CHAPTER IV
RESULTS AND DISCUSSION

4.1 Microemulsion Phase Formation

A microemulsion is a surfactant-oil-water system, which has important properties that correspond to the detergency such as the very high oil solubilization and the very low oil-water interfacial tension (Bourrel *et al.,* 1998). Formulation of Surfactant for detergency depends on the kinetics of solubilization or wetting as well as surfactant adsorptions. A complex dynamic process that depends on several factors, such as the nature and composition of the washing solution, salinity, temperature, surfactant concentration, washing time, agitation speed, water hardness, and hydrodynamic conditions (Germain 2002; Linfiled *et al.* 1962; Webb et al. 1988). In this work a mixture of 0.1 wt.% Alfoterra 145-3PO, and 5 wt.% Tergitol 15-S-5 was used as base conditions to form microemulsions with motor oil

4.1.1 <u>Fish diagram of motor oil with the selected formulation</u>

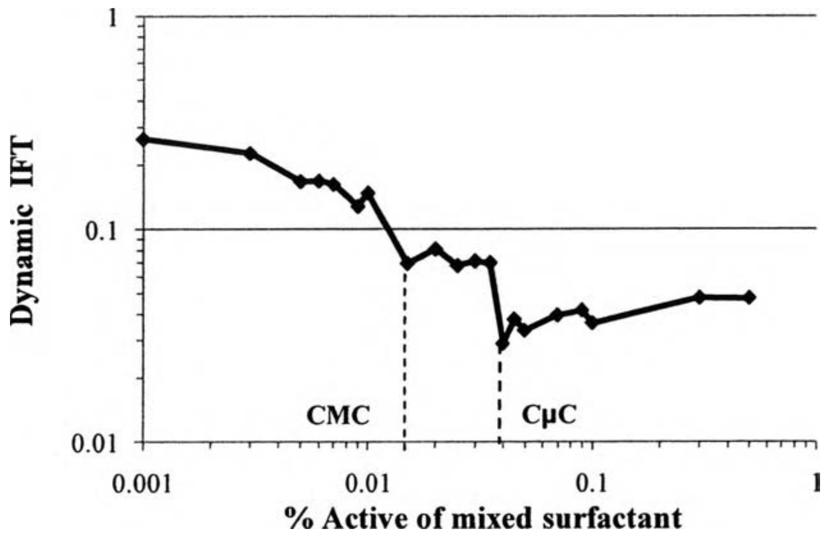


Figure 4.1 Dynamic IFT at 20 min as a function of total surfactant concentration at 30 °C using a mixed surfactant of 0.1 wt.% Alfoterra 145-3PO and 5 wt.% Tergitol 15-S-5.

In Figure 4.1 show IFT of a dynamic system at 20 min as a function of total surfactant concentration at a mixture of 0.1 wt.% Alfoterra 145-3PO, and 5 wt.% Tergitol 15-S-5, and 5% salinity was used as base conditions to form microemulsions with motor oil. It illustrated the dynamic IFTs tended to decrease with increasing total surfactant concentration. There are two steps sharply decreased in IFT, with increasing surfactant concentration. The first step occurs at concentrations less than the CMC. The second step corresponds to the changing in curvature of the micelles which ends at the point, where the first droplet to form a Winsor Type III microemulsion (CμC). From this observation, the CMC and CμC were found at 0.015 and 0.04% of total active surfactant concentration, respectively.

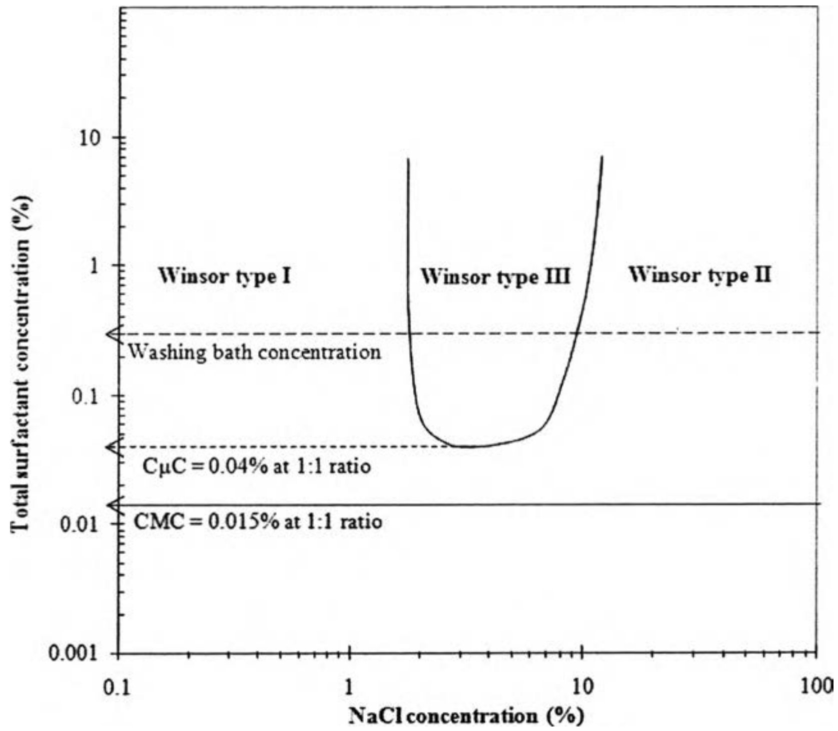


Figure 4.2 Fish phase diagram of selected formulation (of 0.1 wt.% Alfoterra 145-3PO and 5 wt.% Tergitol 15-S-5, and 5% salinity) at an oil-to-water volumetric ratio of 1 to 1 at 30 °C.

The phase behavior of microemulsion systems can describe by the fish diagram, as shown schematically in Figure 4.2. The fish diagram of the selected formulation at 1:1 oil-to-surfactant solution ratio. The fish diagram was constructed by using IFT data. Normally, it show the Winsor Type I microemulsion at low salinity, a Type III inside the closed loop and Type II at high salinity. A Winsor Type IV microemulsion occurs at high surfactant concentration and corresponds to the whole solution being a single homogeneous surfactant rich phase. At the lowest surfactant concentration on the fish diagram, the system formed the middle phase Microemulsion or Type III microemulsion. At this point is known as the critical microemulsion concentration or CμC. Surprisingly, it was found at a very low surfactant concentration of 0.04% total active surfactant concentration which investigated by dynamic IFT. In this study, the surfactant concentration (0.3%) in the washing bath used for the detergency experiment is located in the Winsor Type III region. The CμC (0.04%) is slightly higher than the CMC (0.015%). Therefore, it can be noted that the diluted surfactant concentration used in the washing bath can still form the middle phase microemulsion.

4.1.2 Effect of oil-to-surfactant ratio on IFT

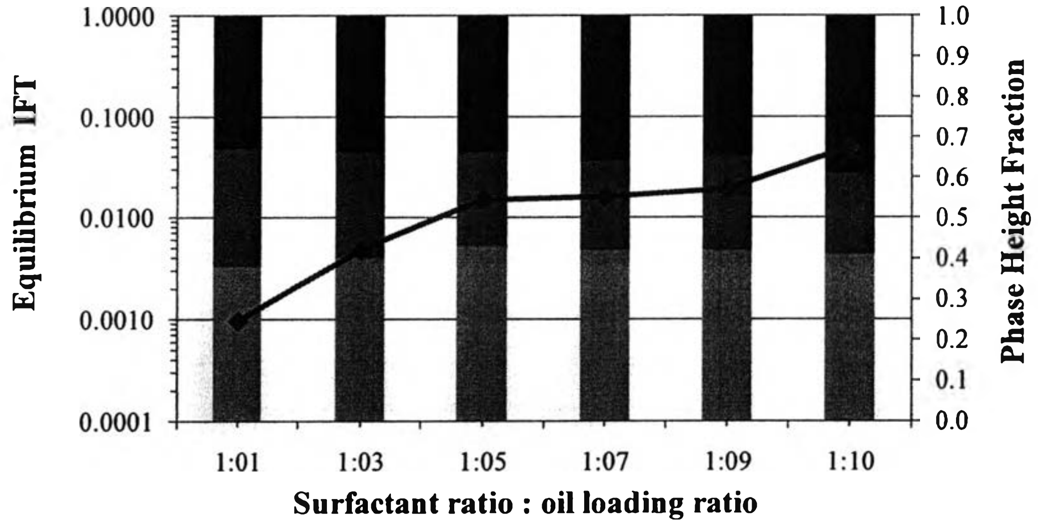


Figure 4.3 Phase Height Fraction and interfacial tension (mN/m) between washing solution (before washing process) and dyed oil as a function of oil-to-surfactant ratio by using a mixed surfactant of 0.1wt.% Alfoterra 145-3PO and 5wt.% Tergitol 15-S-5, and 5% salinity.

In general ratio of oil-to-surfactant much less unity, unlike the one to one ratio normally used in most microemulsion phase studies. Due to preferential partitioning of the different surfactant components into the bulk oil or water phases on the detergency performance, the oil-to-surfactant solution ratio may affect the IFT. For microemulsion formation with motor oil, a mixture of 0.1 wt.% Alfoterra 145-3PO, an extended anionic surfactant, and 5 wt.% Tergitol 15-S-5, a nonionic surfactant which is a secondary alcohol ethoxylate, and 5% salinity were used as a base condition in this study, the system form Winsor type III micremulsions. The experiment was kept at 30°C and the phase behavior equilibrium time was about 1 month. The equilibrium IFT of the oil and surfactant solution at different oil-to-surfactant solution ratios is show in Figure 4.3. It observed that the equilibrium IFT value was increased, with increasing oil loading, as showed

4.2. Detergency Performance

4.2.1 <u>Effect of oil loading on the detergency performance</u>

To study the Effect of oil loading on detergency performance in terms of the oil loading and detergency as a function of oil loading with the selected formulation at 0.3% total surfactant concentration, 5% NaCl and 30°C as illustrated in Figure 4.4. From this graph, both of oil removal and Detergency decreased, with increasing oil loading. It interpreted that oil loading slightly affected the detergency performance.

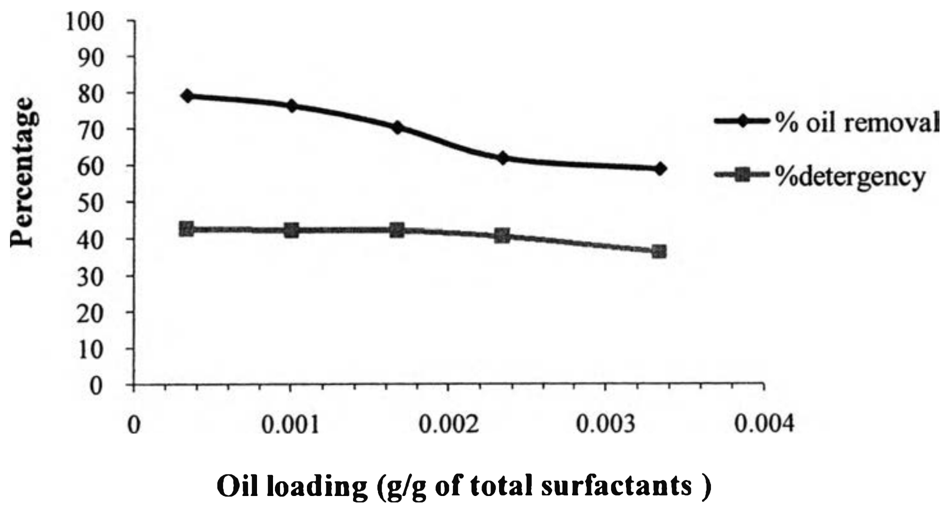


Figure 4.4 Percentage of oil removal and detergency for studied the effect of oil loading on detergency performance with difference oil loading by using fixed amount of total surfactant concentration at 0.3%.

Furthermore, Figure 4.5 shows the oil removal at wash step, the first rinse step and the second rinse step, respectively. The oil weight increased, with the oil removal slightly decreased. The oil removal in the first rinse was found to be much higher than the wash step. This present result was good agreement with previous works [8]. It was indicated that the oil to surfactant ratio affected to efficiency of detergency performance, which is the most influencing parameter in detergency performance.

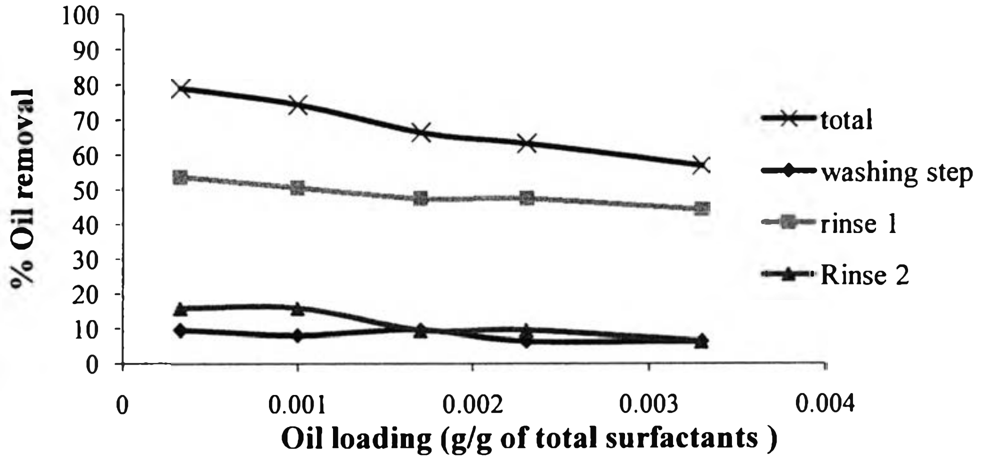


Figure 4.5 Oil removals in each step on studied the effect of oil loading on detergency performance with difference oil loading by using fixed amount of total surfactant concentration at 0.3%.

4.2.2 <u>Effect of fabric weight on the detergency performance</u>

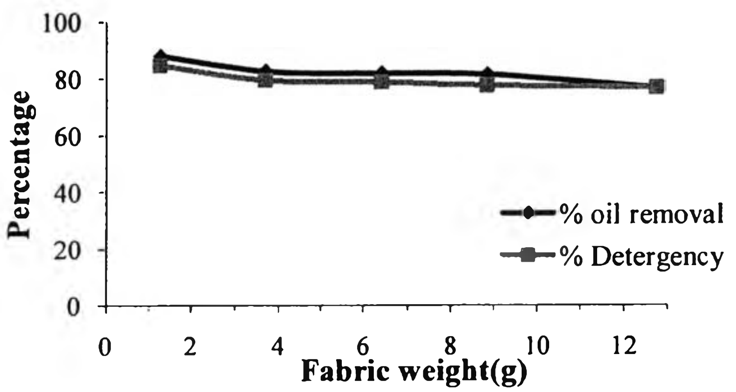


Figure 4.6 Percentage of oil removal and detergency for studied the effect of fabric weight on detergency performance at the total surfactant concentration of 0.3%.

In Figure 4.6 shows the oily soil detergency performance in terms of % oil removal and % detergency as a function of fabric weight. In the detergency experiments, the selected formulation which had a ratio of Alfoterra 145-3PO and Tergitol 15-S-5, and 5% salinity of 1 to 50 was diluted to have the total surfactant concentration of 0.3%. It was conducted a constant temperature of 30°C. Both of oil removal and detergency efficiency tended to slightly decrease with increasing fabric weight. The oil removal and detergency results still show the similar trends. It is interesting to point out that the fabric weight not affect to detergency performances.

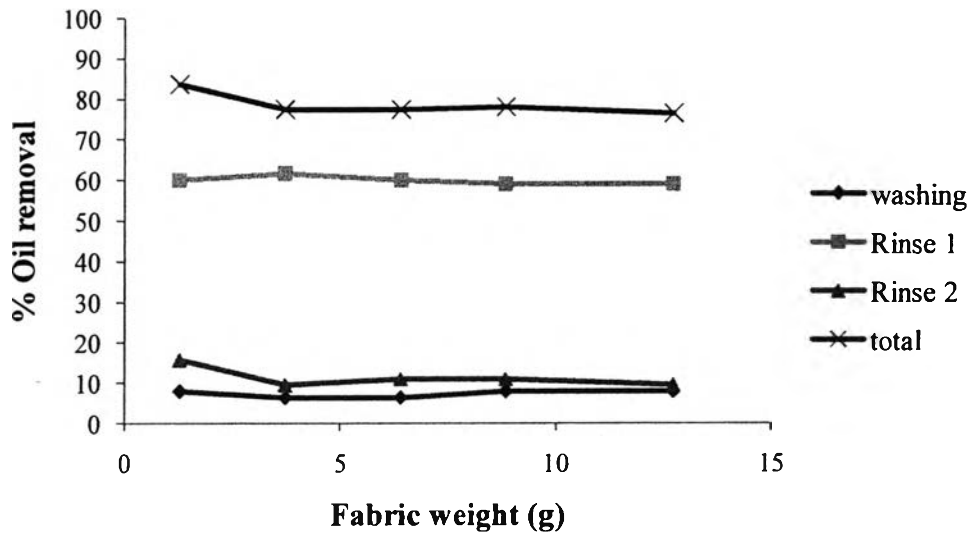


Figure 4.7 Oil removal in each step studied the effect of fabric weight on detergency performance at the total surfactant concentration of 0.3%.

In order to obtain a better understanding of the washing process, the oil removal in the each step was investigated apart from the total oil removal. Figure 4.7 show the oil removal of wash step, the first rinse step and the second rinse step, respectively as a function of fabric weight with the selected formulation of the total surfactant concentration of 0.3% (0.1 wt.% Alfoterra 145-3PO and 5 wt.% Tergitol 15-S-5, and 5% salinity). When fabric weight increased, the oil and surfactant adsorption of wash step, the first rinse step and the second rinse step showed the same trends. In a comparison between the total oil removal and the oil removal in the wash step, most oil was removed in the first rinse step instead of the wash step. The present results are in good agreement with the previous study [10]. It observed that oil removal of weight varied does not different % Oil removal value which support with previous result.

4.2.3. Correlation between mixed surfactant adsorption and % oil removal

Surface tension and contact angle experiments; this graph shows the Critical Micelle Concentration (CMC) values. The Critical micelle concentration (CMC) value was the first point to form micelle, which was determined by surface tension measurements, as plot in Figure 4.8 as a function of surfactant concentration. The CMC values of mixed-surfactant (Alfoterra and Tergitol), single Alfoterra, single Tergitol were 250, 125, and 550 μM respectively. The secondary substitution of the alkyl chain of surfactant interferes with the packing of the surfactant molecules within the micelles do not form so that the CMC of nonionic surfactant was slightly highest the CMC value. Increase ionic strength, micelle can form more easily so that the CMC value of Anionic surfactant was lowest the CMC value [12].

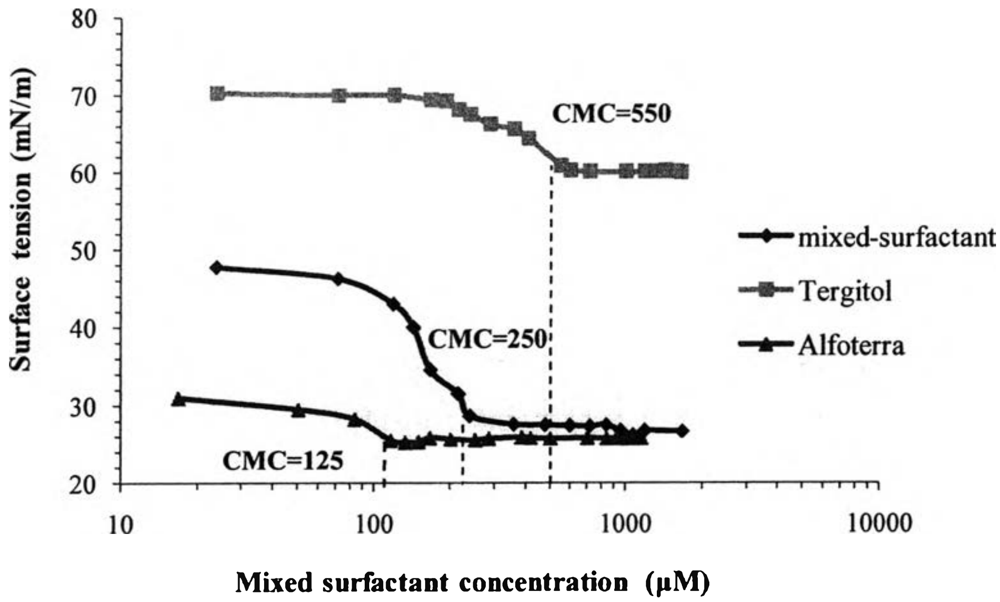


Figure 4.8 The Critical Micelle Concentration (CMC) values were measure by Surface tensions measurement as a surfactant concentration of different surfactant system at 30°C.

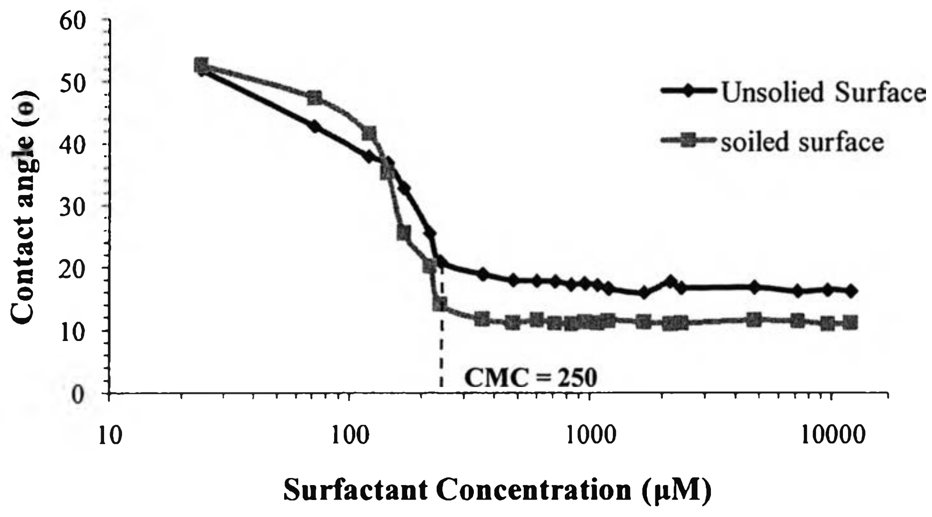


Figure 4.9 Contact angles of mixed surfactant solution on soiled fabric surface and unsoiled fabric surface versus surfactant concentrations.

In addition, the contact angles of mixed surfactant solution on both soiled and unsoiled surfaces shapely decreased significantly with increasing surfactant concentration and reached to contact angles minimum values. The break point in the slope was CMC, as show in Figure 4.9. At equilibrium, the soiled surface shows Contact Angles lower than unsoiled surface. Molecule of mixed surfactant attach oil on surface, it expected that Surfactant spread on soiled fabric surface more than unsoiled fabric surface.

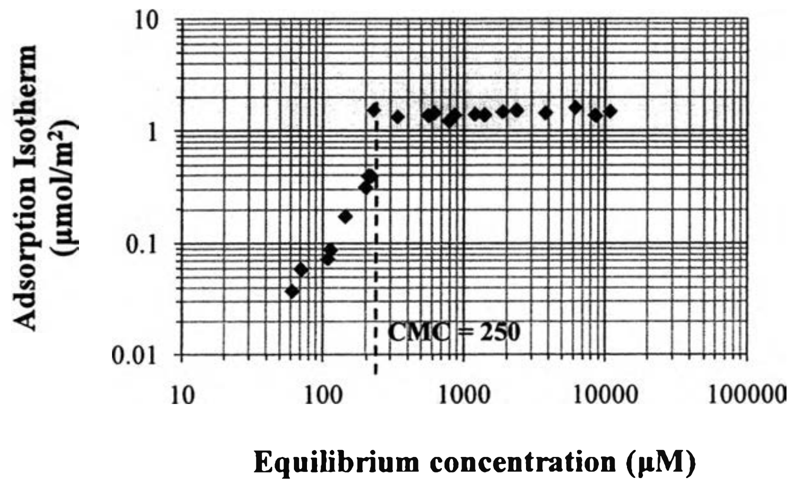


Figure 4.10 Adsorption isotherms for mixed surfactant solutions of 0.1 wt.% Alfoterra 145-3PO and 5 wt.% Tergitol 15-S-5 with 5% salinity.

The adsorption isotherm was studied for mixed surfactant solutions of mixed surfactant of 0.1 wt.% Alfoterra 145-3PO and 5 wt.% Tergitol 15-S-5 with 5% salinity by varied % total active surfactant concentrations in terms of different total mixed surfactant concentration onto polyester/cotton blend, as shown in Figure 4.10. This representation was interpreted that surfactant adsorption increase, with increasing surfactant concentration and reached a plateau above the CMC at 250 μM.

Figure 4.11 illustrates the correlation between the oil removal and the surfactant at different total surfactant concentrations. The result shows a good relation between the oil removal and the surfactant adsorption. The surfactant adsorption is known as a first step occurring in the washing process. In this washing experiment, the total surfactant concentration in washing solution was kept constant at 0.3%, suggesting that the system possessed both maximum levels of surfactant adsorption and oil removal.

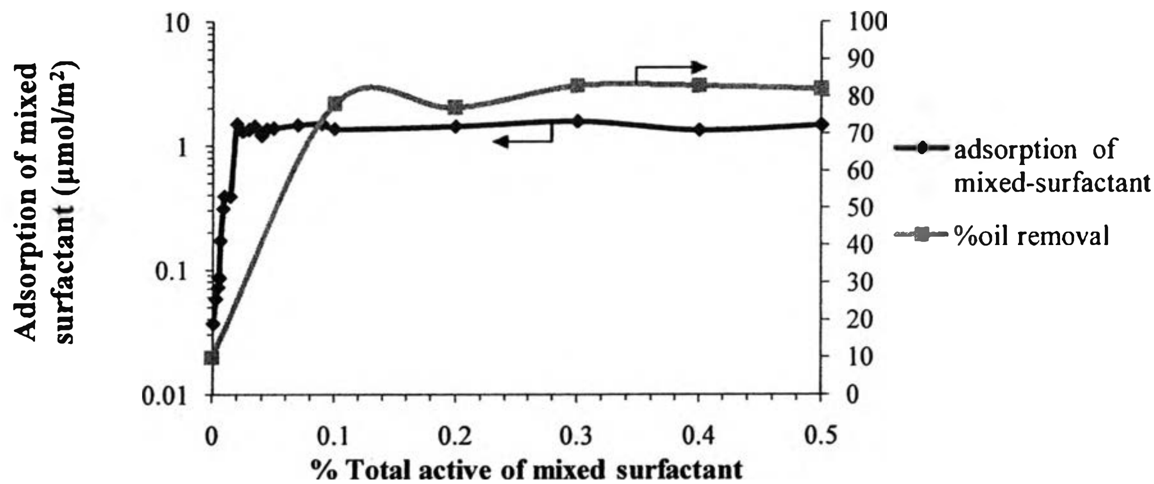


Figure 4.11 Correlation between adsorbs of mixed surfactant solution and % oil removal by different % total active mixed surfactants.

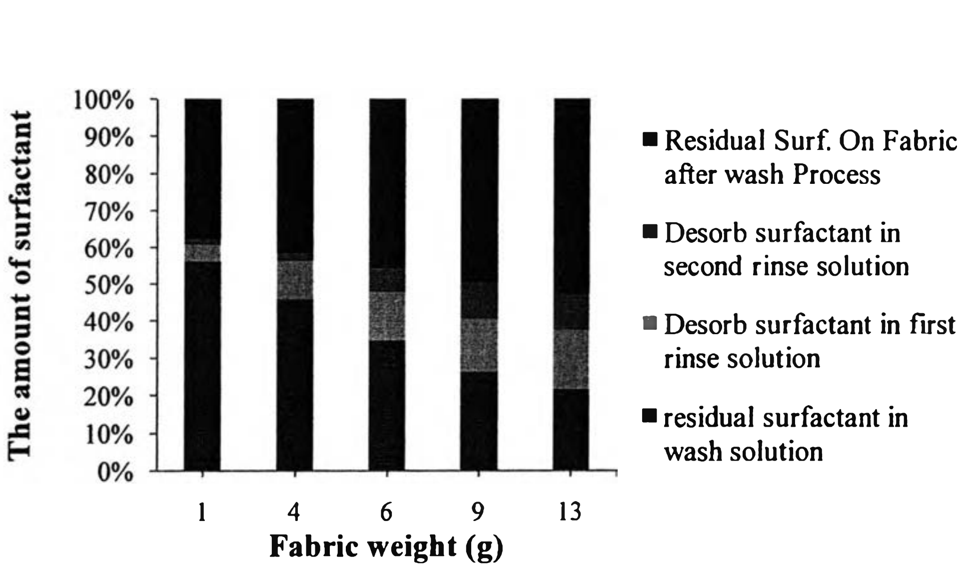


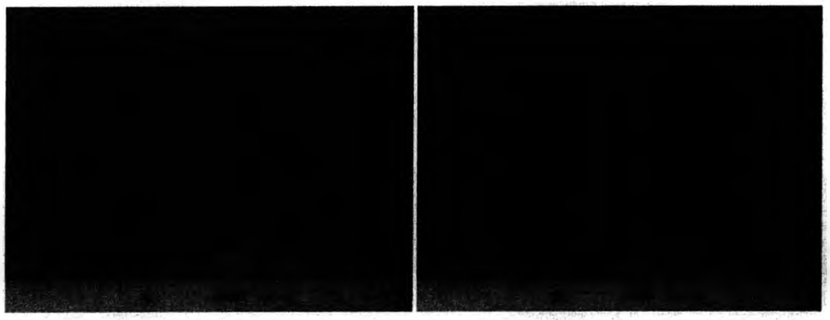
Figure 4.12 The amount of mixed surfactant in each step of washing process of soiled polyester/cotton blend fabric, which varied fabric weights by using a % total active mixed surfactant concentration of 0.3% total active surfactant concentration with 5% salinity.

For this experiment, the washing and the two-rinsing solution after washing process of blend polyester/cotton fabric at 5% salinity with a selected formulation of mixed surfactant was studied the amount of surfactant on detergency performance. Titration method is reach to amount of Surfactant in detergency experiments. The amount of anionic surfactant in the washing and the rinsing solutions were measured by titration with the cationic surfactant, following the standard testing method for synthetic anionic active ingredient in detergents by cationic titration procedure. The titration method followed ASTM standard guide D1681-92. In this case we assume the amount of anionic surfactant equal to the amount of nonionic surfactant. The cationic surfactant, which was used for this experiment was 0.005 M Hyamine. Figure 4.12 show the amount of mixed surfactant in each step and the residual surfactant on the fabric surface after washing process supported by the result of Ratchatawetchakul (2005). The excess surfactant was used in the wash step and the residual surfactant that occurs in the washing process. Increasing of fabric weight, with increased amount residual surfactant after wash process it mentions that surfactants were adsorped on fabric after wash process.

4.2.4 Oil detachment at different concentrations

(a) 5400 s (b) 12600 s

(c) 18000 s (d) 24950 s



(e) 25000 s (f) 25062 s

Figure 4.13 Consecutive photos of the motor oil detachment from horizontal dry compressed fabric surface in 0.07 % active mixed surfactant solution at 30°C.

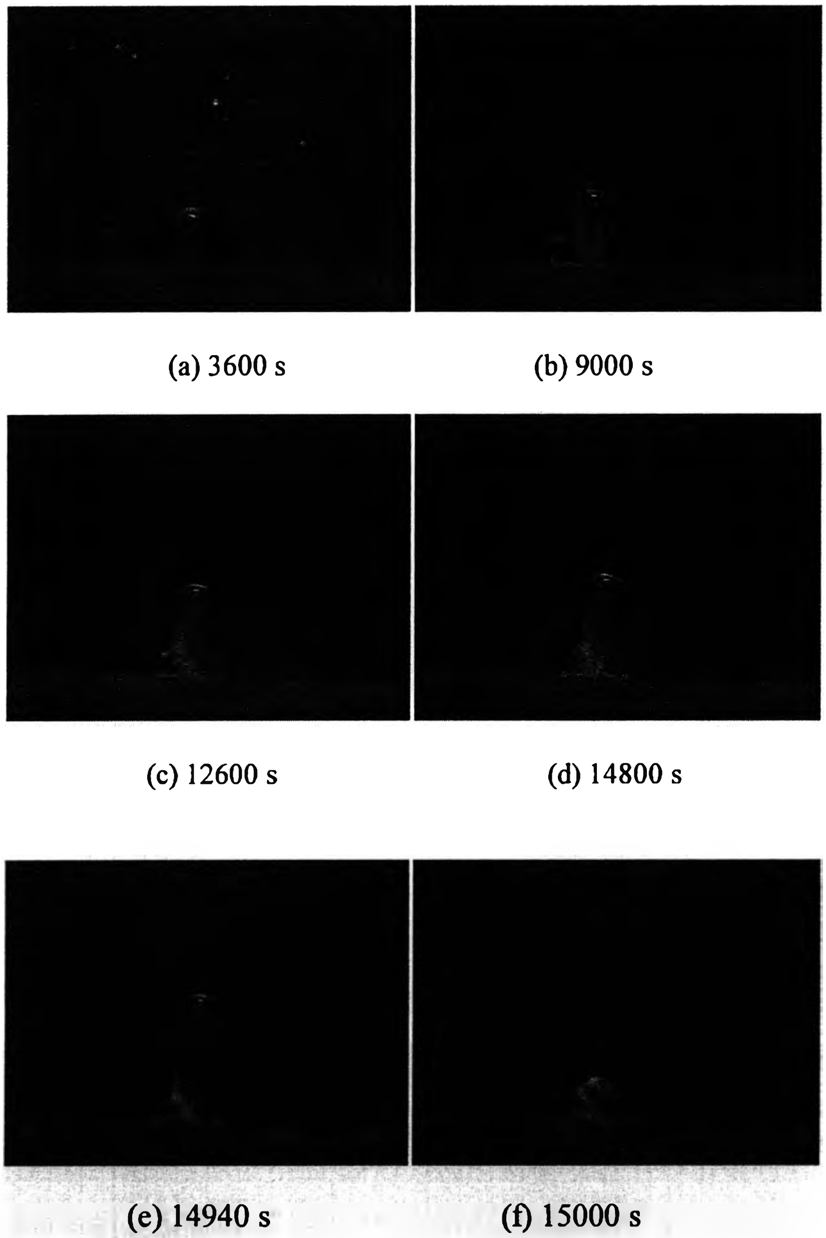


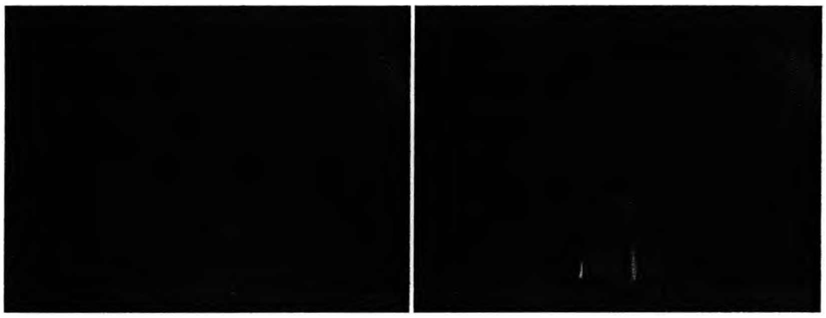
Figure 4.14 Consecutive photos of the motor oil detachment from horizontal dry compressed fabric surface in 0.1 % active mixed surfactant solution at 30°C.


(a) 600 s (b) 3600 s


(c) 7200 s (d) 10540 s

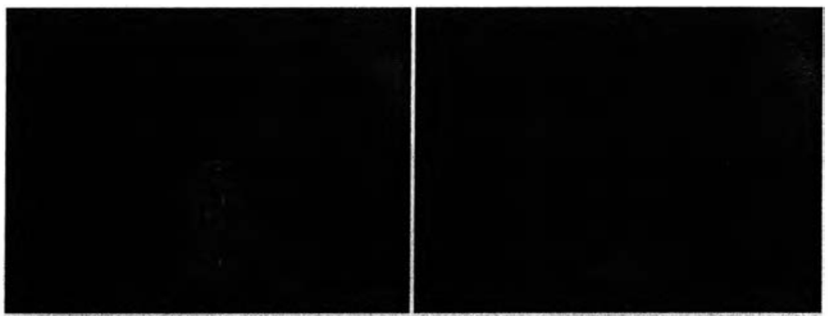

(e) 10600 s (f) 10604 s

Figure 4.15 Consecutive photos of the motor oil detachment from horizontal dry compressed fabric surface in 0.3 % active mixed surfactant solution at 30°C.



(a) 1200 s (b) 2000 s

(c) 3600 s (d) 5400 s



(e) 7800 s (f) 8000 s

Figure 4.16 Consecutive photos of the motor oil detachment from horizontal dry compressed fabric surface in 0.5 % active mixed surfactant solution at 30°C.

The integration technique was used to determine the residual oil detachment from compress fabric surface. And % oil detachment was shown in figure 4.17. It show increased % oil detachment with increasing % active of mixed surfactant. It mentions that at higher concentration can enhance volume of oil removal.

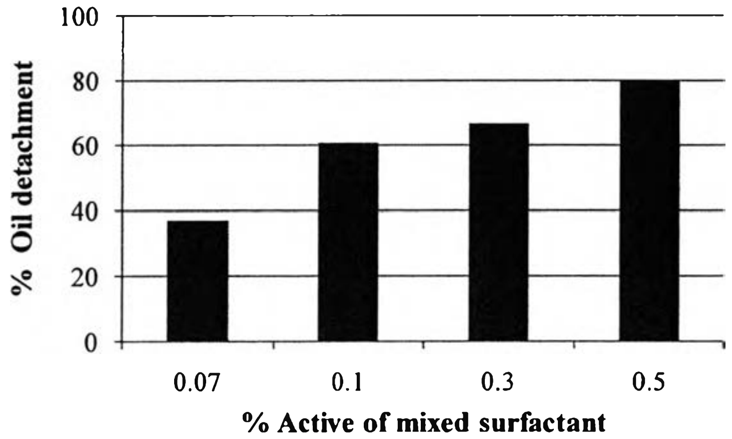


Figure 4.17 % oil detachment as a function of % active of mixed surfactant concentration of the motor oil detachment from dry compressed fabric surface at 30°C.

In figure 4.18 illustrated the contact angle at different % active of mixed surfactant concentration. The result showed that at higher % active of mixed surfactant concentration has the higher the equilibrium contact angle value. It interpreted that surfactant concentration can enhance the equilibrium contact angle value.

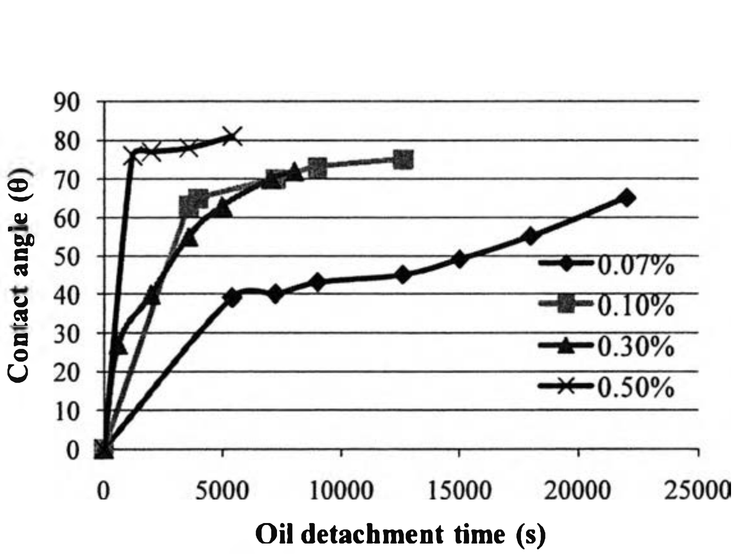


Figure 4.18 Contact angle as a function oil detachment time at different percentage total surfactant concentration of the motor oil detachment from dry compressed fabric surface at 30°C.

On detachment experiments, this research studied the specific the parameters that was used to quantitatively characterize the rate of oil detachment of oil drops from compressed fabric surface in solutions of mixed surfactant. It is worth to mention that the oil detachment time was measured at different total surfactant concentrations without mixing. This is because the solution became turbid and could not be observed the oil detachment. Hence, the oil detachment experiments were conducted under no mixing instead. Figure 4.19 shows the correlation between oil detachment time, oil removal and oil detachment by difference % total active of mixed surfactant. The oil detachment time decreased markedly with increasing total surfactant concentration. The oil removal and oil detachment increased with increasing surfactant concentration. It can indicate that the lower the oil detachment time, the higher the % oil removal and % oil detachment at higher surfactant concentration.

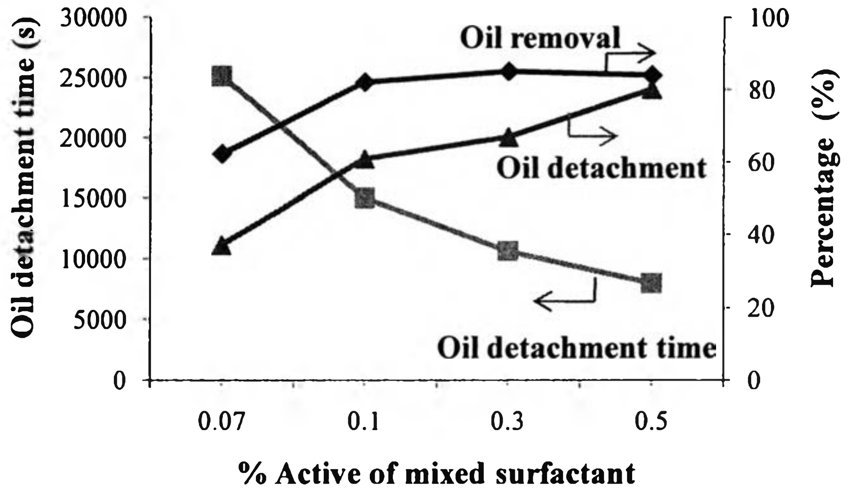
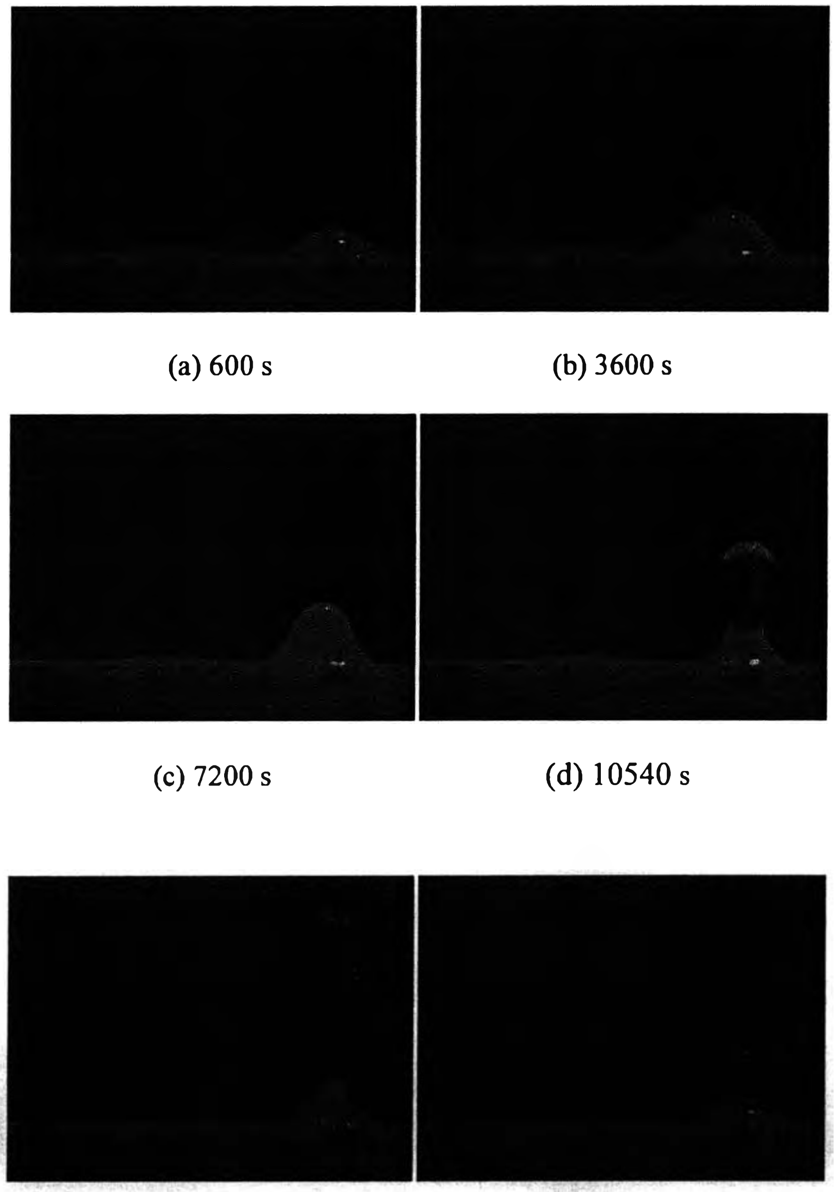


Figure 4.19 Correlation between oil detachment time, % oil removal, and % oil detachment by difference % active of mixed surfactant of 0.1 wt.% Alfoterra 145-3PO and 5 wt.% Tergitol 15-S-5.

4.2.5 Oil detachment at different temperature

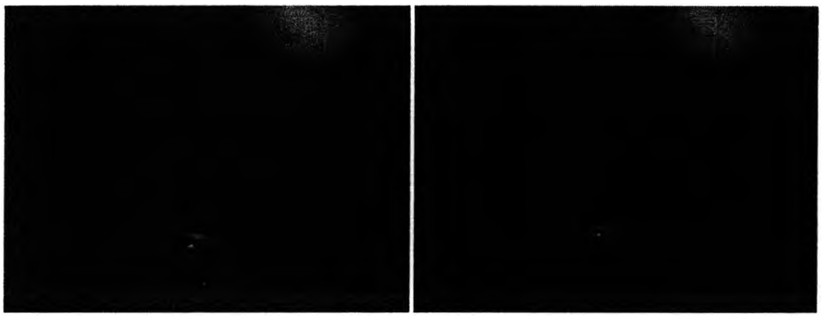


(a) 600 s (b) 3600 s

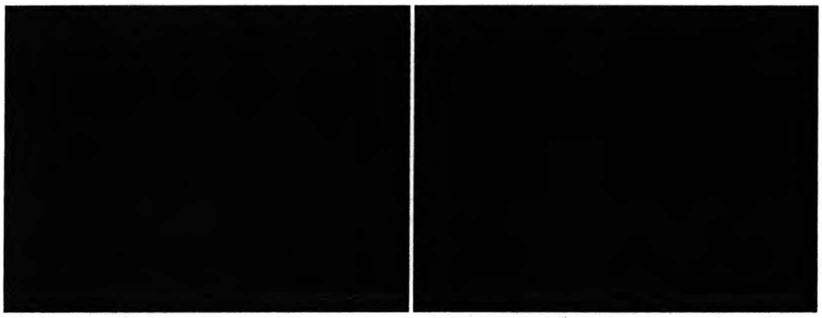
(c) 7200 s (d) 10540 s

(e) 10600 s (f) 10604 s

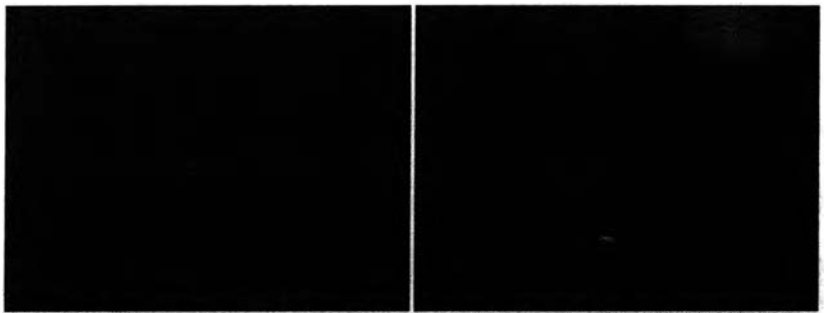
Figure 4.20 Consecutive photos of the motor oil detachment from horizontal dry compressed fabric surface in 0.3 % active mixed surfactant solution at 30°C.



(a) 1800 s (b) 3600 s

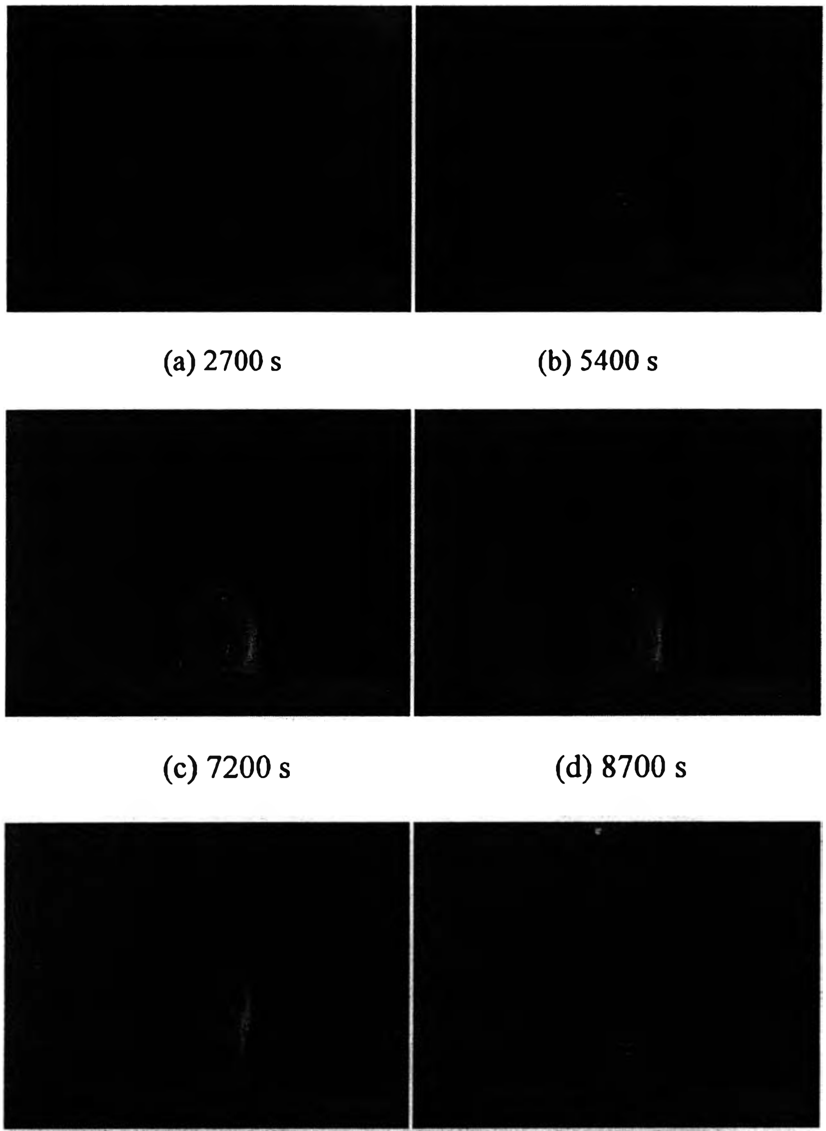


(c) 5400 s (d) 7200 s



(e) 9038 s (f) 9042 s

Figure 4.21 Consecutive photos of the motor oil detachment from horizontal dry compressed fabric surface in 0.3 % active mixed surfactant solution at 40°C.



(a) 2700 s (b) 5400 s

(c) 7200 s (d) 8700 s

(e) 9012 s (f) 9072 s

Figure 4.22 Consecutive photos of the motor oil detachment from horizontal dry compressed fabric surface in 0.3 % active mixed surfactant solution at 50°C.

From oil detachment photo, the residual oil on the compressed fabric surface was determined by integration technique. Figure 4.23 illustrated % oil detachments remained almost unchanged at different temperature. Correspondingly, the contact angle at different temperature remained almost unchanged also as show in figure 4.24. It mentions that temperature can decreased viscosity and increased mobility of oil but can not improve efficiency of % oil detachment.

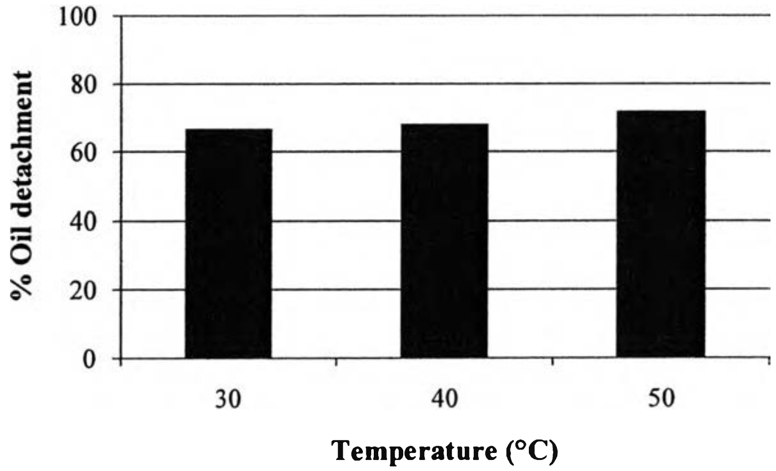


Figure 4.23 % oil detachment as a function of different temperature of the motor oil detachment from dry compressed fabric surface at 30°C.

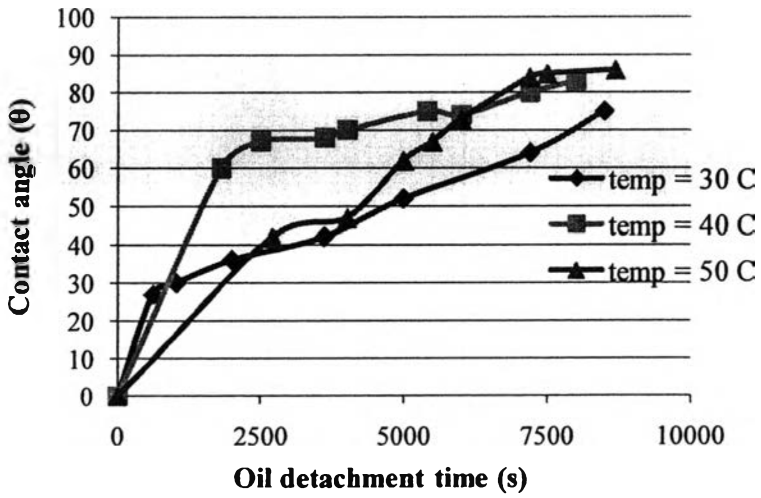


Figure 4.24 Contact angle as a function oil detachment time at different temperature of the motor oil detachment from dry compressed fabric surface.

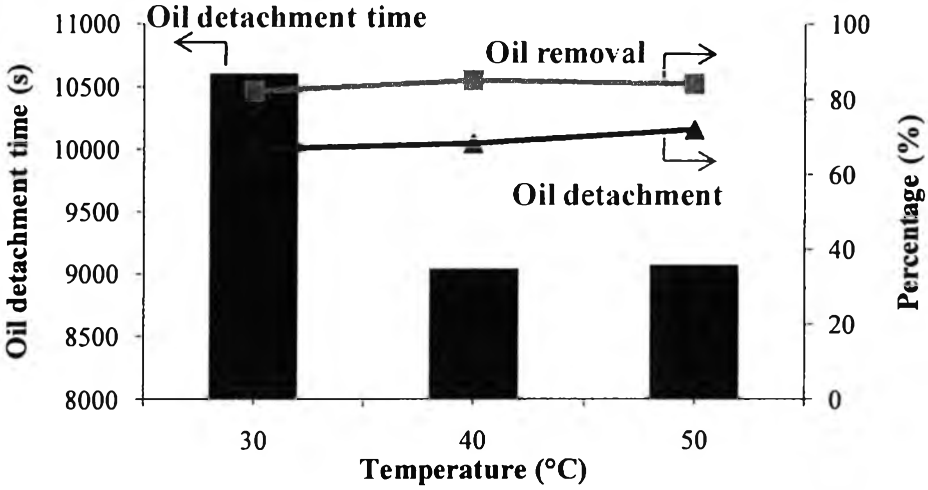


Figure 4.25 Correlation between oil detachment time, % oil removal and oil detachment by different temperature of system of mixed surfactant of 0.1wt% Alfoterra 145-3PO and 5%wt Tergitol 15-S-5.

The correlation between oil detachment time and % oil removal by different temperature system of mixed surfactant, Figure 4.25 shows the correlation between the oil detachment time, % oil removal and % oil detachment at different temperatures. In the studied temperature rang of 30-50°C, the % oil removal and % oil detachment remained nearly unchanged. The oil detachment time decreased significantly when the washing temperature increased up to 40°C.