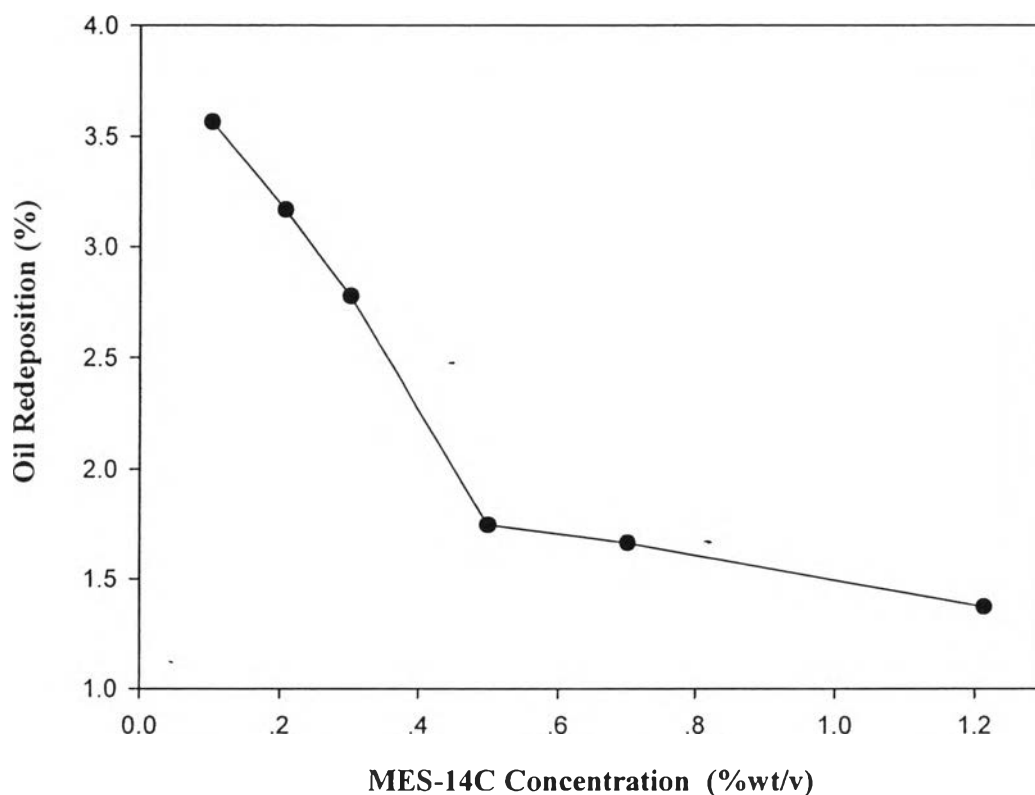


**Figure 4.1** Percentage of detergency, dynamic IFT at 20 min between washing solution and palm oil as a function of total surfactant concentration of single MES-14Cat 30 °C.



**Figure 4.2** Percentage of total oil removal, dynamic IFT at 20 min between washing solution and palm oil as a function of total surfactant concentration of single MES-14C at 30 °C.

Figure 4.3 shows percentage of palm oil re-deposition as a function of MES-14C concentration. The result indicated that percentage of palm oil re-deposition on the fabric dramatically decreased with increasing the surfactant concentration and reached the plateau at the surfactant concentration approximately 0.5 %w/v. It was due to surfactant usually preventing the re-deposition of soil by keeping the soil suspended in surfactant micelles. Therefore, the surfactant concentration was increased, the levels of re-deposition significantly decrease because there is sufficient surfactant to keep the soil suspended (Ayuthya, 2010).



**Figure 4.3** Percentage of palm oil re-deposition as a function of MES-14C concentration at 30 °C.

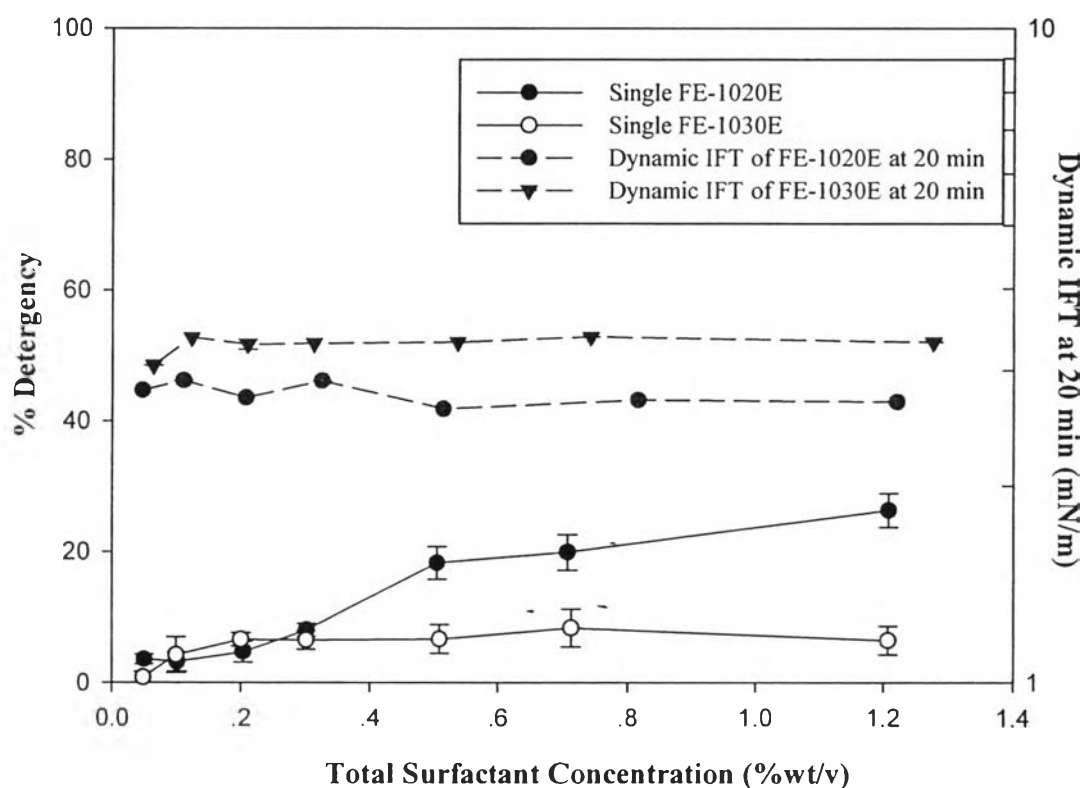
#### 4.1.2.2 Effect of EO Groups and Concentration of Nonionic Surfactants

Solubilization has long been known to be a one of oily soil removal mechanism. Nonionic surfactants have, in general, much lower CMC than anionic and cationic surfactants and are therefore often used as solubilizing agents. Accordingly, nonionic surfactants are believed that it is good for oil removal (Rosen, 2012, Tehrani-Bagha *et al.*, 2012).

To enhance solubilization of surfactants, the size of the micelles must be increased. Therefore, any factors that cause an increase in either the diameter of micelle or its aggregation number affect an increase in solubilization capacity resulting an increase in oil removal efficiency. For nonionic surfactants, the

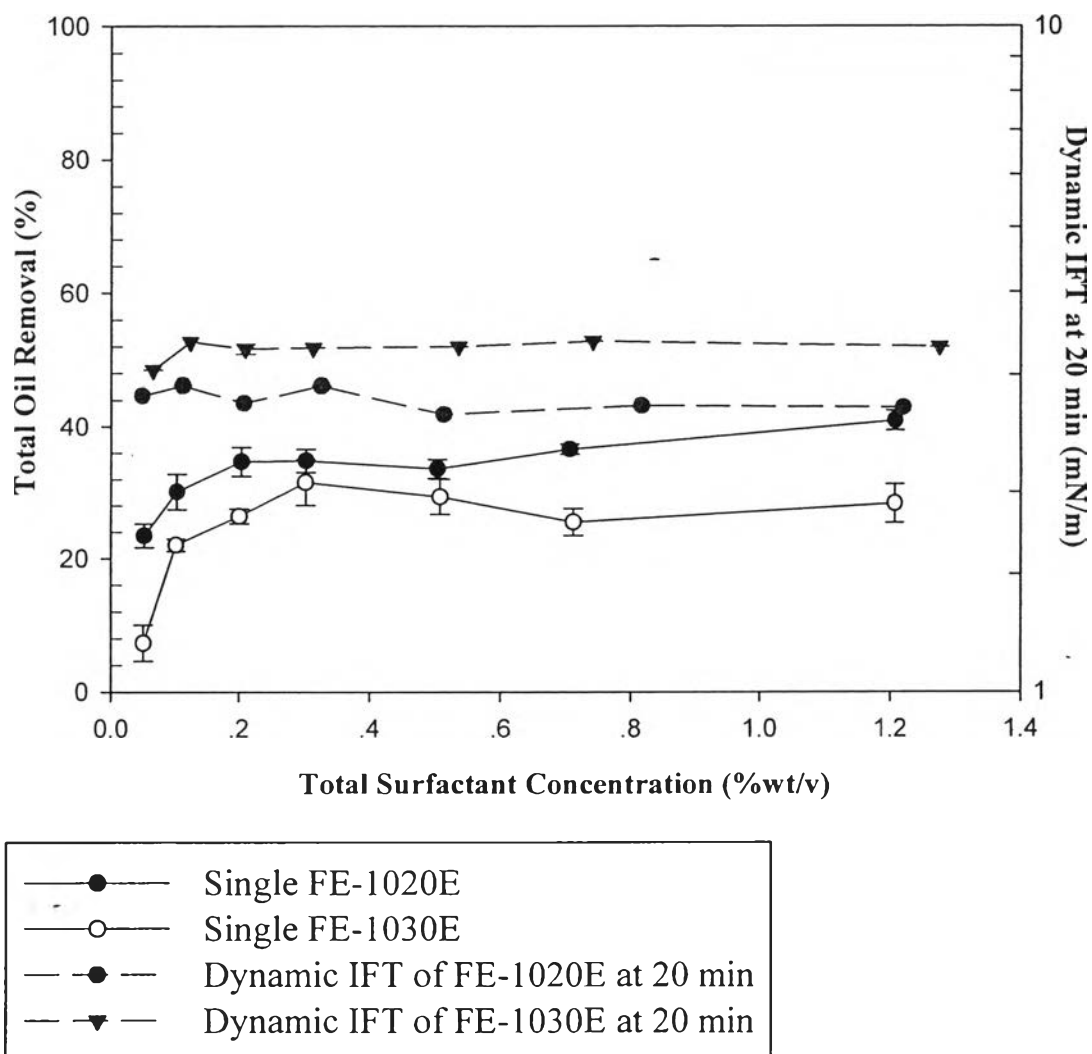
number of ethylene oxide groups is the one of factors that affects solubilization capacity of nonionic surfactants since an increase in the number of ethylene oxide group causes a decrease in aggregation numbers. Furthermore, an increase in the number of ethylene oxide groups appears to decrease the adsorption efficiency of surfactant onto most materials affecting a decrease in detergency (Rosen, 2012). However, a decrease in the number of ethylene oxide group results in a decrease in solubility of surfactant in the cleaning bath. Consequently, in this work, the various number of ethylene oxide groups of nonionic surfactants are studied to find the number of ethylene oxide group which is suitable for palm oil removal.

#### 4.1.2.2.1 Gemini Surfactants



**Figure 4.4** Percentage of detergency, dynamic IFT at 20 min between washing solution and palm oil as a function of total surfactant concentration of single FE-1020E and single FE-1030E at 30 °C.





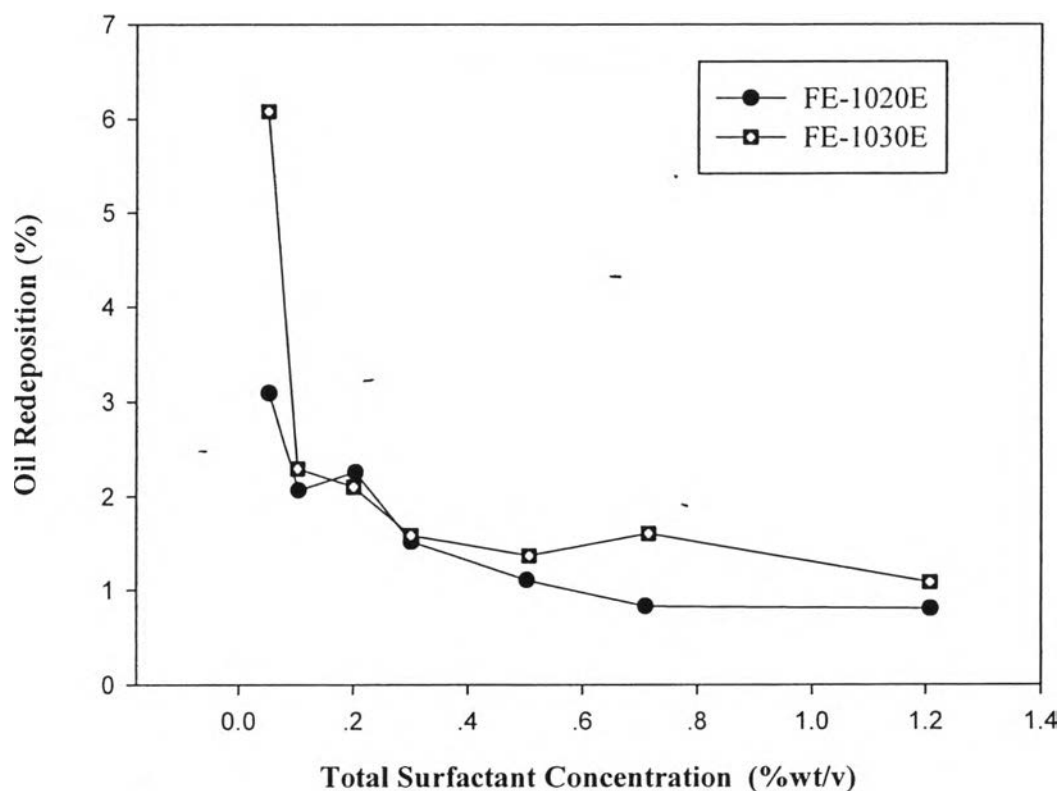
**Figure 4.5** Percentage of total oil removal, dynamic IFT at 20 min between washing solution and palm oil as a function of total surfactant concentration of single FE-1020E and single FE-1030E at 30 °C.

In this study, number of ethylene oxide (EO) groups of gemini surfactants was varied from EO groups 20-30 groups. According to Figure 4.4 and 4.5, FE-1020E gave the highest percentage of detergency and total oil removal corresponding to IFT.

The reason that why FE-1020E gave the lower interfacial tension than another can be explained using the HLB method, which is use for selection of surfactant as emulsifying agents. In this method, to achieve any type of the emulsification, the HLB value of surfactants must match to that of materials. High HLB materials, are O/W emulsifiers and low HLB material are W/O emulsifiers. The HLB value of palm oil is in range 9 to 11(Inc., Hodate *et al.*, 1997). So, a gemini surfactant used to form emulsification with palm oil, must has HLB value being in range 9 to 11.

According to analytical sheet, the HLB values of FE-1020E and FE-1030E are 12.7 and 15.1 respectively. Thus, it is clear that HLB value of FE-1020E is nearer-HLB value than HLB value of FE-1030E matching to HLB value of palm oil. Consequently, FE-1020E gave lower interfacial tension than FE-1030E.

Dimov *et al.* (2000) believed that the electrostatic or steric repulsion between the oil drops and the solid substrate could prevent the oil drop re-deposition. Figure 4.6 shows percentage of palm oil re-deposition as a function of total surfactant concentration of FE-1020E and FE-1030E at 30 °C. The experimental results showed that EE-1030E gave the highest percentage of palm oil re-deposition. This result might be explained that an increasing in the length of the POE group decreased adsorption of surfactant molecule at the interface between bath and substrate. This phenomenon was due to the larger area occupied by the surfactant molecule at the interface as the length of the POE group is increased (Rosen, 2012). At low coverage, the surfactant molecule might lie prone on the surface resulting in lower repulsive force than high coverage. Thereby, FE-1030E had lower repulsive force than another resulting in higher oil re-deposition.

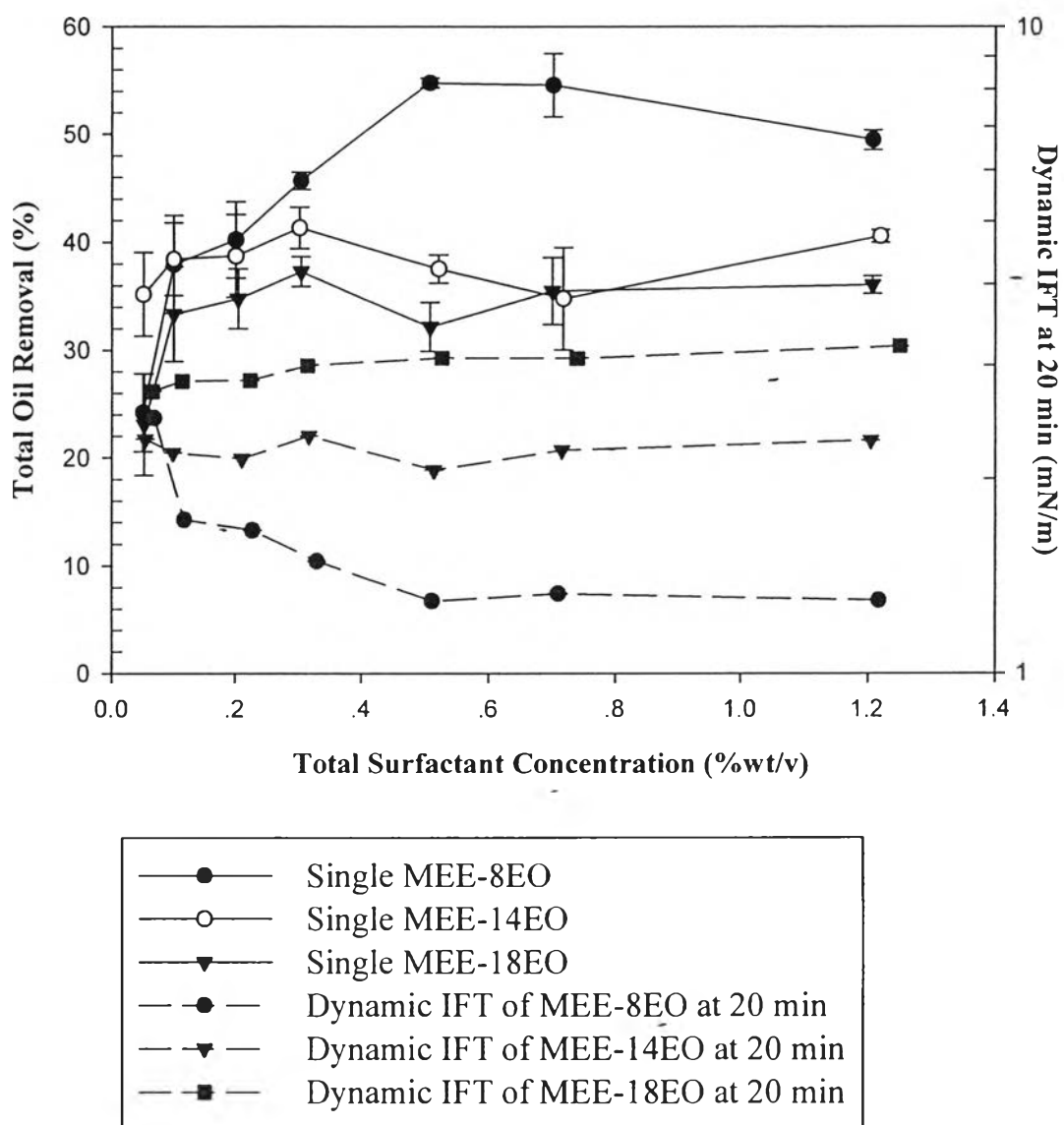


**Figure 4.6** Percentage of palm oil re-deposition as a function of total surfactant concentration of FE-1020E and FE-1030E at 30 °C.

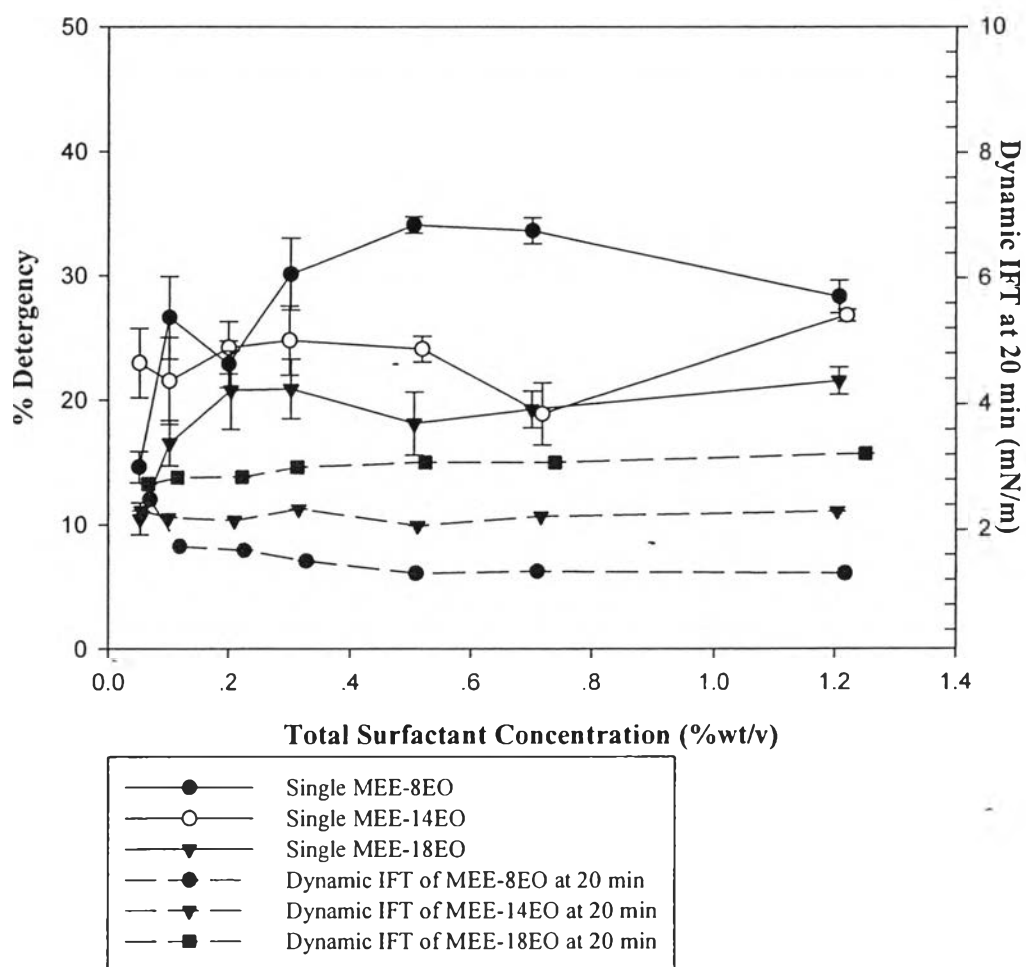
From these results, FE-1020E was selected for mixing with MES-14C in order to study phase behavior and detergency performance of mixed surfactant system.

#### 4.1.2.2.2 Methyl Ester Ethoxylates (MEE)

In this study, number of ethylene oxide (EO) groups of MEE was varied from 8-18 groups. The results as shown in Figure 4.7 and 4.8, the lowest IFT was found at MEE-8EO.



**Figure 4.7** Percentage of total oil removal, dynamic IFT at 20 min between washing solution and palm oil as a function of total surfactant concentration of single MEE-8EO, MEE-14EO and MEE-18EO at 30 °C.



**Figure 4.8** Percentage of detergency, dynamic IFT at 20 min between washing solution and palm oil as a function of total surfactant concentration of single MEE-8EO, MEE-14EO and MEE-18EO at 30 °C.

The reason that why MEE-8EO gave the lowest interfacial tension can be explained using the HLB method as prior discussion. To calculate HLB value of nonionic surfactants, the following equation is used.

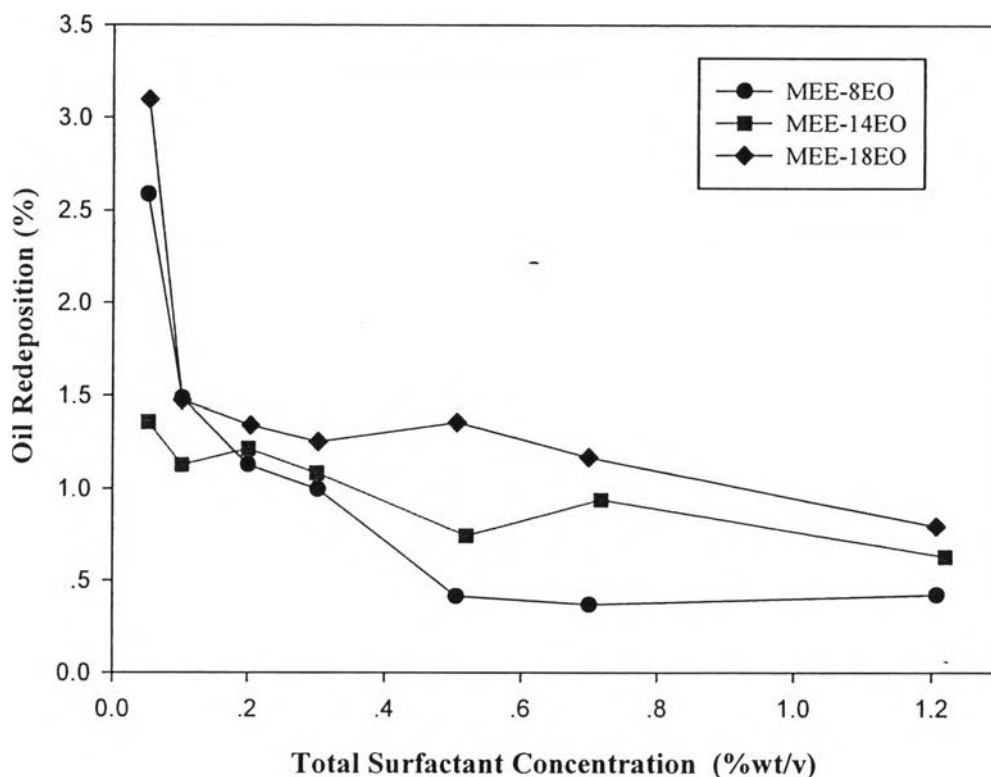
$$HLB = 20 \times \frac{M_H}{M_H + M_L}$$

Where  $M_H$  is the formula weight of the hydrophilic portion of the molecule and  $M_L$  is the formula weight of hydrophobic portion of the molecule.

**Table 4.3** HLB value of MEE-8EO, MEE-14EO and MEE-18EO

Sample	Average EO number	$M_H$	$M_L$	HLB
C12MEE-8EO	8.3	365.2	216	12.57
C12MEE-14EO	13.6	598.4	216	14.70
C12MEE-18EO	17.6	774.4	216	15.64

After calculating the HLB values of MEE-8EO, MEE-14EO and MEE-18EO by using above equation, their HLB value are shown in the Table 4.3, it is clear that HLB value of MEE-8EO is the nearest HLB value matching to HLB value of palm oil. Consequently, MEE-8EO gave the lowest interfacial tension.

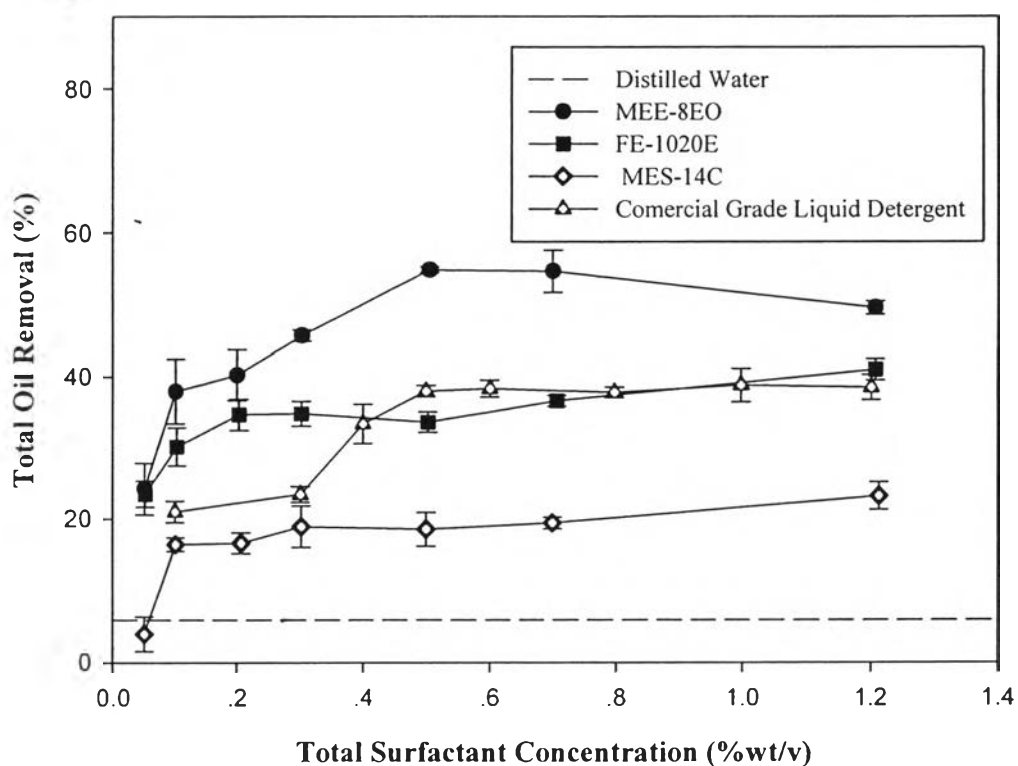


**Figure 4.9** Percentage of palm oil re-deposition as a function of total surfactant concentration of MEE-8EO, MEE-14EO and MEE-18EO at 30 °C.

Figure 4.9 shows percentage of palm oil re-deposition as a function of total surfactant concentration of MEE-8EO, MEE-14EO and MEE-18EO at 30 °C. The experimental results indicated that percentage of palm oil re-deposition of MEE-8EO is approximately 0.5 % while percentage of palm oil re-deposition of MEE-14EO and MEE-18EO are approximately 0.7 and 1 % respectively. From the result, percentage of palm oil re-deposition of MEE-8EO is the lowest that means MEE-8EO could prevent more oil re-deposition than others. This result might be explained that an increase in the number of ethylene oxide groups appears to decrease the adsorption efficiency of surfactant onto fabric affecting a decrease in repulsion force between the fabric and the oil drops (Rosen, 2012).

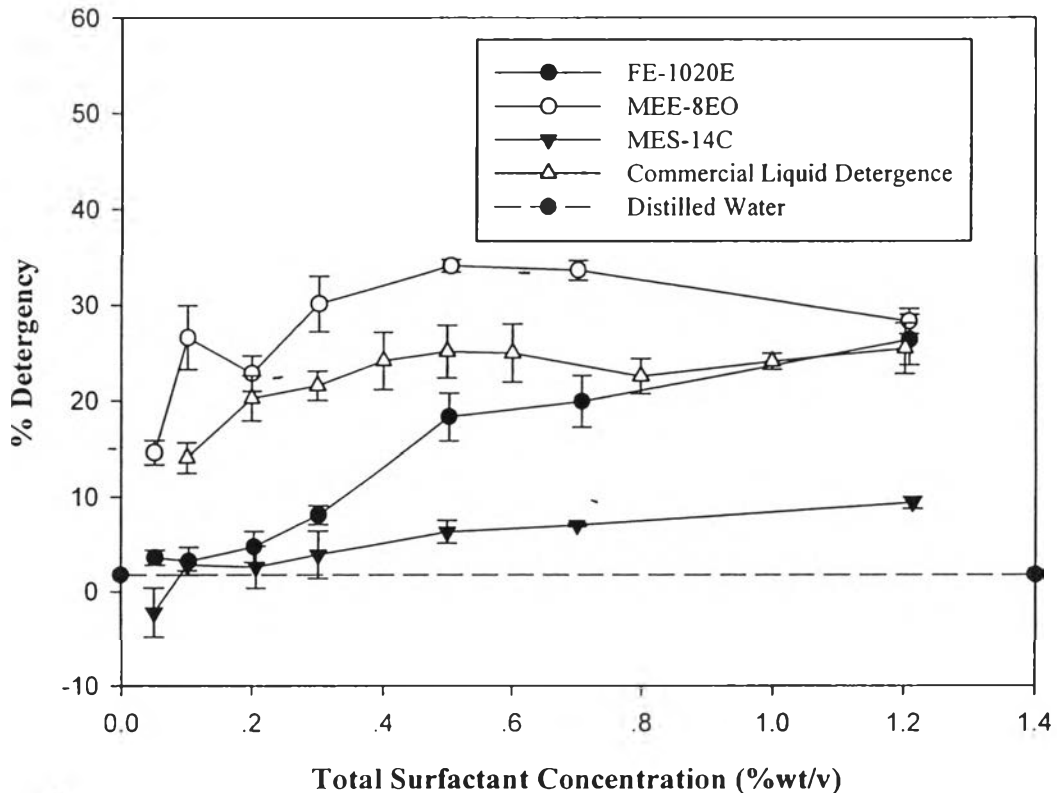
From these results, MEE-8EO was chose for mixing with MES-14C in order to investigate phase behavior and detergency performance of mixed surfactant system.

#### 4.1.2.3 Single Surfactant Systems Compare to a Commercial Grade Liquid Detergent



**Figure 4.10** Percentage of total oil removal and dynamic IFT between washing solution and oil as a function of total surfactant concentration with the single surfactant systems as compared to the commercial grade liquid detergent.





**Figure 4.11** Percentage of detergency and dynamic IFT-between washing solution and oil as a function of total surfactant concentration with the single surfactant systems as compared to the commercial grade liquid detergent.

Figure 4.10 and 4.11 showed percentage of oil removal, percentage of detergency and dynamic IFT between washing solution and palm oil as a function of total surfactant concentration with the single surfactant systems as compared to the commercial grade liquid detergent. The experimental results indicated that MEE-8EO gave the highest detergency performance while FE-1020E gave detergency performance as much as the commercial grade liquid detergent. Accordingly, in terms of detergency performance, both MEE-8EO and FE-1020E had potential to replace the commercial grade liquid detergent.

## 4.2 Mixed Surfactant Systems

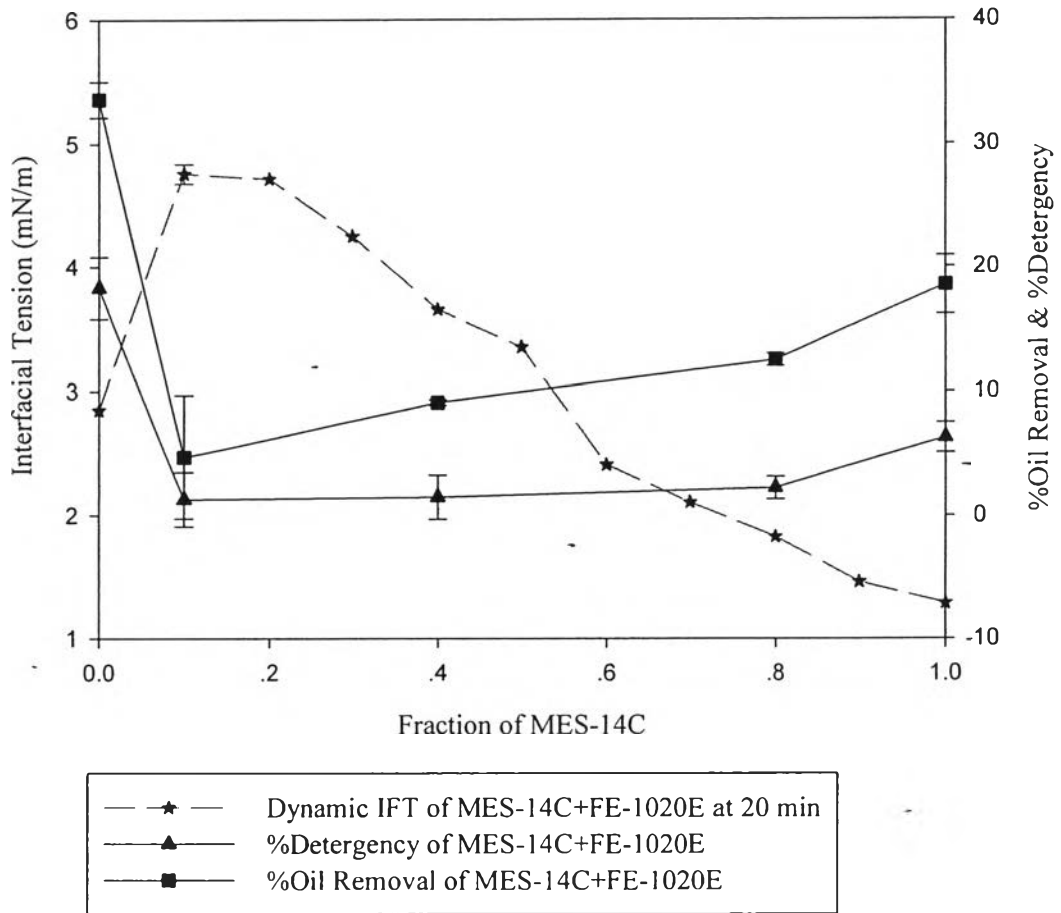
Synergism in mixed surfactant systems has been observed in cationic-anionic, nonionic- cationic, nonionic- anionic and even nonionic–nonionic mixtures. Many studies pointed out that mixed surfactant systems could remove oily soil greater than single surfactant systems (Tongcumpou *et al.*, 2003, Preechasil, 2009, Tanthakit *et al.*, 2010).

According to the previous result, FE-1020E and MEE-8EO were selected for mixing with MES-14C. Therefore, in this study, mixture between MES-14C and FE-1020E, and mixture between MES-14C and MEE-8EO, were used to investigate phase behavior and detergency performance by using palm oil as an oily soil.

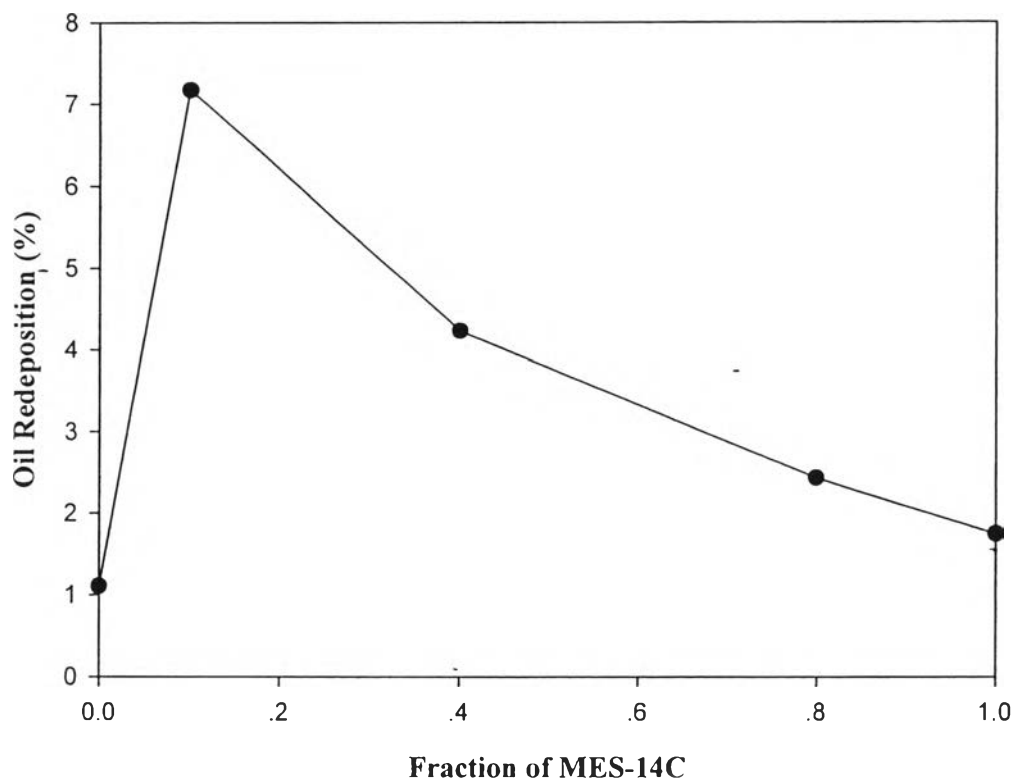
### 4.2.1 Mixture between MES-14C and FE-1020E

Figure 4.12 shows percentage of detergency, percentage of total oil removal and dynamic IFT at 20 min between washing solution and palm oil as a function of fraction of MES-14C of mixture between MES-14C and FE-1020E. This result indicated that all weight ratio of the mixed surfactant system gave lower detergency performance than single surfactant system corresponding to the IFT. The results might be explained that adding MES-14C moved the system away from the optimum point which led to higher IFT value resulting in lower detergency performance.

According to Figure 4.13, all weight ratio of the mixed surfactant system gave higher percentage of palm oil re-deposition than single surfactant system corresponding to the IFT. Thereby, this mixed surfactant system was not suitable for palm oil removal.



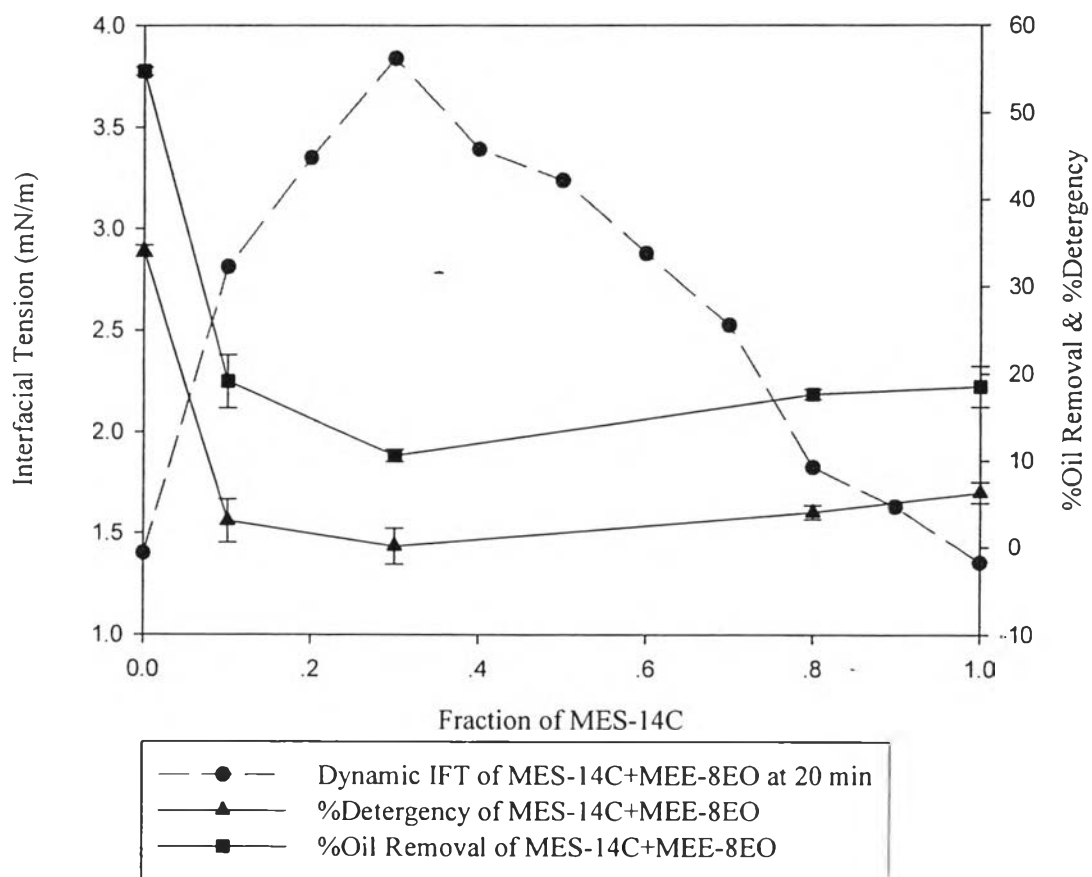
**Figure 4.12** Percentage of detergency, percentage of total oil removal and dynamic IFT at 20 min between washing solution and palm oil as a function of fraction of MES-14C of mixture between MES-14C and FE-1020E.



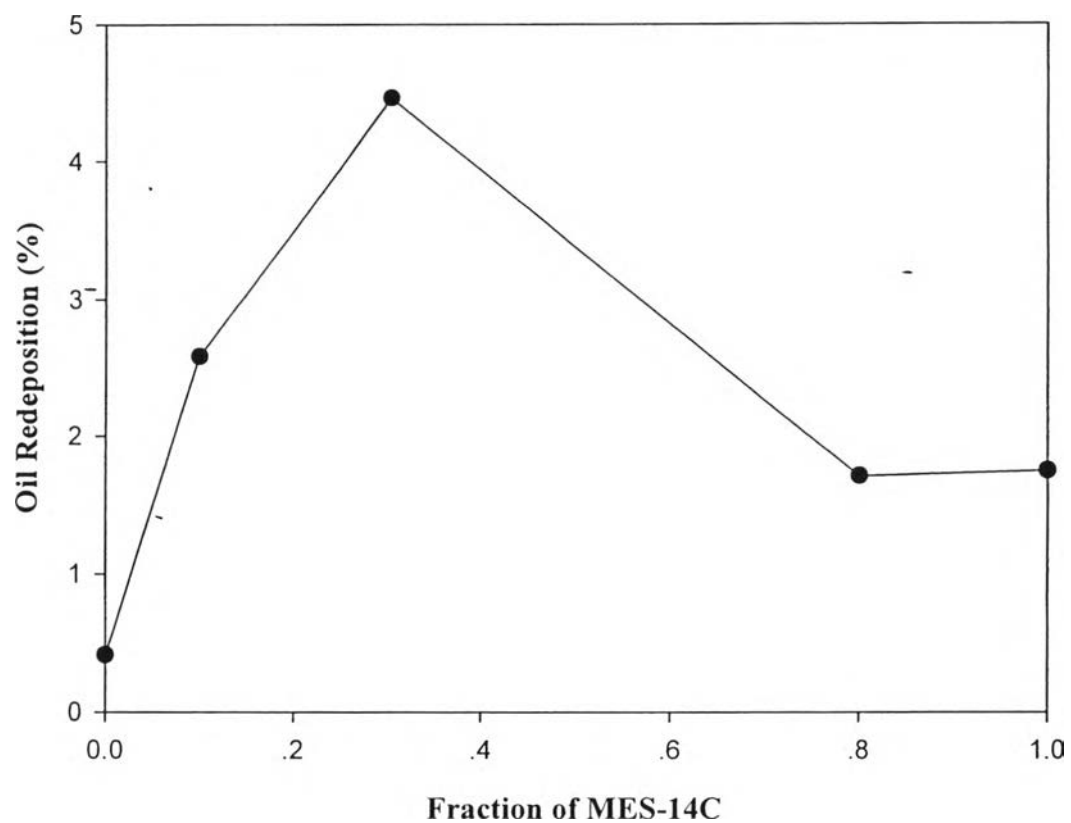
**Figure 4.13** Percentage of palm oil re-deposition as a function of fraction of MES-14C of mixture between MES-14C and FE-1020E at 30 °C.

#### 4.2.2. Mixture between MES-14C and MEE-8EO

From Figure 4.14, all weight ratio of this mixed surfactant system gave lower detergency performance than single surfactant system corresponding to the IFT. Moreover, this system gave higher percentage of palm oil re-deposition than single surfactant system as shown in Figure 4.15. Consequently, this system was not appropriate for use as a detergent solution when compared with the single surfactant systems, in terms of palm oil removal and re-deposition.



**Figure 4.14** Percentage of detergency, percentage of total oil removal and dynamic IFT at 20 min between washing solution and palm oil as a function of fraction of MES-14C of mixture between MES-14C and MEE-8EO.



**Figure 4.15** Percentage of palm oil re-deposition as a function of fraction of MES-14C of mixture between MES-14C and MEE-8EO at 30 °C.