CHAPTER IV
RESULTS AND DISCUSSION

4.1 Basic Properties of Methyl Ester Sulfonate (MES)

The basic properties of surfactants are needed to know in order to understand how surfactants perform in uses and application. In this work, some basic properties useful in detergency application were investigated including CMC, surface tension reduction, solubility and foaming power.

4.1.1 Critical Micelle Concentration and Surface Tension

Critical micelle concentration (CMC) and surface tension are surfactant basic properties which can affect detergency. That means surfactant which has a lower CMC, will give easier micelle formation at a lower concentration affecting to the use of a lower surfactant concentration in detergency. Figure 4.1 shows the surface tension of the methyl ester sulfonate (MES), linear alkylbenzene sulfonate (LAS) and Alfotera as a function of surfactant concentration. The CMC of MES is approximately 0.012 %wt/v. While the CMC of Alfotera and LAS are approximately 0.050 and 0.080 %wt/v respectively. From the results, the critical micelle concentration (CMC) of MES is less than that of Alfotera and LAS about 5 and 8 times, respectively suggesting that the MES is easier to form micelle than both Alfotera and LAS. Therefore, it was hypothesized that the MES can help in cleaning fabrics better than both Alfotera and LAS at a lower concentration.

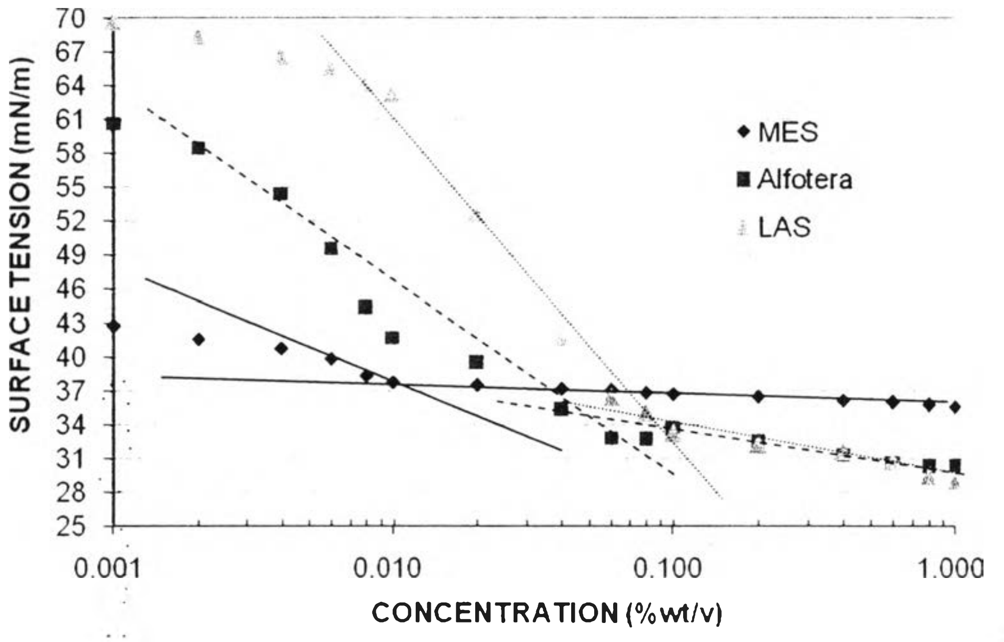

Figure 4.1 Surface tension and Critical micelle concentration (CMC) of Methyl Ester Sulfonate (MES), Alfotera and LAS

There are several factors affecting the value of the CMC in aqueous media: (1) the surfactant structure, (2) addition of electrolyte in the system, (3) the presence of various organic compounds in the system, (4) second liquid phase presence, and (5) temperature of the system. However, the most important factor affecting the CMC is the structure of surfactant. The surfactant structure can be divided into 2 parts: The first part of a hydrophobic group and the second part of hydrophilic group.

The hydrophobic group can affect the CMC depending on the alkyl chain length. First, The CMC decreases significantly when the number of carbon atoms in the hydrophobic group increases to about 16 carbons. If the number of carbon atoms exceeds 16, the CMC decreases slightly with increasing alkyl chain length and if the number of carbon atoms exceeds 18 carbons, the CMC doesn't change with a further increase in the alkyl chain length. An addition of one carbon atom to the main chain of hydrophobic group can halve the CMC, as expressed in the below equation

$$\text{Log CMC} = \text{A-Bn} \qquad (2)$$

where A is a constant for a particular ionic head group at a given temperature, B is a constant ≈ 0.3 and n is the number of carbon atoms in the hydrophobic chain.
If the hydrophobic group has a branch chain, the carbon atoms in the branch chain is about one half of the carbon atom on a straight chain. For a surfactant containing bulky hydrophobic, it will have a higher CMC than that of one containing no a bulky group.

For the effect on the hydrophilic group, nonionic surfactants have a lower CMC value than ionic surfactants with the same number of carbon atoms in the hydrophobic group. In addition, the effect of the hydrophilic group, the order of decreasing CMC was aminium salts > carboxylates > sulfonates > sulfates. A surfactant containing more than one hydrophilic group will have a higher CMC values than that with one hydrophilic group.

The MES is a mixture of C16 – C18 homologues in hydrophobic group. Each homologue is a mixture of different isomers, depending on the position of the SO_3 being hydrophilic group. The LAS is also a mixture of C10 – C13 homologues in hydrophobic group. Each homologue is a mixture of different isomers with a phenyl ring attached to the alkyl chain and SO_3 being hydrophilic group. Alfotera is a mixture of C14 – C15 homologues in hydrophobic group. There are two hydrophilic groups which are propylene oxides and sulfate. Therefore, then studied surfactants are considered as mixed surfactant and so they lend to have lower CMC value than their homologues with single carbon number.

The MES hasa lower CMC value than both Alfotera and LAS because The MES has a higher number of carbon atoms in the alkyl group than those of both Alfotera and LAS. In addition, the structure of the MES hydrophobic group is a linear chain but those of Alfotera and LAS hydrophobic group are branch chains. Moreover, the hydrophobic group of the MES consists of a less bulky group than the LAS, having a bulky phenyl group, and Alfotera, having a bulky oxypropylene(OP) units. For a comparison between Alfotera and the LAS, the LAS has a higher CMC value than Alfotera since Alfotera has a higher the number of carbon atoms than that of the LAS. For the results, the effect of carbon number in alkyl group is higher than the bulky structure of the tail group on the CMC.

There are several works to reveal that the CMC of MES is lower than than that of LAS. In 1998, Cohen and Trujillo investigated the surface property of MES. They found that MES had a significantly lower CMC than LAS. The CMC values of MES and LAS were found to be 7.5 and 150 ppm, respectively. Moreover, Lion Corporation studied the CMC of MES. They found that the CMC of MES was about one-tenth of LAS, which were 25 and 300 ppm, respectively.

4.1.2 Solubility

Solubility is an important factor, affecting detergency performance. Many studies have indicated that detergency increases when the length of hydrophobic group increases (Schwuger, 1992). This is because an increase in the length of hydrophobic group results in an incrase in solubility for organic solutes but a decrease in solubility of surfactant in the cleaning bath. It is necessary to known the solubility of surfactant for the development of detergent formulation. Figure 4.2 shows the solubility values of the MES, Alfotera and the LAS at room temperature. As shown in Fig.4.2, the solubility of the MES in water is approximately 14.1 g/100 ml of water at room temperature which is slighty higher than that of the LAS. This is because the ester group of the MES can form hydrogen bond with water, leading to higher solubility in water. Moreover, the benzene group in the LAS increases the hydrophobicity, causing lowerings the water solubility.

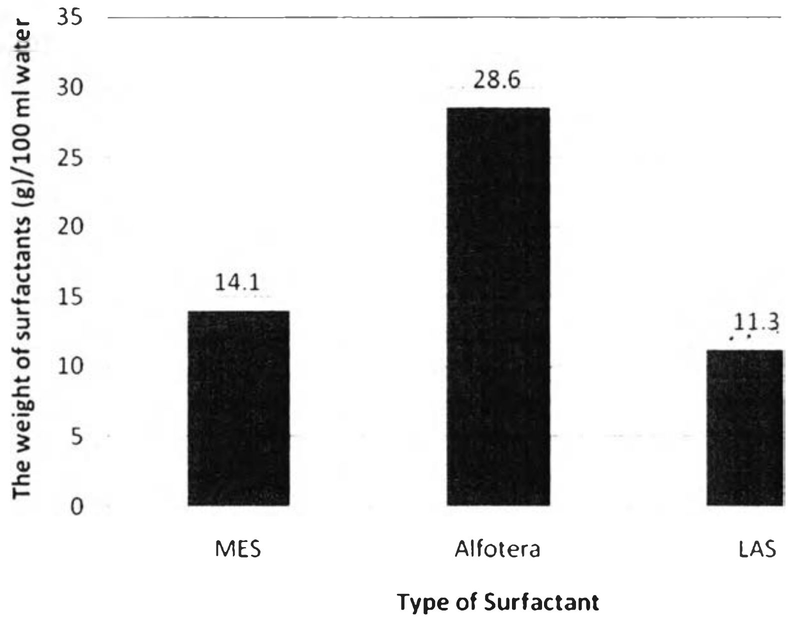

Figure 4.2 Solubility of different surfactants at room temperature.

In a comparison among three surfactant solubility values, Alfotera has the highest water solubility and this may be due to the face that Alfotera consists of three propylene oxide groups which are preferently soluble in water. In 1998, Cohen and coworkers measured the solubility of MES. They used turbidity point to indicate solubility that means the lower the turbidity point temperature, the higher the solubility in water. They found that the turbidity point temperature of MES is lower than that of LAS. It means MES has higher solubility than LAS.

4.1.3 <u>Foaming Power</u>

Foam is an important aspect of detergent products. The most important foaming properties of surfactant are how easily foam is formed (foam ability) and how the foam resists in collapses (foam stability). Any surfactant that has foam height > 120 mm is considered to be a high foaming surfactant (Germain, 1973). Factors affecting foam properties include concentration and structure of surfactant, water hardness, electrolyte concentration and temperature. Figure 4.3 shows the results in term of foamability and foam stability by the Ross Miles method in the absence of water hardness, at a surfactant concentration of 800 ppm (0.08 %wt/v) and temperature 30°C.

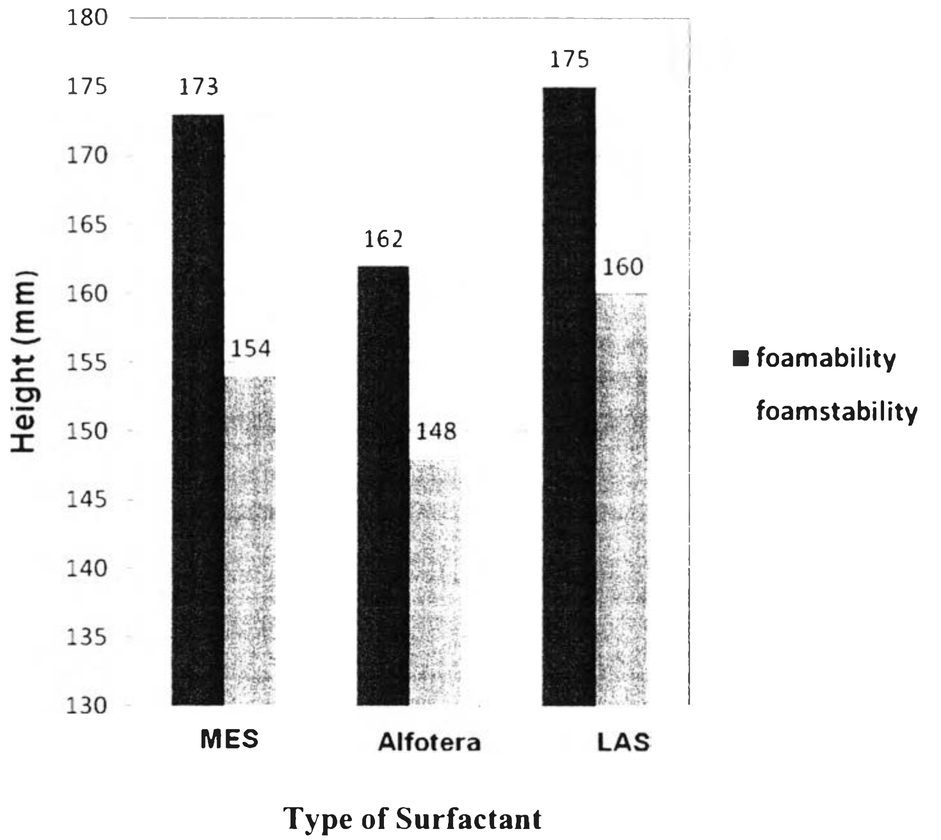

Figure 4.3 Foamability and Foam stability of MES, Alfotera and LAS at 800 ppm surfactant concentration and 30°C

From Figure 4.3, both foamability and foam stability of MES are higher than those of Alfotera since the MES has a linear chain of hydrocarbon in the hydrophobic part and lower molecular weight (MW=382.71). The Alfotera has a higher molecular weight (MW=483) and has a solvated hydrophilic part (propylene oxide (PO) group) and has a branched chain of hydrocarbon. Hence, Alfotera diffuses to the interfacemore slowly than the MES. Moreover, the surfactant that has a lower CMC, it is more efficient to foam foam (Rosen, 2004). The MES has a lower CMC than Alfotera, so the MES is a better foamer than Alfotera.

For comparisons between the MES and the LAS, the foam properties of MES in terms of foamability and foam stability were not much different from those of the LAS since the MES's molecular weight is close to that of the LAS.

For comparisons between the foaming results of this work and other works, Lion Corporation studied foaming power by using Ross-Miles method. They found that the foam height of the MES was not much less than that of LAS at 316 ppm water hardness, surfactant concentration 500 ppm and temperature 25°C. In 1999, Cohen et al. determined foaming power of MES by using the Ross-Miles method at different water hardness, a surfactant concentration of 1 g/l and temperature of 49°C. They found that the foam height of MES was just slightly lower than that of LAS.

For detergency application, foaming doesn't directly affect performance efficiency because it does not help to remove soils. However, foaming is concerned about this application in terms of foaming requirement or non-foaming requirement. For the development of formulation for automatic washing machines, foaming is undesirable. If detergency application is used for hand washing, foaming is used to indicate cleaness psychologically. For any surfactant having high foaming properties greater than 120 mm, they are not possible for using in an automatic washing machine. An antifoaming substance is needed to reduce foam formation if these surfactants are used in formulations for automatic washing machines.

4.2 Microemulsion Formation Results

To enhance the oily soil detergency performance, a microemulsion-based formulation is used. There are many factors governing microemulsion conditions such as type of surfactant, type of soil, surfactant concentration, salinity, temperature and etc. A mixed surfactant system has been demonstated to provide the detergency performance better than a single surfactant system (Chantra, 2003). To develop a mixed surfactant system, single surfactant systems must be studied first.

4.2.1 Single Surfactant Systems for Microemulsion Formation

4.2.1.1 Effect of MES Concentration

In this study, the MES concentration was varied from 0.1% to 10%wt./v to find which MES concentration gave the lowest interfacial tension (IFT). The results as shown in Figure 4.4, the lowest IFT of MES was found at 5 %wt./v MES concentration. The lowest IFT at the 5 %wt./v MES concentration was approximately 0.35 mN/m. This IFT value is not ultralow interfacial tension because the ultralow interfacial tension is between 10^{-2} – 10^{-3} mN/m.

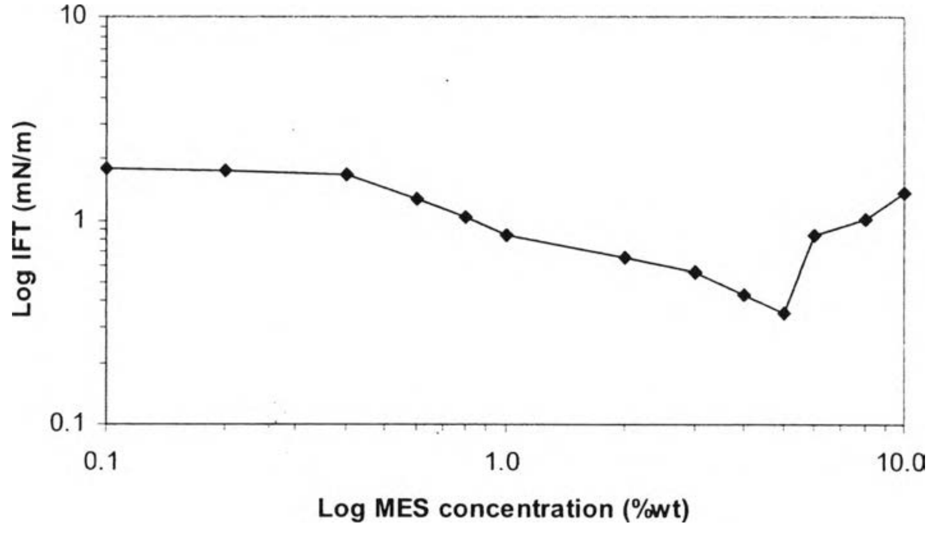

Figure 4.4 Interfacial tension (IFT) of palm oil and aqueous solution at various MES concentrations.

4.2.1.2 Effect of salinity

The effect of salinity on microemulsion formation was studied by adding salt in the system is known as salinity scan. When increasing salinity, the microemulsion system transforms from a Winsor Type I microemulsion to a Winsor Type III microemulsion since increasing salinity causes the system become more lypophilic or more surfactant moving out from the water phase to the oil phase. As a result, adding salt will help to reduce interfacial tension (IFT) since salt reduces the repulsive force between the charged ionic surfactant head groups which can lead to decreasing the CMC and increasing the aggregation number or decreasing HLB value (Rosen, 2004).

From the previous result, the 5%wt MES concentration giving the lowest IFT, was selected for varying the salinity to find which salinity would give the lowest IFT.

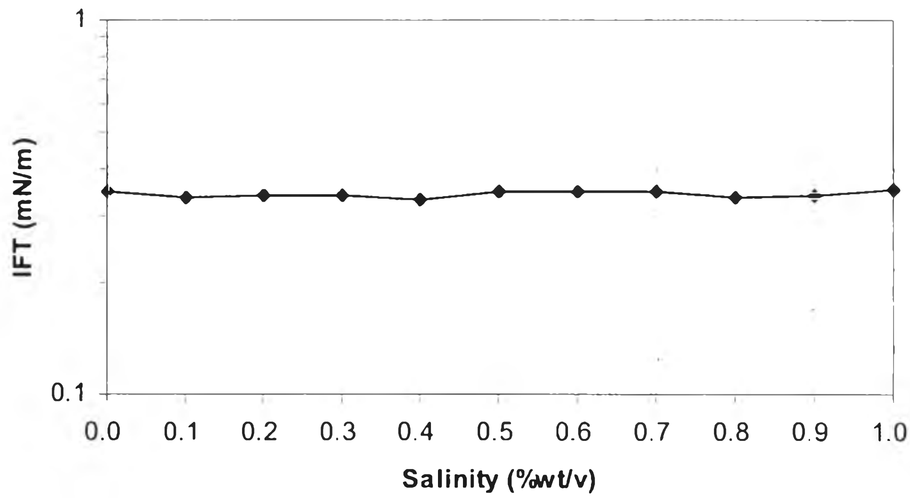

Figure 4.5 Interfacial tension as a function of salinity at 5% MES concentration at 30°C

Figure 4.5 shows that the IFT does not significantly with increasing salinity in the studied range of salinity. Beyond 1% salinity, the MES solution was found to have very high viscosity which is not suitable for use in detergency. This is because the system already contained a very high Na^+ concentration derived from the MES.

4.2.1.3 Effects of EO groups and Concentration of Alcohol Ethoxylate

A nonionic surfactant is believed that it is good for oil removal because it provides better solubilizing property than an ionic surfactant. Moreover, nonionic surfactants have a much lower CMC than ionic surfactants containing equivalent hydrophobic group.

To enhance solubility 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 can lead to an increase in solubilization capacity, resulting an increase in oil removal efficiency. For nonionic surfactants, the number of ethylene oxide groups is one of factors that affect solubilization capacity since an increase in the number of ethylene oxide group causes a decrease in aggregation numbers resulting in decreasing solubilization capacity of surfactant. 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, 2004). Consequently, a high number of ethylene oxide groups of nonionic surfactants is not suitable for oily soil removal.

In this work, the AEs with different numbers of ethlylene oxide groups were studied to find the optimum number of ethylene oxide group which was suitable for microemulsion formation with palm oil.

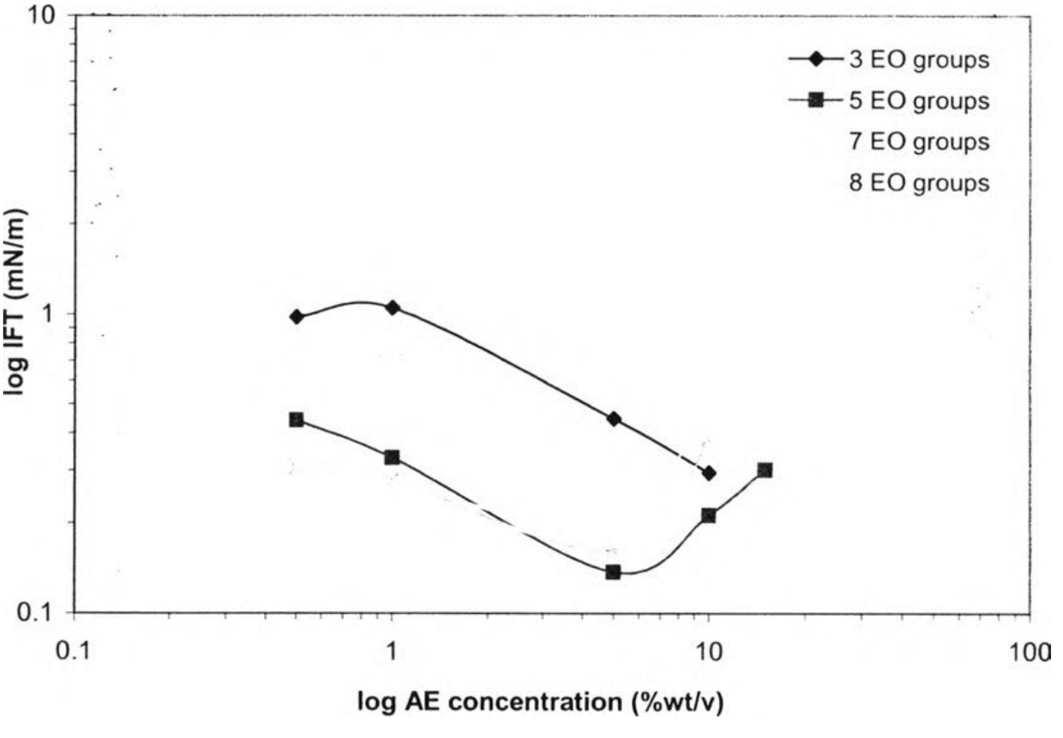

Figure 4.6 Interfacial tension as a function of AE ethylene oxide (EO) groups and concentration at 30°C

From Figure 4.6, the lowest IFT was found at the 5 EO groups of AE at a 5% wt/v AE concentration. The reason that why the AE with 5 EO groups gave the lowest interfacial tension can be explained using the HLB method, which is used 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 a studied oil. High HLB surfactant are O/W emulsifiers and low HLB surfactant are W/O emulsifiers. The HLB value of palm oil is in the range of 10 to 11 (Hodate, 1996 and US Patent Emulsification, 1992). Hence, an Alcohol Ethoxylate used to form emulsification with palm oil, must has a HLB value being in this range. To calculate HLB value of nonionic surfactants, the following equation is used.

$$HLB = 20 \times \frac{M_H}{M_L - M_I}$$

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.

An AE with 5 EO group, ($C_{12}H_{25}O(CH_2CH_2O)_5H$), will have 237 formula weight of hydrophilic portion (M_H) and 169 formula weight of hydrophobic portion (M_L). Hence, the HLB value is 11.7. This HLB value is close to HLB value of the palm oil.

4.2.2 Mixed system of surfactants

The mixture of surfactants is known that it can provide a better oily soil removal because it exhibits a lower oil-water interfacial tension and greater solubilization than a single surfactant system (Verma, 1998, Ogino, Abe, 1997, Tongcumpou, 2003). In this study, a mixture of the MES, an anionic surfactant, and the AE, a nonionic surfactant, was used to form microemulsions with the palm oil. From the previous results of AE microemulsion formation, the AE with 5 EO groups gave the lowest interfacial tension at 5%wt./v AE concentration. To form the mixed system, the AE 5 concentration was fixed at 5%wt./v and the MES concentration was varied from 1% to 10%. From Figure 4.7, as the MES concentration increases, the interfacial tension remains almost unchange. In addition, the interfacial tension of the mixed surfactant systems was not much different from those of both single systems as showing in igure 4.5 and 4.6. The results suggest that the presence o the MES does not help to reduce the interfacial tension of the mixed system probably because the AE which has better solubilization capacity and a lower CMC plays important role in microemulsion formation and has more domination in microemulsion formation than the MES. However, at 5%wt./v o the MES showed the lowest interfacial tension in the mixed surfactant system which corresponds to the single MES system providing the lowest interfacial tension at the same concentration. Therefore, The mixture of 5% MES and 5% AE was selected for further study.

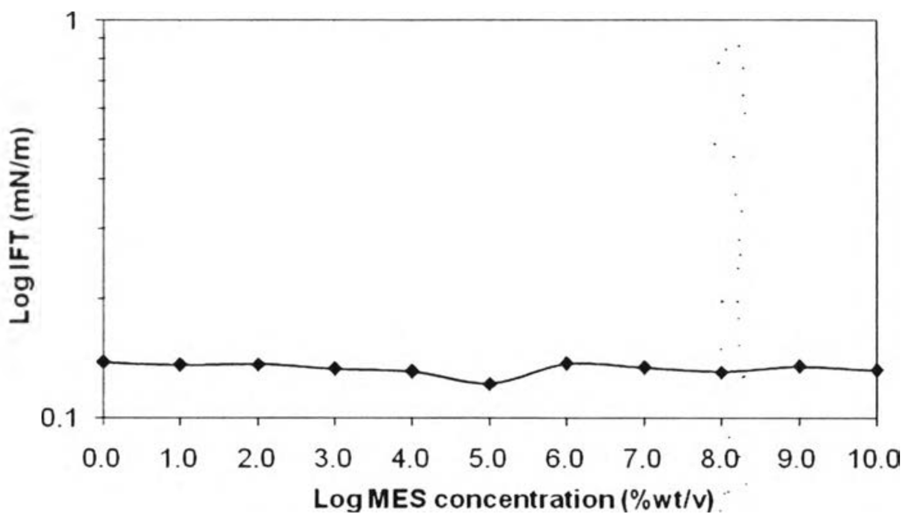

Figure 4.7 Mixed system interfacial tension as a function of MES concentration at fixed 5%wt/v AE concentration at 30°C

4.2.2.1 Effect of salinity to Mixed surfactant system

As mentioned before, salinity can affect the reduction of interfacial tension due to the reduction of repulsive force between the charged ionic surfactant head groups. However, as described before this effect did not affect significantly the reduction of interfacial tension in the MES pure system.

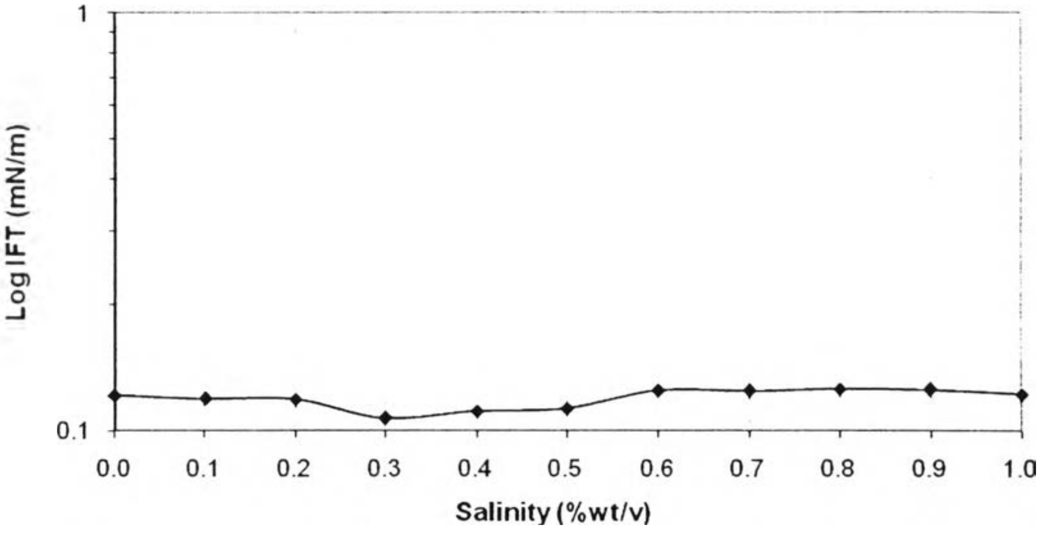

Figure 4.8 Interfacial tension of the mixed surfactant system of 5%wt AE and 5%wt MES as a function of salinity at 30°C

Effect of salinity on the mixed surfactant system is shown in Figure 4.8. The result showed that salinity did not affect significantly the system interfacial tension because the system already had a very high Na^+ concentration.

4.2.2.2 Effect of Active Surfactant Concentration

The active total surfactant concentration o the mixture of 5% MES and 5% AE was varied in order to find an optimum active total surfactant concentration for using in detergency experiment. In this study, the total surfactant concentration of the mixed surfactant of 5% MES and 5% AE was varied from 0.3% to 1.4%. The results are shown in Fig 4.9. The interfacial tension decreased with increasing total surfactant concentration and reached the plateau at around 0.5 % total surfactant concentration. Therefore, 0.5% active surfactant concentration was selected as the optimum concentration for detergency experiments.

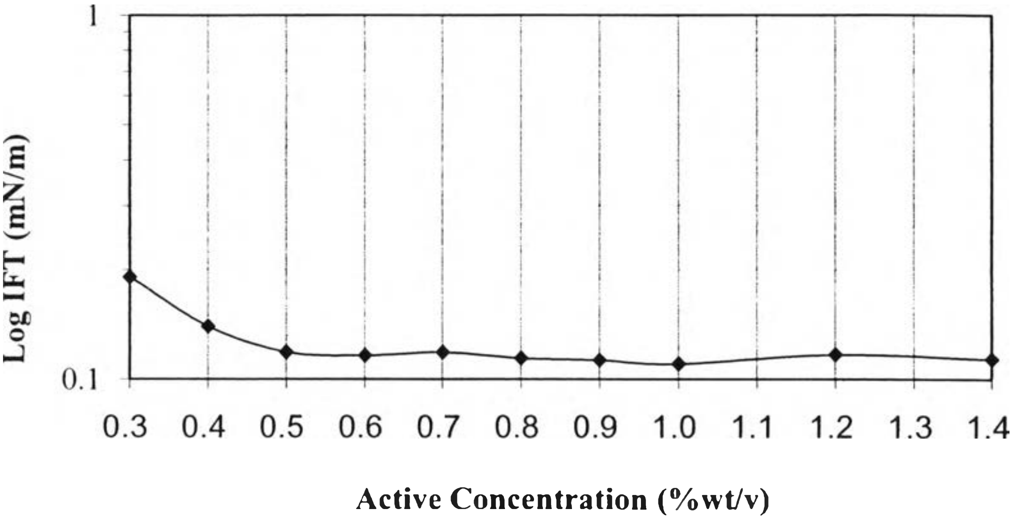

Figure 4.9 Interfacial tension as a function of active surfactant concentration of the mixed surfactant system at 30°C

4.3 Detergency Performance Results

4.3.1 Correlation of Microemulsion Formation and Detergency Performance

Maximum detergency performance is known to correspond to the lowest IFT (Chantra, 2005). Hence, both IT and oil removal were considered in this work.

4.3.1.1 Effect of MES Concentration

Figure 4.10 shows the correlation of IFT , %oil removal and %detergency. From this result, when the IFT decreased, %oil removal and %detergency increased and reached the maximum levels at the MES concentration greater than 5%. The results indicate that an increase in MES content greater than 5% cannot improve the detergency performance. Hence, 5% MES was selected for further investigation.

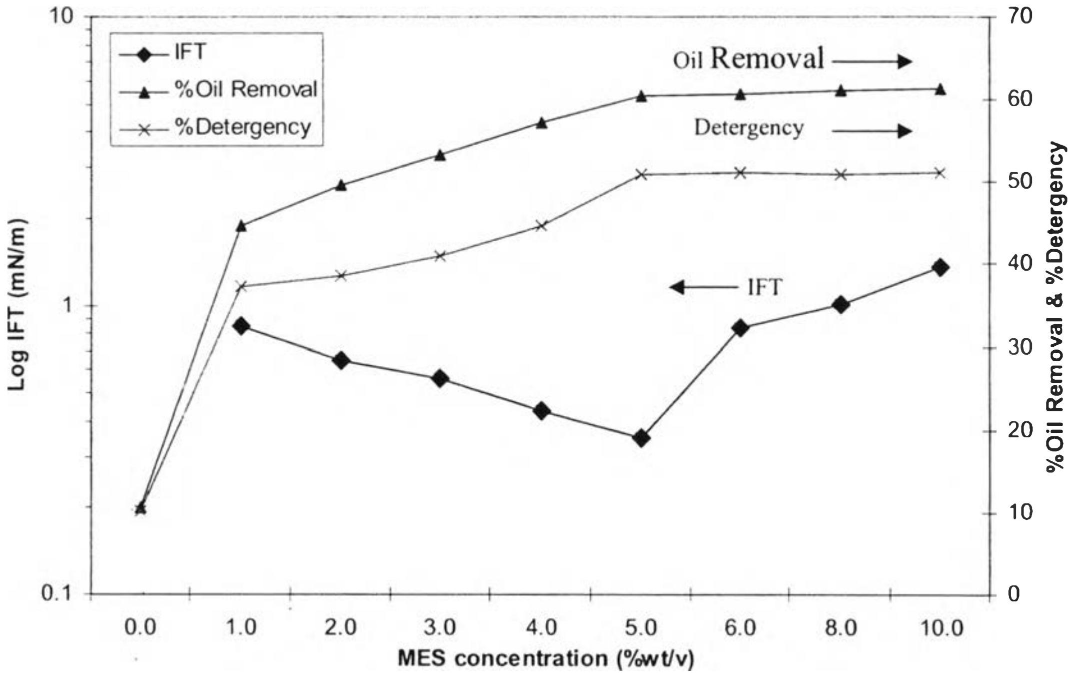

Figure 4.10 The correlation of interfacial tension (IFT) %oil removal, and %detergency at different MES concentration and an AE concentration of 5% and 30°C

4.3.1.2 Effect of Alcohol Ethoxylate (AE) Concentration

Figure 4.11 shows the correlation of IFT, %oil removal and %detergency of he mixed surfactant system. When the IFT decreased, both %oil removal and %detergency increased reached the maximum levels at an the AE concentration greater than 5 %. The maximum of palm oil removal and detergency were approximately 76% and 60% respectively. Hence, 5% MES and 5% AE 5 were used as the selected formulation.

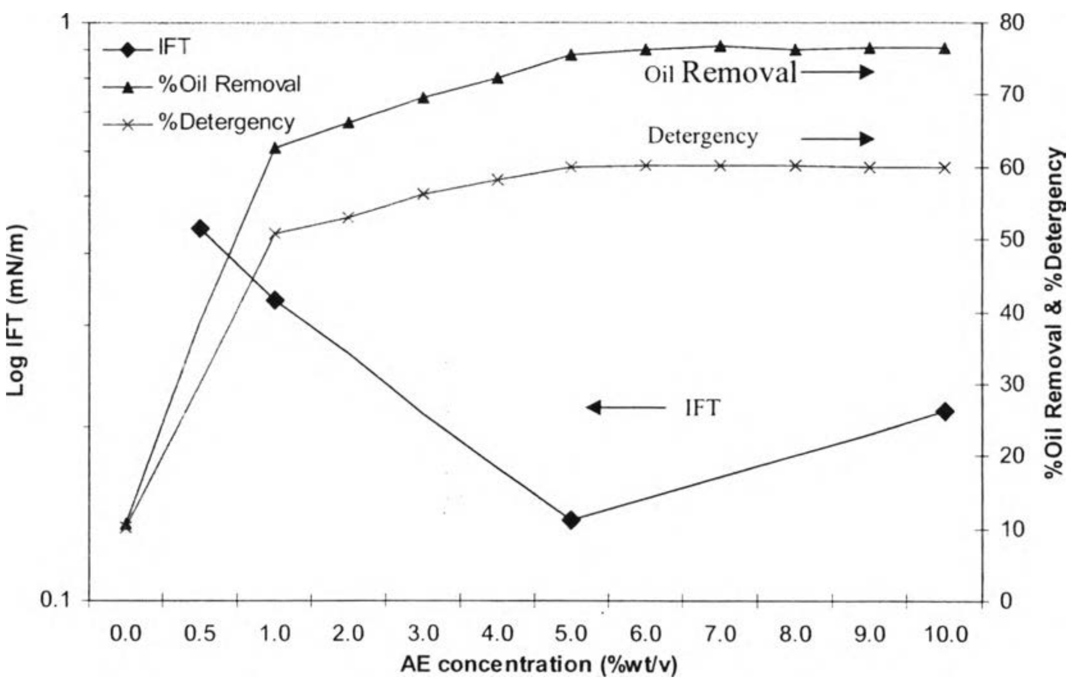

Figure 4.11 The correlation of interfacial tension (IFT) and %oil removal and %detergency of AE at different AE concentration and 30°C.

4.3.1.3 Effect of LAS Concentration

To compare oil removal efficiency of the LAS to that of other surfactants, the LAS concentration was varied from 1% to 10%wt/v. Figure 4.12 shows the correlation of the IFT, %oil removal and %detergency at different LAS concentration. With increasing LAS concentration, the system IFT decreased whereas both oil removal and detergency increased. However, the oil removal and detergency reached the maximum levels when the LAS concentration was greater than 7 %wt./v. With the use of pure LAS, the maximum oil removal and detergency were found to be 46.9% and 41.3%, respectively.

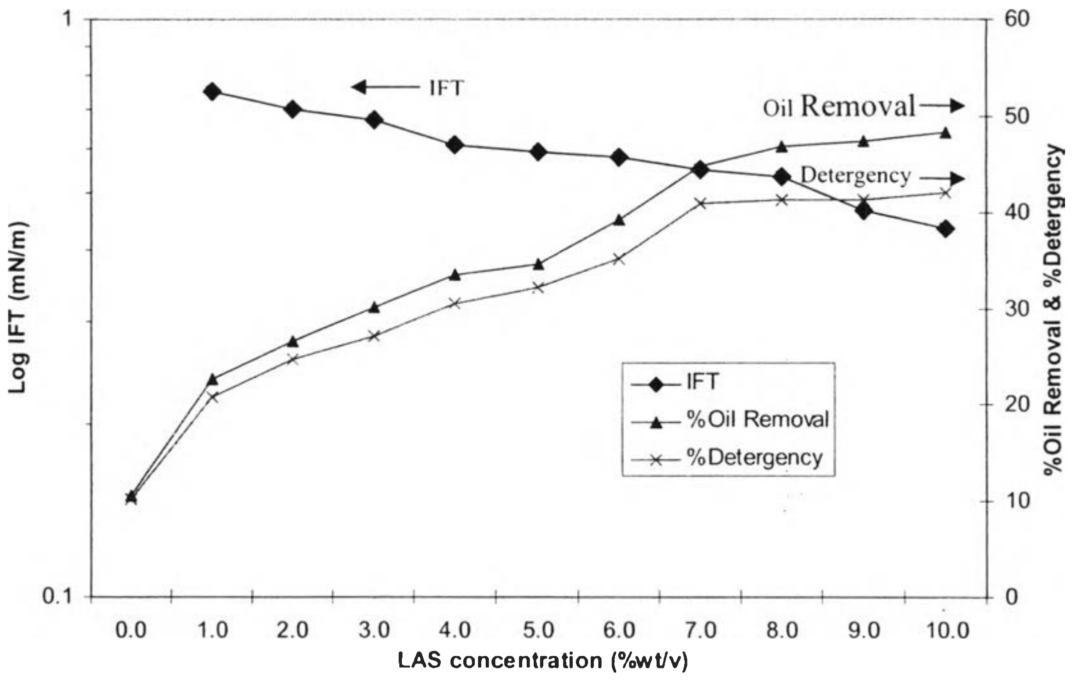

Figure 4.12 The correlation of interfacial tension (IFT) and %oil removal and %detergency of LAS at different LAS concentration and 30°C.

4.3.1.4 Effect of Mixed System

The mixture of 5% AE5 and various MES concentrations from 1% to 10%wt/v was used to remove the palm oil from fabric. Figure 4.13 shows the cleaning performance in terms of oil removal and detergency as a function of MES concentration at constant AE5 concentration of 5% and 30°C. Both oil removal and detergency increased with increasing MES concentration whereas the system IFT remained almost unchanged. However, both oil removal and detergency reached maximum when the MES concentration increased beyond 5%. The experimental results can be explained in that an increase MES concentration does not help to reduce the interfacial tension of mixed system. In comparisons among the studied surfactants, the mixed surfactants of AE5 and MES gave the highest detergency performance in terms of oil removal and detergency. As a consequence, the mixture of 5% AE5 and 5% MES was used as the selected formulation for further washing experiments.

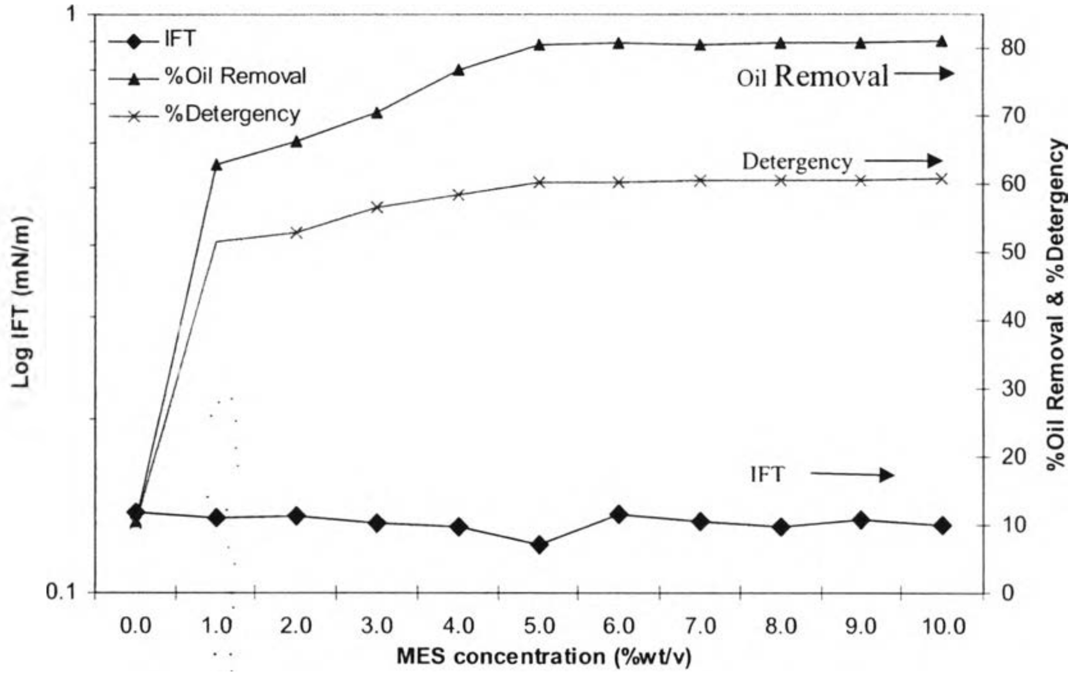

Figure 4.13 The correlation of interfacial tension (IFT), %oil removal and %detergency of mixed surfactant system of 5% AE and different MES concentration at 30°C.

4.3.1.5 Effect of Active Surfactant

The selected formulation of 5% AE5 and 5% MES was diluted to obtain different active total surfactant concentration for washing experiments. Figure 4.14 shows the oil removal as a function of active total surfactant concentration of the selected formulation as compared with the commercial detergent.

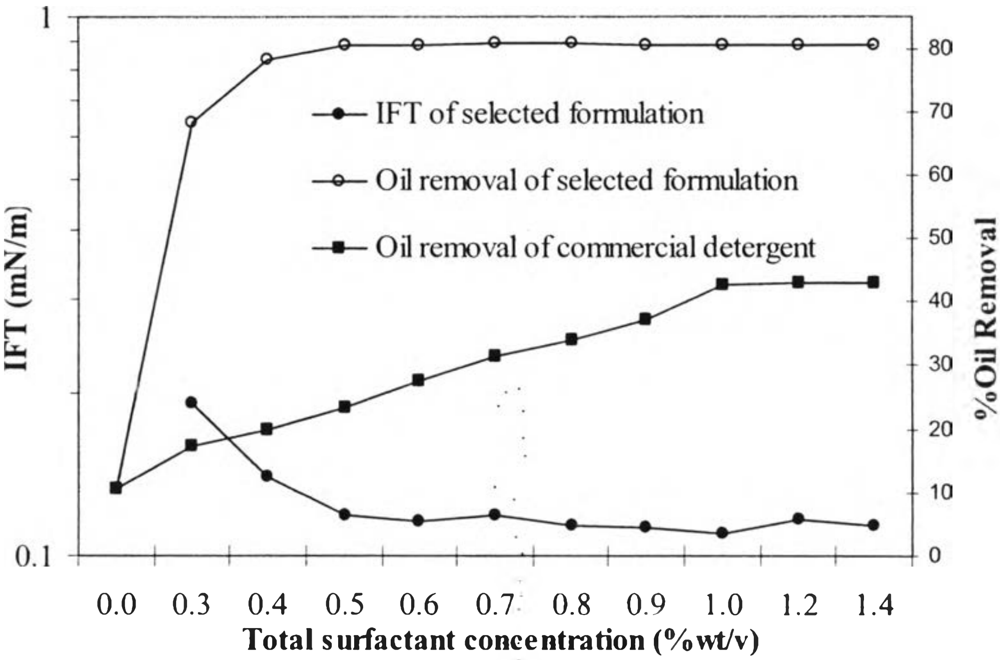

Figure 4.14 % Oil removal as a function of active surfactant concentration of selected formulation (5% AE5 and 5% MES) as compared with commercial detergent at 30°C.

As shown in Figure 4.14, the oil removal increases with increasing active total surfactant concentration for both the selected formulation and the commercial detergent. For the selected formulation, the oil removal reached a maximum of about 80% when the active total surfactant concentration was around 0.5% whereas the maximum oil removal for commercial detergent was very low about 42% at a very high concentration of 1%. Hence, the selected formulation of AE5 and MES can provide much better oily soil detergency than the commercial detergent.

The detergency performance for removing palm oil in this work is compared to the previous as summarized in Table 4.1.

Comparison	Chantra ,2003	Parichat , 2004	Pantipa , 2005	Thitima , 2006	This study
Type of Oily Soils	Motor Oil	Motor Oil	Motor Oil	Motor Oil	Palm Oil
Selected Formulation	2% ADPODS 3% AOT 2% SPAN 80	1.5% ADPODS 5% AOT 5% SPAN 80	0.5% ADPODS 5% AOT 3% SPAN 80	0.1% Alfoteral45-3PO 5% Tergitol 15S6	5% MES 5% AE (5 EO groups)
% Total Surfactant Concentration	7	11.5	8.5	5.1	10
% Active Concentration	0.112	0.115	0.119	0.3	0.5
% Salinity	16	2.83	3	5	-
Temperature	30°C	30°C	30°C	30°C	30°C
% Maximum Detergency (At selected formulation)	78	80	80	82.04	80.40

Table 4.1 The detergency performance of oily soil removal comparison table, Chantra T. (2003), Parichat K. (2004), Pantipa R. (2005), Thitima R. (2006), and Apisol P. (2009).

4.3.2 Effect of Temperature on Detergency Performance

Temperature is the one of factors that can affect detergency performance. For an ionic surfactant and especially nonionic surfactant, an increase in temperature enhances the extent of solubilization because an increase in temperature causes an increase in thermal agitation increasing the space available for solubilization in the micelle (Rosen, 2004). There was a report about optimum detergency efficiency temperature of alcohol ethoxylate, $C_{12}(EO)_5$, nonionic surfactant-hexadecane system. The optimum temperature for the maximum detergency performance was found to be at 52°C (Azemar et al., 1993).

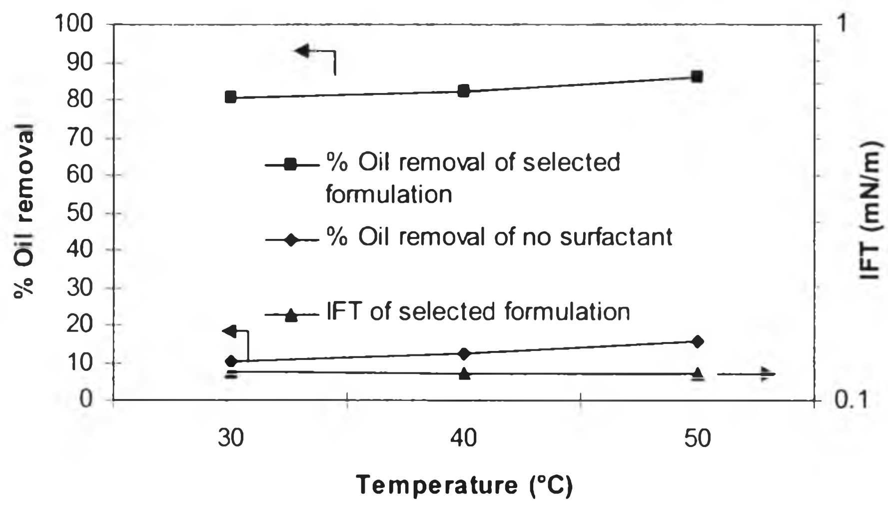

Figure 4.15 Oil removal efficiency as a function of temperature of the selected formulation at an active total surfactant concentration of 0.5% and 30°C.

In Fig. 4.15, an increase in temperature causes a slight increase in oil removal of both selected formulation and no surfactant. However, an increase in temperature did not affect the IFT. Therefore, the increased oil removal with increasing temperature does not rely on an increase in solubilization capacity of micelle with increasing temperature. The explanation in that an increase in temperature can decrease the viscosity of palm leading to facilitate the detachment of the attached palm oil. Moreover, an increase in temperature weakens the hydrogen bond between palm oil molecules and the fabric.

4.3.3 Residual Surfactant on Fabric after Washing Process

Since remaining surfactant on the fabric after washing can cause skin irritation (Rosen, 2004), the remaining surfactant on fabric after washing has to be minimized.

To study the residual surfactant, all surfactant systems at their optimum concentrations giving maximum oil removal, including single systems of MES and LAS, the selected formulation and commercial detergent (consisting of LAS, AE, and Lauryl Ether Sulphate), were tested to determine the amount of remaining surfactant in each step of washings by using titration method. However, this method is a standard test method for anionic surfactant interacting with cationic in titration. Therefore, the single system of anionic surfactant could be directly measured for the residual surfactant but the mixed system consisting of anionic and nonionic which cannot be analyzed by the titration with a cationic surfactant. Hence, the determination of residual surfactant had to be assumed that the amount of residual nonionic surfactant is equivalent with the amount of residual anionic surfactant on the fabric.

Types of surfactants	Optimum concentration (%wt/v)	Amount of residual surfactant on the fabric (g)	Amount of residual surfactant per Fabric area (g/in^2)
Single system of MES	5	0.3353	0.009313
Single system of LAS	7	0.3023	0.008397
Mixed system of 5% MES and 5% AE (Selected formulation)	0.5	0.3282	0.009116
Commercial detergent	1	0.3897*	0.010826

Table 4.2 Comparison of the amount of residual surfactants on the fabric after washing process using different surfactant systems.

* Using the average molecular weight of LAS (12 carbons) for calculating

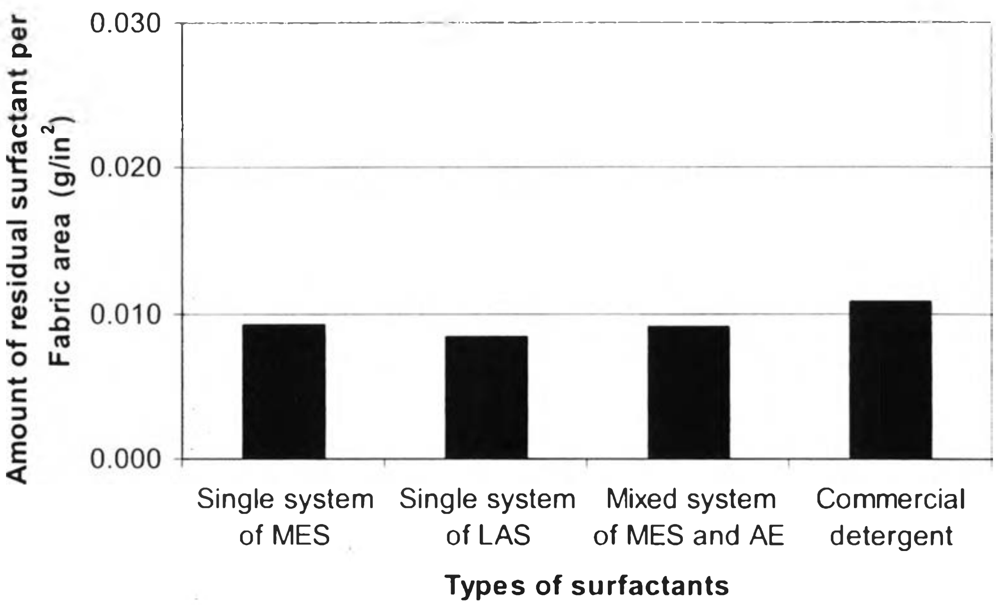

Figure 4.16 Comparison between the amount of residual surfactant per fabric area and typed of surfactants.

From Table 4.2 and Figure 4.16, the amount of residual surfactant on the fabric after the washing process and the amounts of residual surfactant per fabric area of all tested surfactants were not much different. Since there are no any references involving with this effect available, we cannot specify that the amounts of residual surfactant adsorption on the fabric after rinsing is too high or too low. Because commercial detergent does not cause the skin irritation from its residual, the use of either pure MES or the selected formulation is believed not to cause skin irritation.