CHAPTER IV

RESULTS AND DISCUSSION

4.1 Microemulsion Formation Study

To enhance the detergency performance, microemulsion formation is used. The maximum of oily soil removal is achieved under microemulsion condition. But, microemulsion condition determination is very difficult since there are many factors affected the system such as type of surfactant, surfactant system, salinity, temperature and etc. However, mixed surfactant system is believed to improve the detergency performance better than single surfactant system (Chantra, 2003).

To form mixed surfactant system, single surfactant system must be studied before. Therefore, the study of single surfactant system is very useful for mixed system. The purpose of single surfactant system study is finding the optimum surfactant concentration, which provides the lowest interfacial tension and maximum oily soil removal, of any single surfactants.

4.1.1 Single System of Surfactant

4.1.1.1 Effect of MES Concentration

In this study, the MES concentration was varied from 0.1 %wt/v to 10 %wt/v to form microemulsion with motor oil. Since the system could not verify the existence of a Winsor Type III microemulsion, IFT measurement was used instead of measuring phase height change in order to indicate the presence of a Winsor Type III microemulsion. The results as showed in Figure 4.1, the lowest IFT of 0.2532 mN/m was found at 2 %wt/v MES concentration. The IFT values were not in the ultralow IFT range (10^{-2}-10^{-3} mN/m), suggesting that the pure MES system cannot produce a Winsor Type III microemulsion.

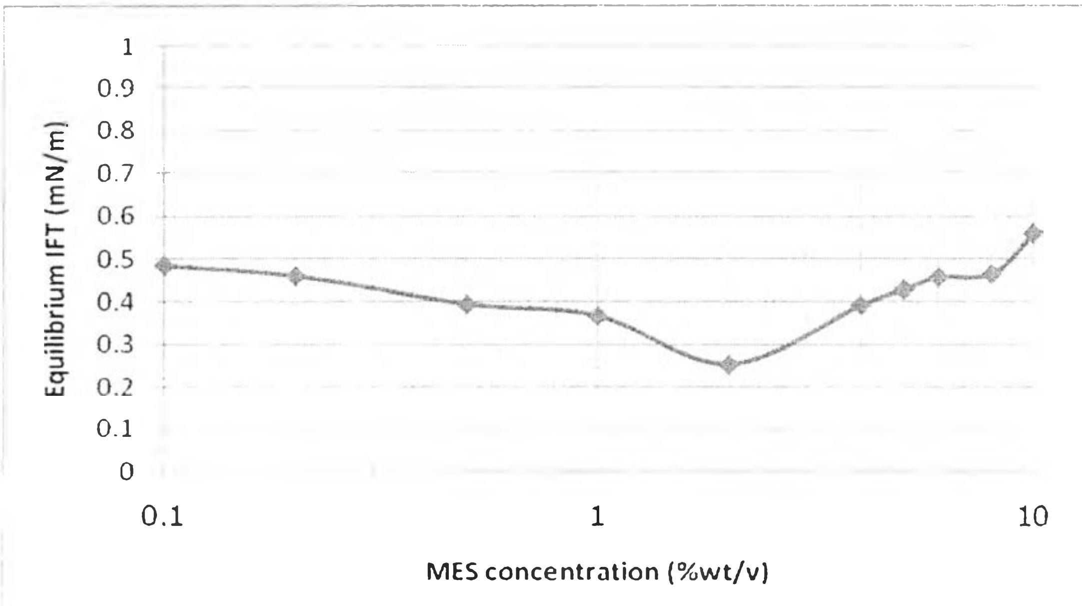

Figure 4.1 Interfacial tension (IFT) of motor oil and various MES concentration solution.

4.1.1.2 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, at 2 %wt MES concentration, the optimum concentration was selected for the salinity experiment in order to find which salinity could provide the lowest IFT.

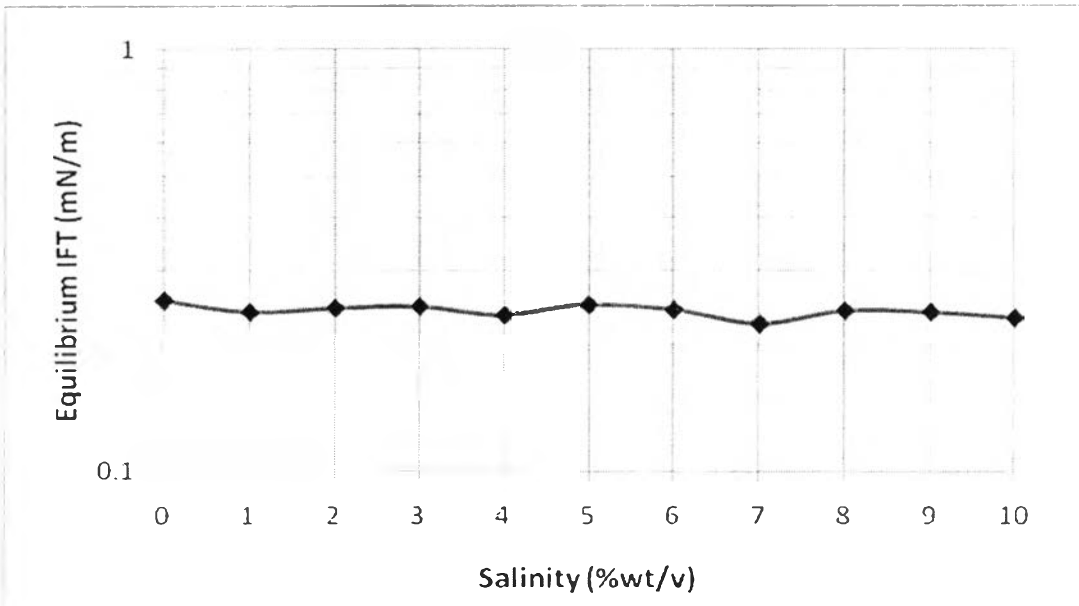

Figure 4.2 Interfacial tension as a function of salinity at 2 % MES concentration.

From the study on the effect of salinity, the correlation of IFT and salinity were plotted as showed in Figure 4.2. The result showed that when salt was added, the IFT of the system did not much change from the system without salt. If salt was further added to the system, IFT would be constant and when the salinity exceeds 1 %, MES solution will have very high viscosity which was not suitable for the detergency application. Therefore, adding salt in this system did not affect to decrease IFT possibly because MES molecule contained a lot of Na^+ ions from the MES production step of neutralization.

4.1.1.3 Effect of EO groups and Concentration of Alcohol Ethoxylate

A nonionic surfactant is believed that it is good for oil removal because an nonionic surfactant is better solubilizing agents than ionic surfactant. Moreover, nonionic surfactants have 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 affect an increase in solubilization capacity which resulting an increase in oil removal efficiency. For Alcohol Ethoxylate, the number of ethylene oxide groups is the one of factors that affects solubilization capacity of nonionic surfactants since a decrease in the number of ethylene oxide group causes an increase in aggregation numbers which resulting an increase in solubilization capacity of surfactant. Moreover, 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 are not suitable for oily soil removal.

In this work. the various number of ethlylene oxide groups of Alcohol Ethoxylate were studied in order to find the number of ethylene oxide group which provided the lowest interfacial tension with motor oil.

In this study, number of ethylene oxide (EO) groups of Alcohol Ethoxylate (AE) and Alcohol Ethoxylate concentration were varied from EO groups 3-9 groups and 0.5-15 %wt/v respectively. In order to find which EO groups and which AE concentration will give the lowest IFT.

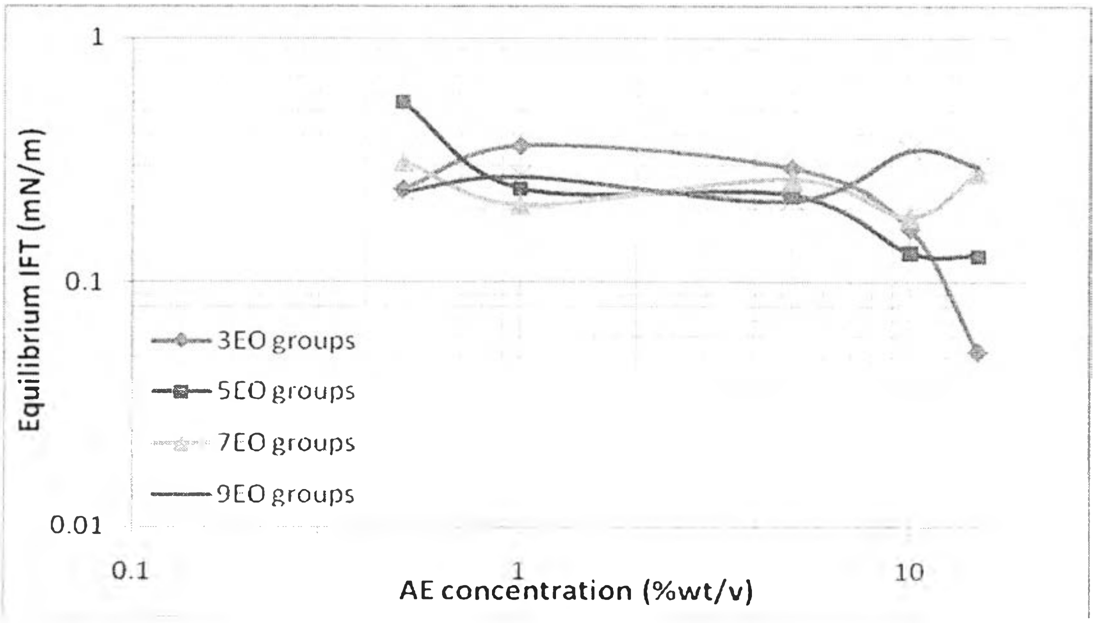

Figure 4.3 Interfacial tension as a function of AE ethylene oxide (EO) groups and concentration.

From Figure 4.3, the result showed that the lowest IFT was found at Alcohol Ethoxylate with 3 EO groups at 15 %wt/v AE concentration but this result is not so clear because at the same concentration, the IFT of each Alcohol Ethoxylate with different EO groups had a very close value to each other's and from the limitation of the instrument, the lowest IFT was also found at Alcohol Ethoxylate with 5 EO groups at 10 %wt/v AE concentration and the IFT at 5 %wt/v of all EO groups were very close to each others. So, to ensure this result that which EO groups should be the optimum, one more experiment was setup. In this study, number of ethylene oxide (EO) groups of Alcohol Ethoxylate (AE) was varied from EO groups 3-9 groups and Alcohol Ethoxylate concentration was constant at 5 %wt/v in order to find the number of EO groups that provided the lowest IFT.

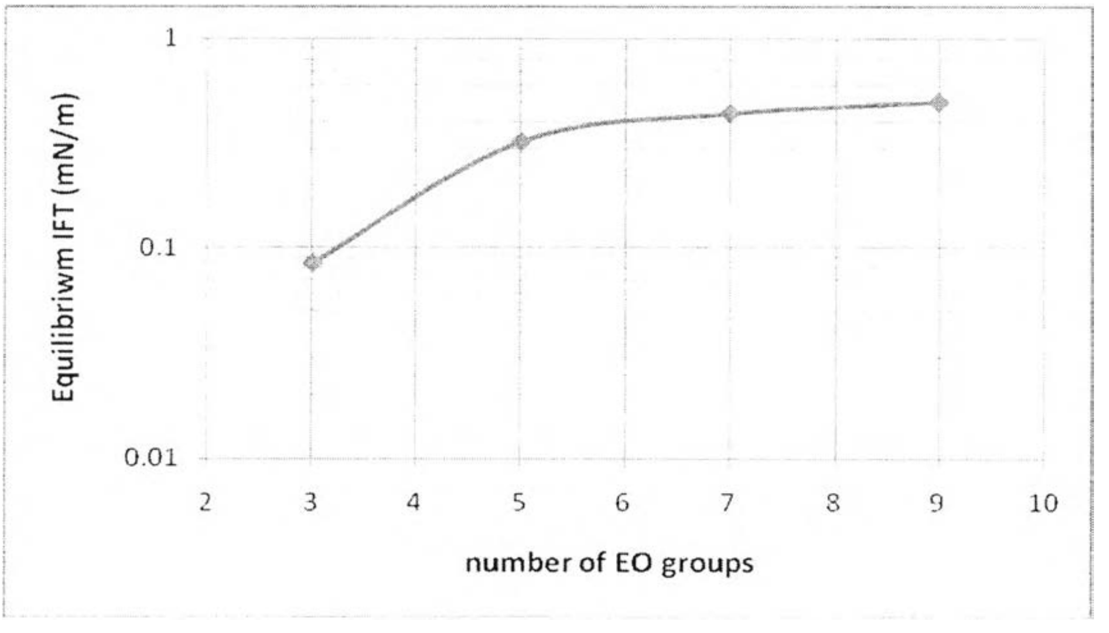

Figure 4.4 Interfacial tension as a function of AE ethylene oxide (EO) groups at constant 5 %wt/v AE concentration.

From Figure 4.4, the lowest IFT was found at Alcohol Ethoxylate with 3 EO groups. The reason that 3 ethylene oxide groups provided the lowest interfacial tension was explained as the previous. For Alcohol Ethoxylate, the number of ethylene oxide groups is the important factor that affects solubilization capacity of nonionic surfactants since a decrease in the number of ethylene oxide group causes an increase in aggregation numbers which resulting an increasing solubilization capacity of surfactant and increase in oil removal efficiency.

4.1.2 Mixed system of surfactants

The mixture of surfactants is believed that it is the best system to remove oily soil as it exhibit a lower oil-water interfacial tension and greater solubilization than single surfactant system (Verma, 1998, Ogino, K and M. Abe. 1997, Tongcumpou, 2003).

In this study, a mixture of Alcohol Ethoxylate with 3 Ethoxylate groups (AE3), a nonionic surfactant and Metyl Ester Sulfonate (MES), an anionic surfactant, was used to form microemulsion with motor oil. The weight ratio between AE3 and MES was varied from pure AE3 to pure MES.

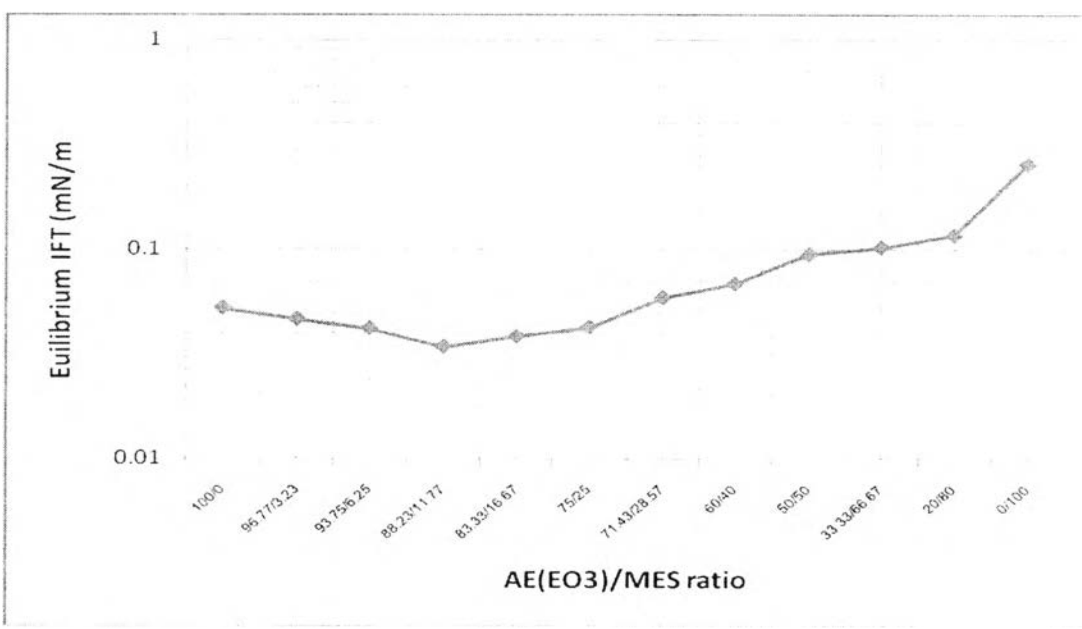

Figure 4.5 Interfacial tension of mixed surfactant system as a function of AE and MES weight ratio at constant 0.3 % active concentration.

From Figure 4.5, as MES concentration increased, interfacial tension was decreased and reached the minimum at 88.23/11.77 of AE3/MES weight ratio. The effect of AE3 concentration was greater than the MES concentration, interfacial tension of mixed system was increasing when the effect of MES concentration became larger. In addition, the interfacial tension of mixed systems at the minimum did not much change from the interfacial tension of pure AE3 system (100/0). As the results, MES did not much help to reduce interfacial tension in microemulsion formation of mixed system probably because AE which had better solubilization capacity and CMC played an important role in microemulsion formation and had more domination in microemulsion formation than MES. However, at the optimum ratio showed the lowest interfacial tension in the mixed system which corresponded to single system of MES and AE.

4.1.2.1 Effect of salinity to Mixed system

It is mentioned that salinity can affect the reduction of interfacial tension due to the reduction of repulsive force between the charged ionic surfactant head groups. However, this effect cannot much affect the reduction of interfacial tension in MES pure system but this effect may affect the reduction of interfacial tension in mixed system. Thus, this study was to find that can salinity result the reduction of interfacial tension in mixed system. To study this effect, the selected formulation of 88.23 %AE and 11.77 %MES concentration which provided the lowest interfacial tension was selected to vary salinity from 0.1 to 1 %wt/v.

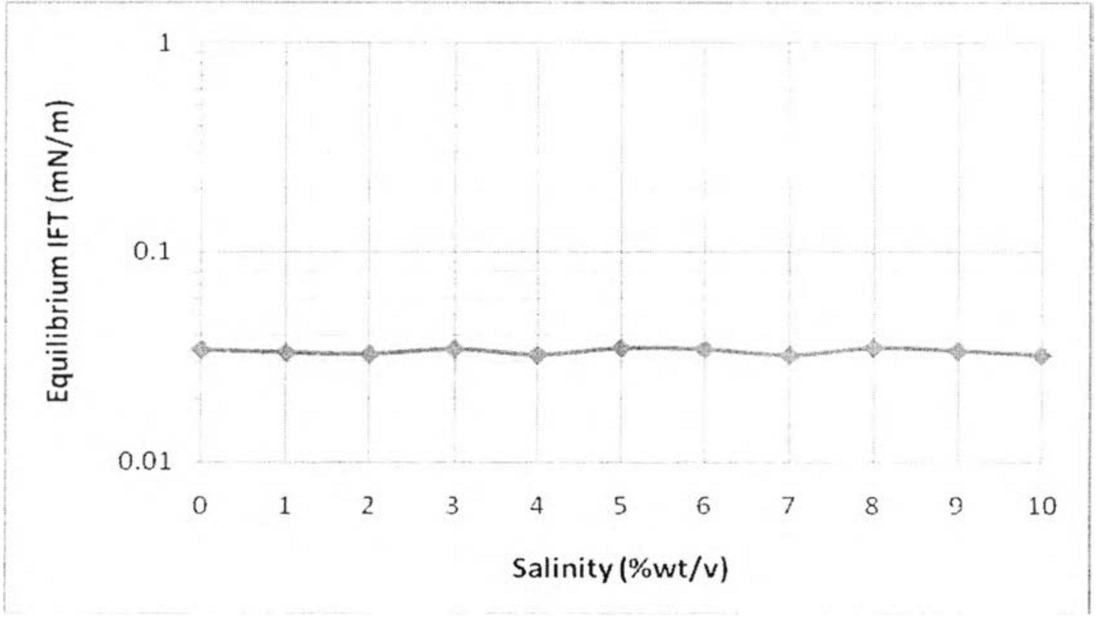

Figure 4.6 Interfacial tension of the mixed system as a function of salinity.

Effect of salinity to mixed surfactant system was showed in figure 4.6. The result showed that salinity could not affect the reduction of mixed system interfacial tension because interfacial tension of mixed system did not change with the increasing salinity. Therefore, the effect of salinity would be cut off in the study of detergency performance.

4.1.2.2 Effect of Active surfactant Concentration

The selected formulation (88.23/11.77 of AE3/MES ratio) was varied %active surfactant concentration in order to find the optimum concentration for using in detergency experiment. In this study, the total concentration of the selected formulation was varied from 0.1 % to 1.0 % active concentration. As the results showed in Fig 4.7, the interfacial tension reached a plateau at around 0.3 % active surfactant. Thus, 0.3 % active surfactant concentration was the optimum concentration for further studying.

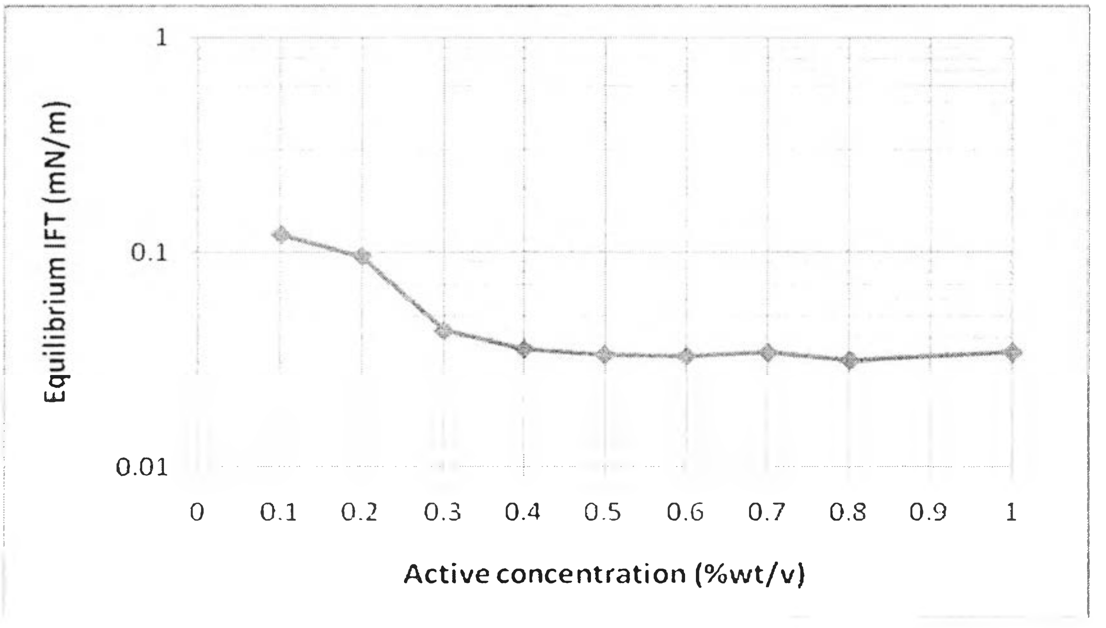

Figure 4.7 Interfacial tension as a function of active surfactant concentration.

4.2 Detergency Performance Study

4.2.1 Correlation of Microemulsion Formation and Detergency Performance

Maximum detergency performance is believed that it will take place when the lowest interfacial tension is present (Chantra, 2005).

4.2.1.1 Effect of MES Concentration

In this study, the different concentrations of MES were varied from 1 to10 %wt/v for washing the fabrics. Figure 4.8 showed the correlation of interfacial tension, detergency (%), and oil removal (%) as a function of MES concentration. From the results, when the interfacial tension decreased, detergency and oil removal were increased until the MES concentration reached 2 %wt/v. At this point, detergency and oil removal reached a plateau which corresponded to the lowest interfacial tension. The maximum of motor oil detergency and oil removal were approximately 42.68 % and 46.55 %, respectively.

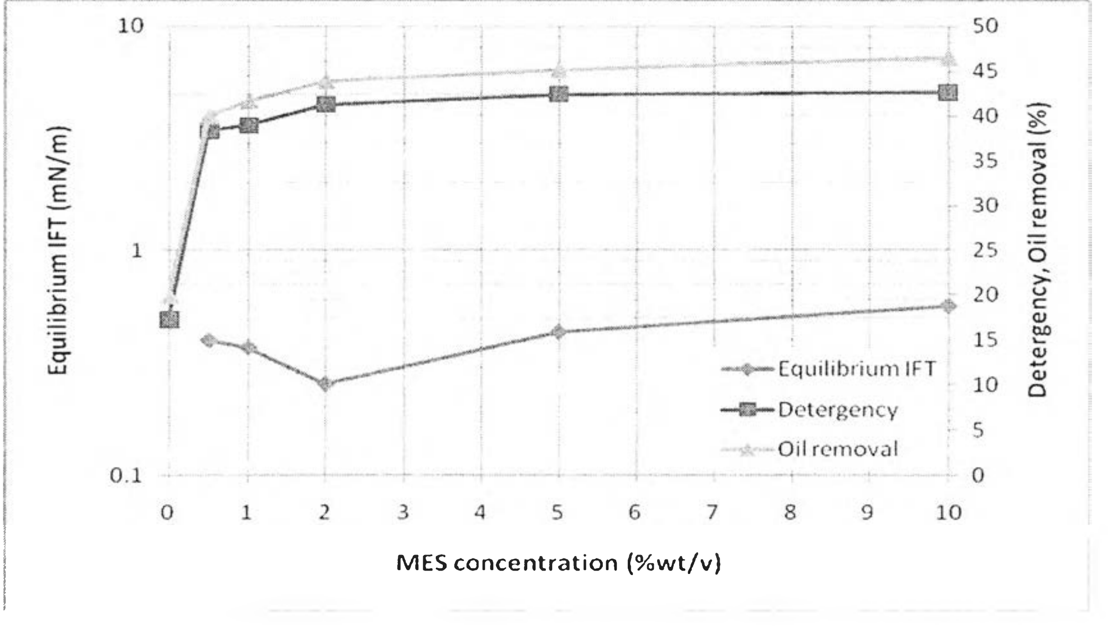

Figure 4.8 The correlation between interfacial tension (IFT), detergency (%), and oil removal (%) of motor oil in pure MES system.

4.2.1.2 Effect of Alcohol Ethoxylate (AE) Concentration

To study this effect, Alcohol Ethoxylate which had ethylene oxide 3 groups (AE3), was varied the concentration from 0.5 to 15 %wt/v. Figure 4.9 showed the correlation of interfacial tension, detergency, and oil removal as a function of AE3 concentrations. From the results, when the interfacial tension decreased, detergency and oil removal increased until AE3 concentration reached 15 %wt/v. At this point, detergency and oil removal had the highest value which corresponded to the lowest interfacial tension. The maximum of motor oil detergency and oil removal were approximately 47.19 and 48.77%, respectively.

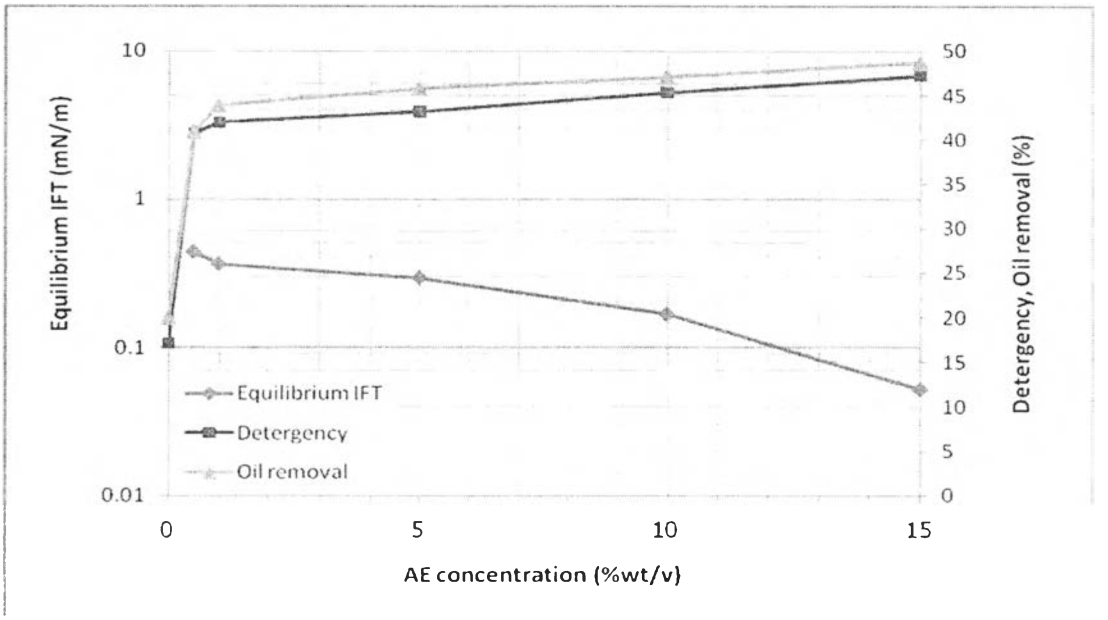

Figure 4.9 The correlation between interfacial tension (IFT), detergency (%), and ooil removal (%) of motor oil in AE single system.

4.2.1.3 Effect of Mixed System

To study the effect of mixed system, the mixtures of different weight ratio between alcohol ethoxylate with 3 ethylene oxide groups (AE3) and Methyl Ester Sulfonate (MES) were prepared to wash the soiled fabrics. The experiment results as showed in figure 4.10 could be explained that the increased of MES concentration did not much help to reduce the interfacial tension of mixed system. However, with the increasing of MES concentration affected an increase in detergency (%) and oil removal (%) which reached a maximum at 88.23/11.77 AE3/MES weight ratio where the maximum of detergency and oil removal were approximately 57.85 % and 83.51%, respectively. The reason that an increase of MES concentration in mixed system help to enhance detergency and oil removal but it could not help to reduce the interfacial tension of mixed system possibly because MES is an ionic surfactant which has negative charged head group. After MES adsorbed on the fabric and in oily soil, the MES head group adsorbing on the fabric repulse with the MES head group adsorbing in oily soil. From this high repulsion force, the oil droplet is more raised from the fabric affecting an increase in oil removal efficiency.

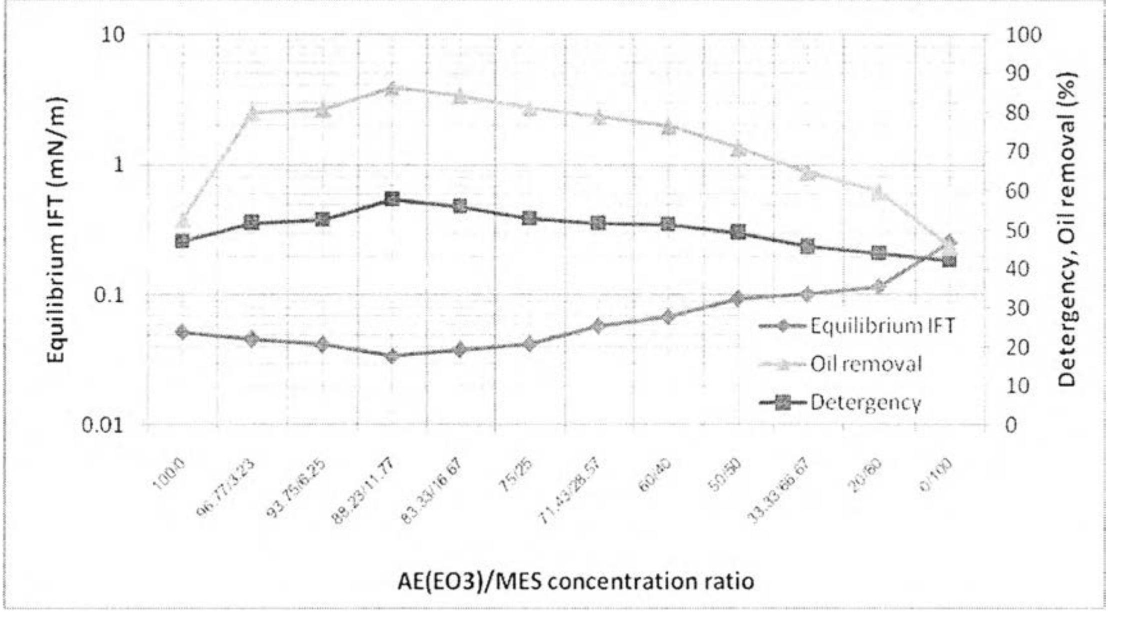

Figure 4.10 The correlation between interfacial tension (IFT) and %detergency of mixed system.

4.2.1.4 Effect of Active Surfactant

Due to the results of microemulsion formation and detergency study, a formulation of 88.23/11.77 of AE3/MES weight ratio was selected for the detergency experiments. Since an optimum surfactant concentration for household applications is recommended in the range of 0.3-0.8 %active concentration of commercial detergents (Jakobi G., 1987), the study for optimum active surfactant concentration of the selected formulations was determined.

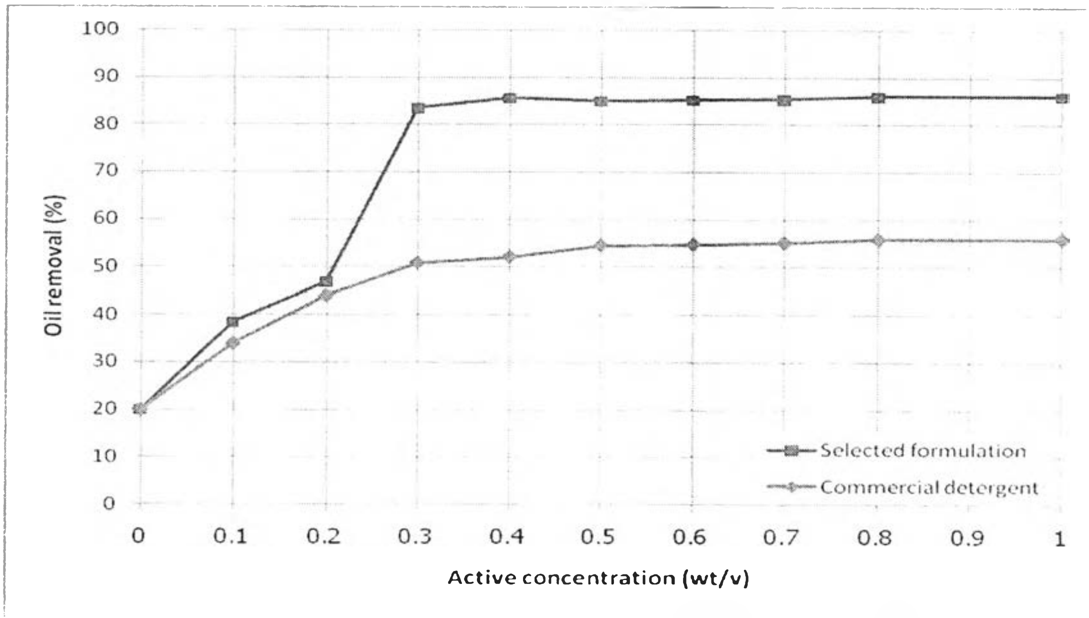

Figure 4.11 Oil removal of the selected formulation and commercial detergent product as a function of active surfactant concentration.

As the results showed in Figure 4.11, the oil removal of the selected formulation increased with an increasing of active surfactant concentration and reached a plateau at around 0.3% active surfactant concentration. Thus, we considered at 0.3% which provided the oil removal about 83.51 % as an optimum concentration for household applications. Moreover, the formulation showed a better detergency performance than the commercial detergent which reached plateau at around 0.3% active surfactant concentration.

4.2.2 <u>Effect of Type of fabrics on Detergency Performance</u>

Type of fabrics is the one of factors that can affect the detergency performance. In the study, three types of fabrics, cotton, cotton/polyester blend, and polyester, were chosen to investigate.

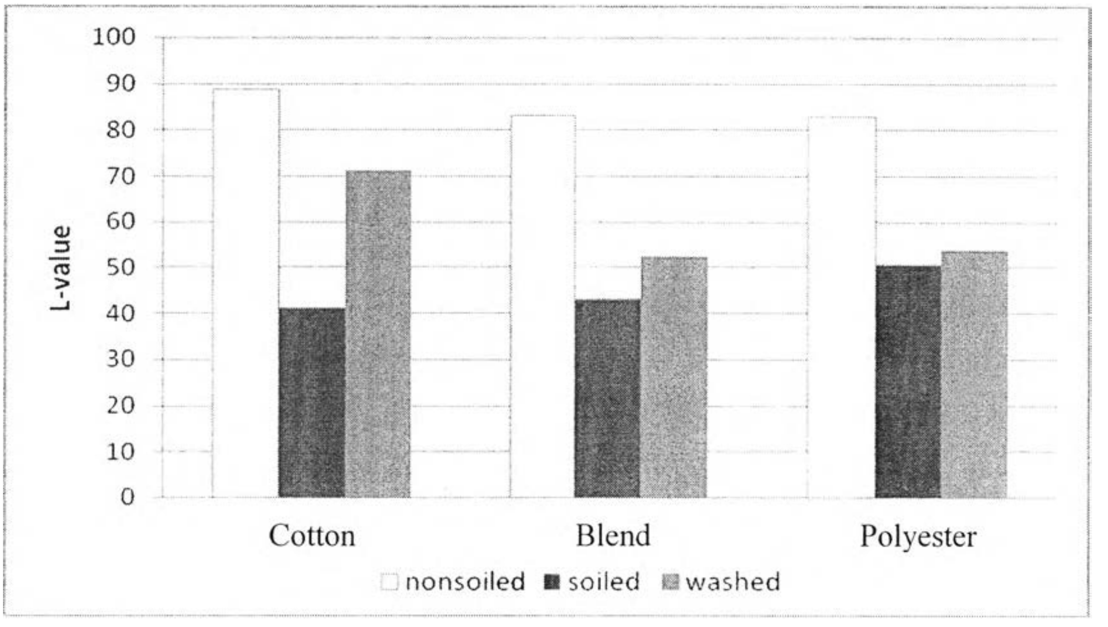

Figure 4.12 Color measurement values (*L*-values) of fabrics soiled with used motor oil.

Type of fabrics was the one of factors that can affect the detergency performance. In the study, three types of fabrics, cotton, cotton/polyester blend, and polyester, were chosen to investigate. Color measurement can measure the amount of motor oil that attached on the fabric. Color measurements of the three fabrics; un-soiled, soiled, and washed, were measured, The L value measured with the spectro-photometer represents the lightness of the sample in a range of white (100) to black (0), the detergency (%) could measure from the difference between before-washed and after-washed fabrics. The motor oil is not easy to remove by laundering. The largest increase in L values after washing was observed for the 100% cotton fabric, and little change occurred with washing of 100% polyester fabric.

To compare the percentage of detergency, the selected formulation was used to wash the soiled fabrics. As the result, the highest detergency (%) was 64.13 % for cotton and only 23.42 % and 10.85 % for blend and polyester respective-ly. The same result for the oil removal, the highest oil removal (%) of cotton, blend, and polyester were 83.51%, 31.56%, and 21.47%, respectively.

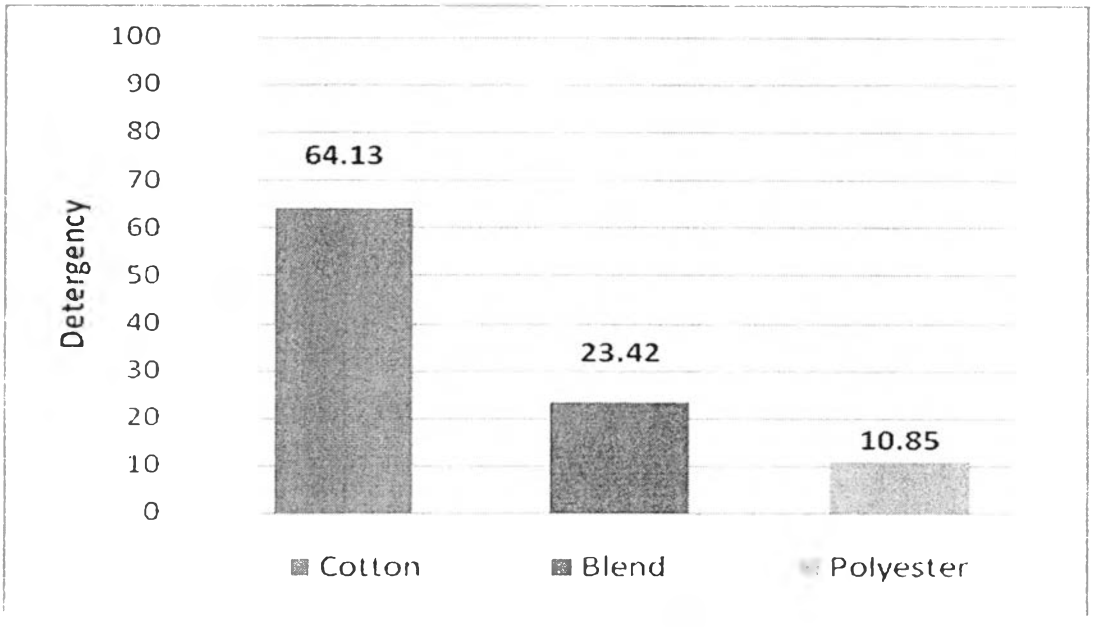

Figure 4.13 The percentage detergency comparison of three types of fabrics.

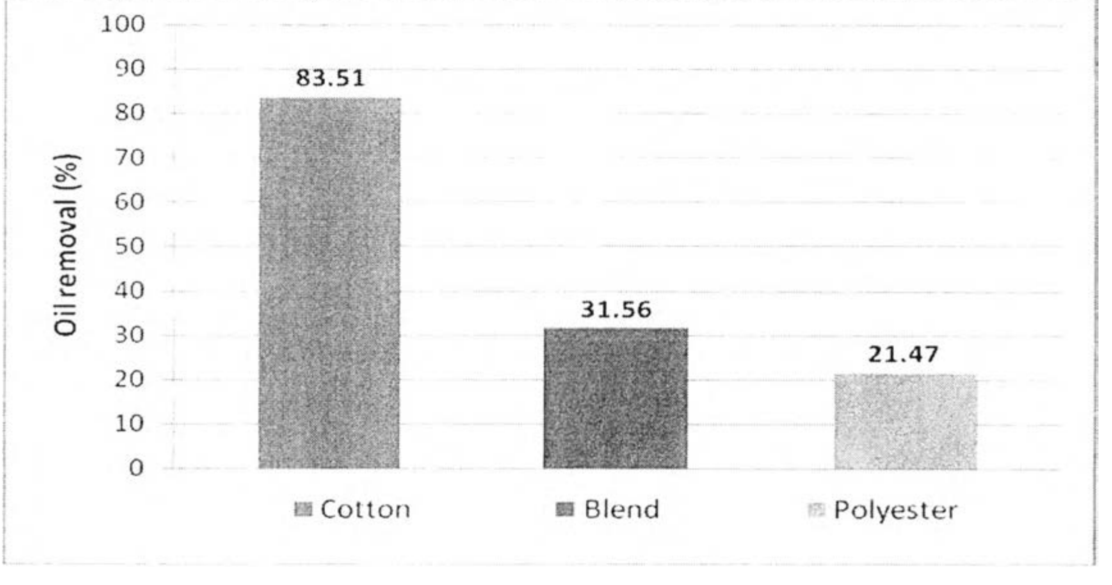

Figure 4.14 The percentage oil removal comparison of three types of fabrics.

The results showed that the color of the motor oil-soiled fabric correlated well with the amount of oil that was present on the fabric (Figs. 4.13, 4.14, and 4.15). The 100% cotton showed the highest detergency of motor oil upon washing. This found that, with motor oil, soil retention measured by a gravimetric method was lower on cellulosic fabrics and cellulosic blends than on synthetics. Because of the high viscosity of aqueous emulsions formed by motor oil and wash water, oil-globule or droplet formation in the fabric matrix, i.e., roll-up, does not proceed on hydrophobic fibers (polyester) to the extent where the soil removal process could be completed by mechanical shear (Kissa E, 1987). The reason that motor oil forms an emulsion fairly easily with detergent solutions compared to other common oily soils may be the presence of dispersant additives in the motor oil, since it is known that motor oils contain dispersant additives (Sanjay, 1994).

4.2.3 Effect of oil redeposition

Surfactants assist in the prevention of redeposition of soil by keeping the soil suspended in surfactant micelles (Rebecca, 2001). Patterns in redeposition were present with the increase of surfactant concentration in the wash solution. As the surfactant concentration increased from low to high, the levels of redeposition significantly decrease because there is sufficient surfactant to keep the soil suspended.

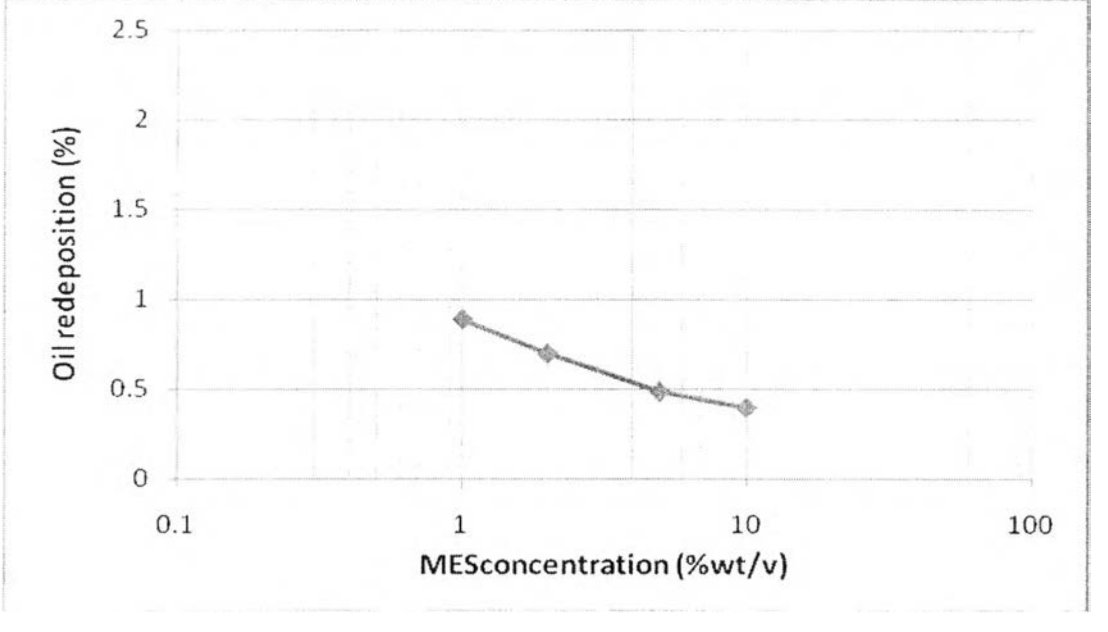

Figure 4.15 The oil redeposition on fabric as a function of MES concentration.

Anionic surfactants are accepted to be good at preventing redeposition of oily soil by surrounding the soil with negatively charged surfactant molecules and enhancing electrostatic repulsion of the surfactant coated soil and the negatively charged fabric surface (Broze, 1994). At the higher concentration of MES there was a smaller increase in the level of soil removal, but a large decrease in redeposition because the presence of more micelles enabled more soil to be suspended.

As the results from Figure 4.15, the redeposition of motor oil was significantly decreased with an increasing of MES concentration because of the repulsion force.

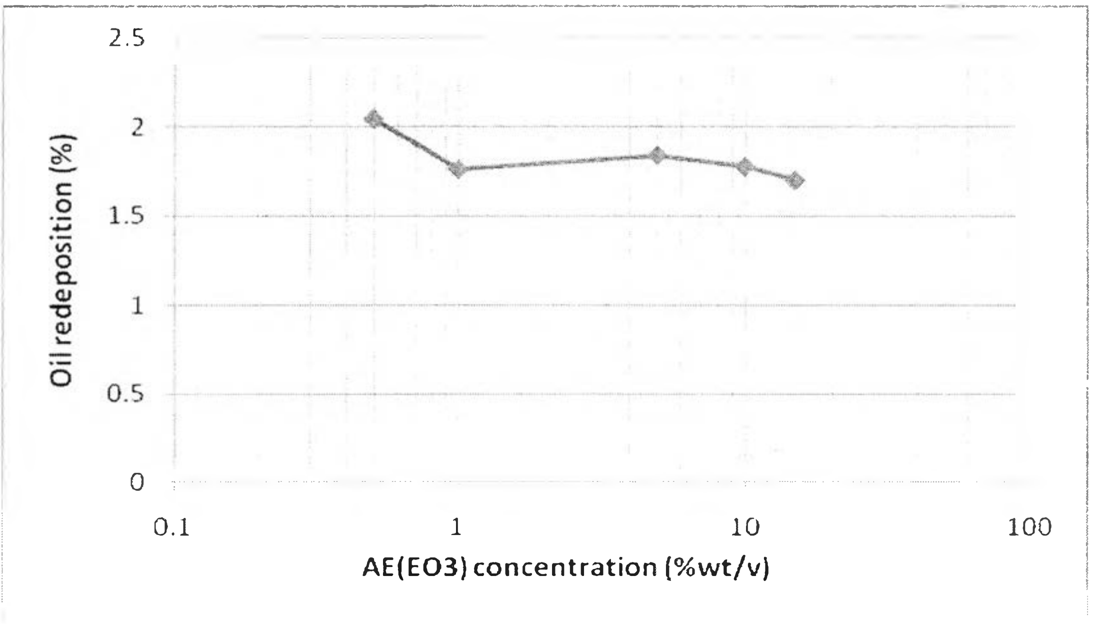

Figure 4.16 The oil redeposition on fabric as a function of AE(EO3) concentration.

The oil redeposition for AE(EO3) single system did not appear to be as effective at keeping soil suspended as MES. Nonionic surfactants prevent redeposition by steric hindrance. The size of the surfactant molecules surrounding the soil particles prevent them from coming physically close enough to the fabric surface to form bonds through van der Waals forces. (Rebecca, 2001)

From Figure 4.16, the redeposition of motor oil was not significantly decreased with an increasing of AE(EO3) concentration.

The systems of mixed surfactant were also studied. The effect of anionic surfactant played an important role to prevent oil redeposition

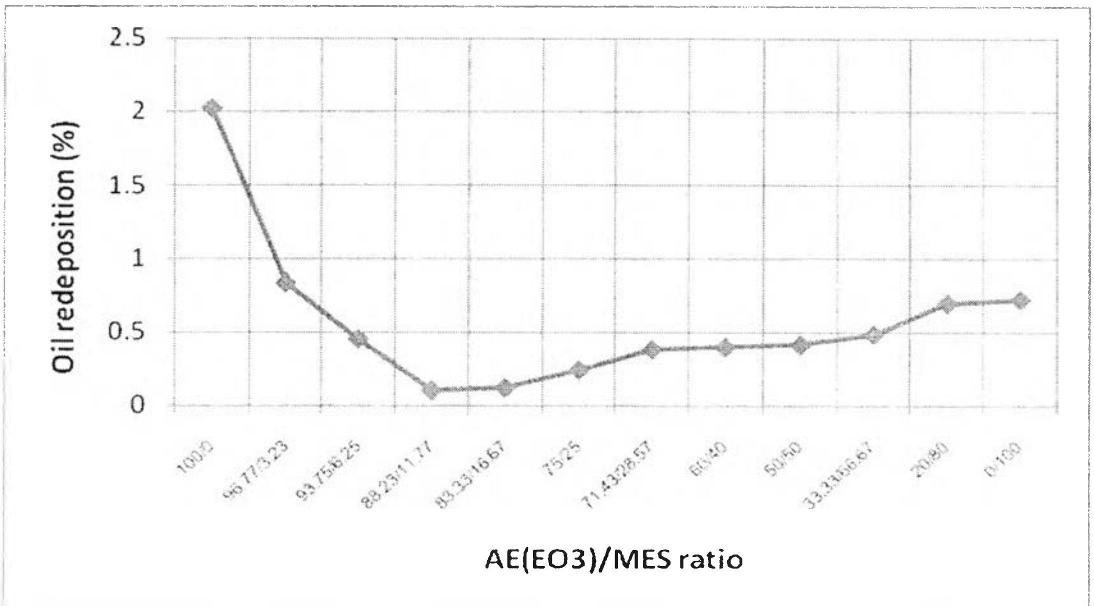

Figure 4.17 The oil redeposition on fabrics as a function of mixed surfactant ratios.

As a result, the oil redeposition was dramatically decreased when an anionic surfactant was added to the system and reached the minimum at the proper fomulation (88.23/11.77). The oil redeposition was slightly increased but not significantly when the ratio of mixed surfactant was changed. The oil redeposition of mixed surfactant system is not much different compared the single system of an anionic surfactant, this is possibly due to the action of the anionic surfactant present in the mixed system and its superior ability to prevent redeposition.

4.2.4 <u>Effect of Residual Surfactant Adsorption on Fabric after Last Rinsing</u>

Since remaining surfactants on the fabric after washing can cause skin irritation (Rosen, 2004). If a high amount of surfactant remains on fabric after washing, we will be itchy when wearing it because the charge of surfactant touches the skin resulting in protein denaturation. Therefore, the study of this effect was to know whether the surfactant remains on the fabric after last rinsing because a good detergent must be able to well remove soils and also must not leave its residue after last rinsing.

To conduct this effect, all surfactant systems at optimum active concentration giving the maximum oil removal, including single system of AE3 and MES, mixture of AE3 and MES, and commercial detergent consisting of LAS, AE, and Lauryl Ether Sulphate, were measured by using High Performance Liquid Chromatography with Light Scattering Detector (HPLC/ELSD) in order to find the residue surfactant in each step of washings. Moreover, this method can also measure the amount of each surfactant type with a high efficiency. The results were shown in Figure 4.18, 4.19, and 4.20.

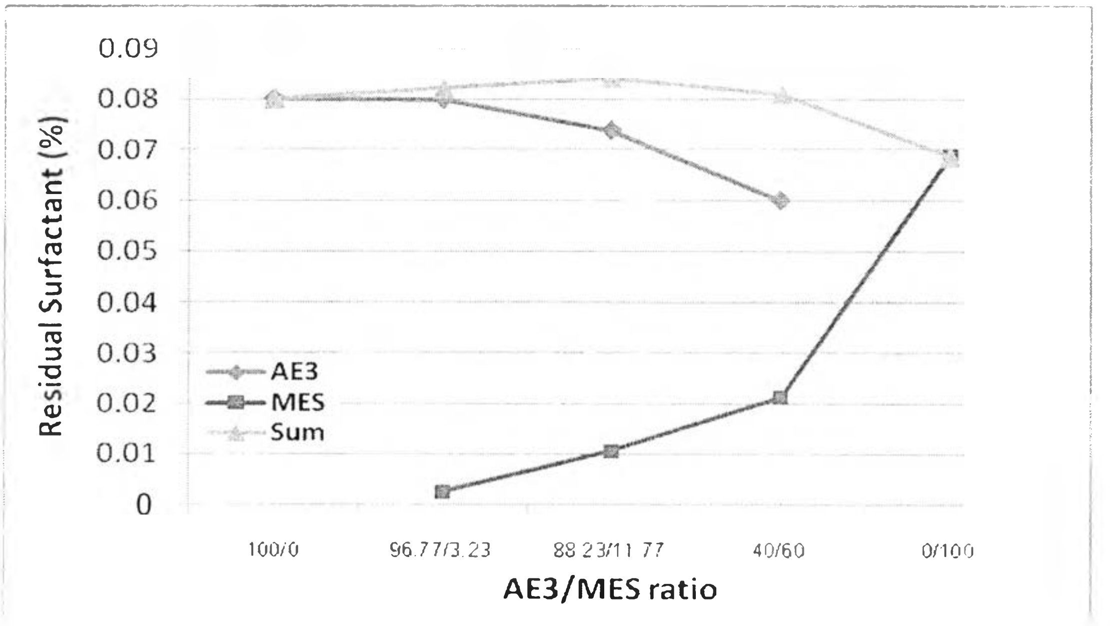

Figure 4.18 The residual surfactant on fabrics as a function of mixed surfactant ratios.

From the results, The total residue surfactant on the fabric after last rinsing was around 0.08 % for all mixed surfactant ratios, this amount was a very low concentration as compared to the 3.90 % of commercial product, thus selected formulation would not cause skin irritation as well. The higher the concentration of surfactants, the higher the amount of the surfactant adsorption. The amount of AE3/MES ratio adsorbed onto the fabric was correlated well with the prepared washing solution. Thus, there was almost the same amount of total residue surfactant on the fabric with a different weight ratio up to the washing solution preparations. Moreover, AE3 seems to adsorb on the cotton fabric more than MES up to their adsorption isotherm.

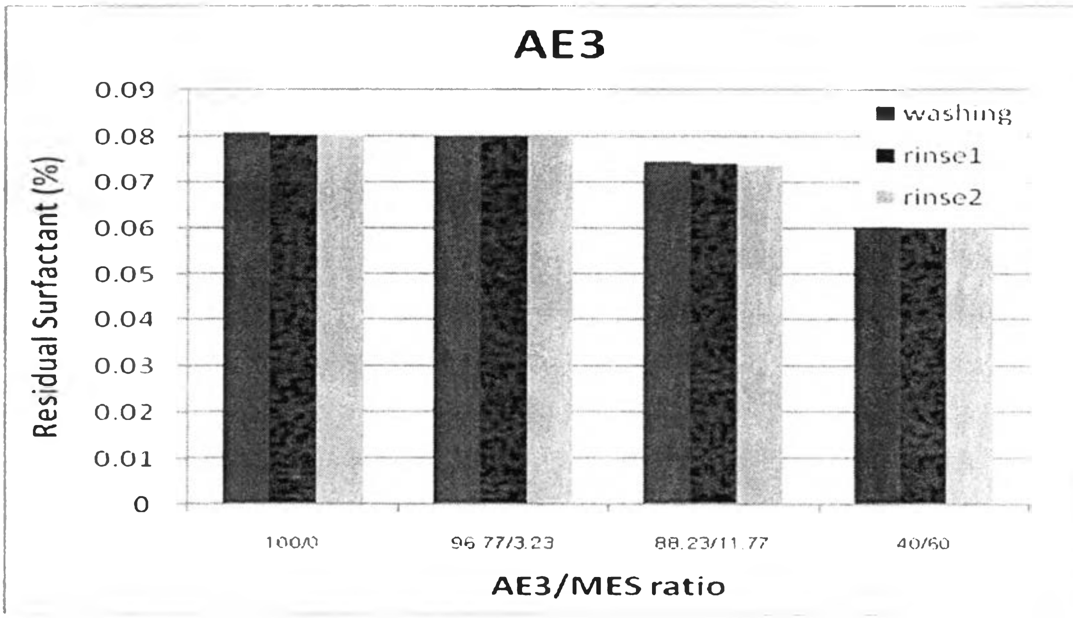

Figure 4.19 The residual AE3 on fabrics in each step of washing as a function of mixed surfactant ratios.

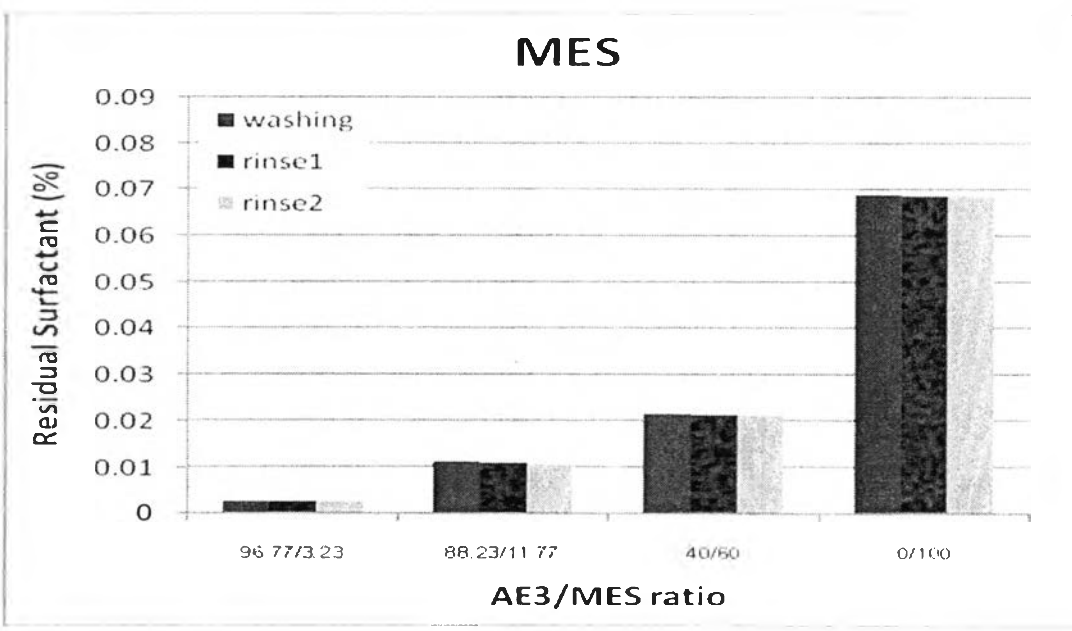

Figure 4.20 The residual MES on fabrics in each step of washing as a function of mixed surfactant ratios.

As the results from figure 4.19 and 4.20, the difference between the amount of residue surfactant after washing, rinse1, and rinse2 steps were not significant in both of AE3 and MES. Therefore, the most of surfactant adsorption was found in the washing step and decreased slightly in both rinse steps.