# CHAPTER IV
# RESULTS AND DISCUSSION

## 4.1 Effect of Surfactant Composition on the Microemulsion Formation

Microemulsion formation is believed to improve the detergency performance during to emulsification and solubilization mechanisms. There are many factors effected the solubilization, such as nature of oil and surfactant, surfactant concentration and temperature (Chantra, 2003)

To achieve the maximum solubilization on the microemulsion formation, each surfactant composition was varied while another surfactant was fixed. Moreover, the salinity scanning with motor oil was studied at each surfactant concentrations.

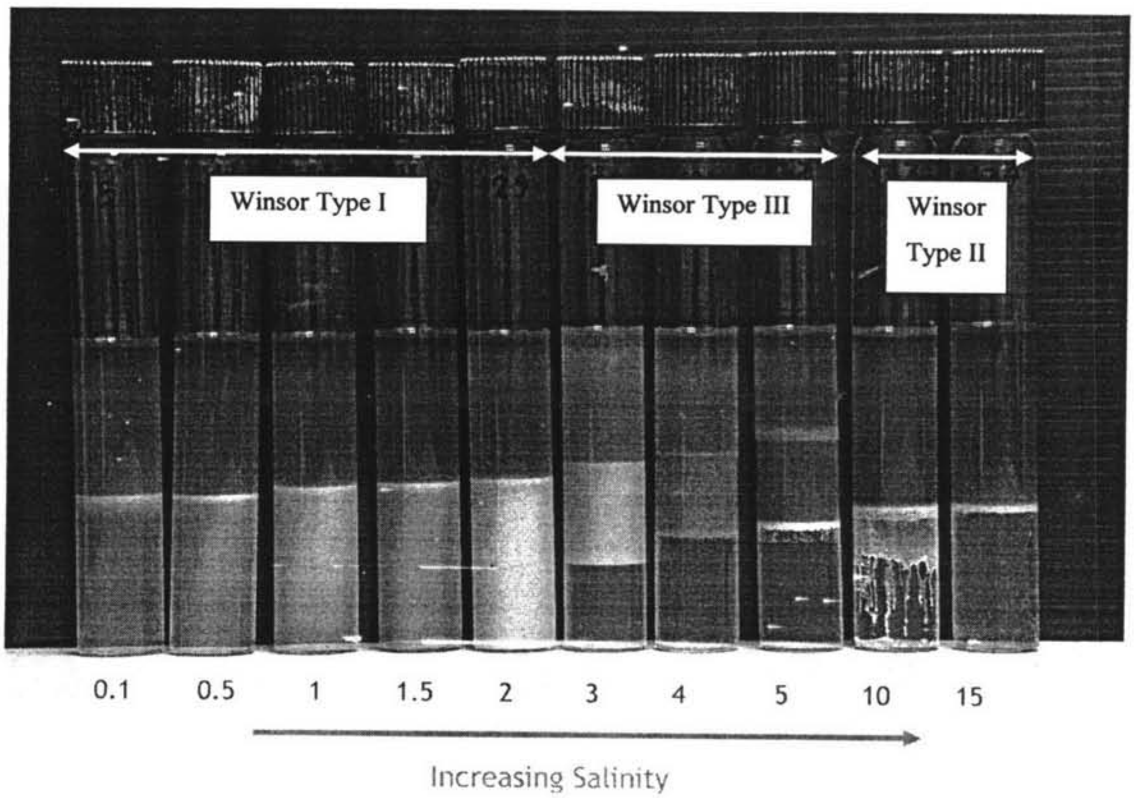


**Figure 4.1** The real microemulsion in the experiment as varying the salinity.

As known from the previous work (Chantra, 2003 and Parichat, 2005), the oil removal in the rinse step is almost as high as that in the wash step for the system operated under the Winsor type III microemulsion condition.

In this study, a mixture of Alfotera 145-3PO, an anionic surfactant, and Tergitol 15S5, a nonionic surfactant which is a secondary alcohol ethoxylate, was used to form microemulsion with motor oil. Many types of nonionic surfactants exist, but the greatest volume used presently in household detergents is oxyethylene or ethoxylate (EO) adducts (Schick, 1967). Mix surfactant systems generally exert grater solubilization than single surfactant system (Ogino, K. and M. Abe, 1997). From Figure 1, microemulsion transition for this system was able to be observed. The optimum salinity ($S^*$) which occurs at the interception of the solubilization parameters between water and oil ($SP_w$ and $SP_o$) can be determined. The $S^*$ provide the highest oil solubilization capacity known as optimum solubilization parameter ($SP^*$). SP is defined as a volume of oil solubilizes or water solubilizes per weight of total surfactants in microemulsion phase.

4.1.1 Effect of Alfotera Concentration

The Tergitol concentration was fixed at 5% and the Alfotera concentration was varied from 0.1% to 1%. The preliminary results show that at higher than 1% of the Alfotera, the mixed surfactant was very turbid and it showed insignificant increase in oil solubilization. Thus the further study was done in this range. Furthermore, the phase transition of each concentration was shown in the Figure 4.1. As expected, an increase in the salinity results the phase transition from Winsor type I to Winsor type III and to Winsor type II. Beside the phase change, the volume of the middle phase is slightly increased when the Alfotera concentration was increased.

In this scanning study, the system of 0.1% Alfotera and 5% Tergitol was selected for further study due to lowest concentration of the Alfotera and the system also provide insignificant different the solubilization from the system with other Alfotera concentrations.

4.1.2 Effect of Tergitol 15S5 Concentration

In the same manner as in the study of the effect of Tergitol 15S, the system was fixed with 0.1% Alfotera and Tergitol was varied at the concentration from 3% to 8%. This is because at lower 3% of the Tergitol, the middle phase microemulsion cannot be observed.

When compared the selected formulation with the previous work (Tongcumpou, C., 2003) which using the mixed of three surfactants to form microemulsion with motor oil, this study found that by using Alfotera which is an extended surfactant, the microemulsion system can be formed with only two surfactants mixture. According to the structure of the Alfotera which contains a very long hydrophobic portion and the Tergitol is the surfactant which is excellent oil soluble emulsifier this leads to an enhancement of hydrophobic oil.

From the study on the effect of surfactant concentration, the solubilization parameter and the optimum salinity were determined and plotted as shown in Figure 4.2 and 4.3 for 4 systems of the varying Alfotera concentrations; (a) 0.1 wt% Alfotera, 5 wt% Tergitol 15S5, (b) 0.3 wt% Alfotera, 5 wt% Tergitol 15S5, (c) 0.5 wt% Alfotera, 5 wt% Tergitol 15S5, (d) 1.0 wt% Alfotera, 5 wt% Tergitol 15S5; and 3 systems of the varying Tergitol 15S5 concentrations; (a) 0.1 wt% Alfotera, 3 wt% Tergitol 15S5, (b) 0.1 wt% Alfotera, 5 wt% Tergitol 15S5, (c) 0.1 wt% Alfotera, 8 wt% Tergitol 15S5, respectively. The result shows an insignificant difference in the solubilization parameter and optimum salinity. However, at the 3% Tergitol concentration, the solution shows phase separation, which is not suitable for liquid detergents. For this reason, the mixture of 0.1% Alfotera and 5% Tergitol was selected for further study. Unfortunately, the effect on detergency performance of the height of the middle phase in the phase study was still ambiguous. This matter remains for our next step.

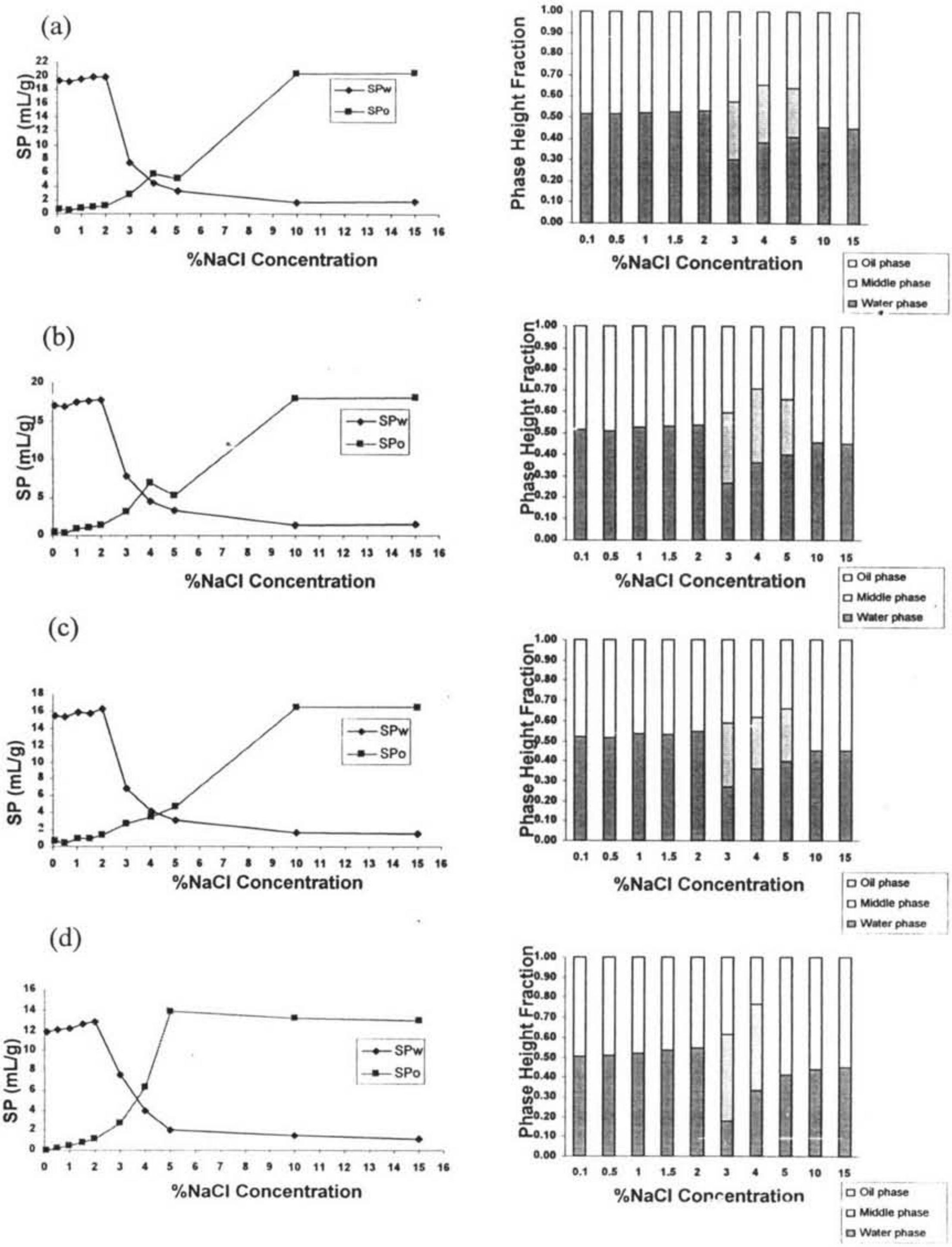


**Figure 4.2** Solubilization parameter as a function of NaCl concentration at different surfactant formulations at the oil to water volumetric ratio of 1 to 1 and Phase transformation , (a) 0.1 wt%Alfotera, 5 wt% Tergitol 15S5, (b) 0.3 wt% Alfotera, 5 wt% Tergitol 15S5, (c) 0.5 wt%Alfotera, 5 wt% Tergitol 15S5, (d) 1.0 wt% Alfotera, 5 wt% Tergitol 15S5.

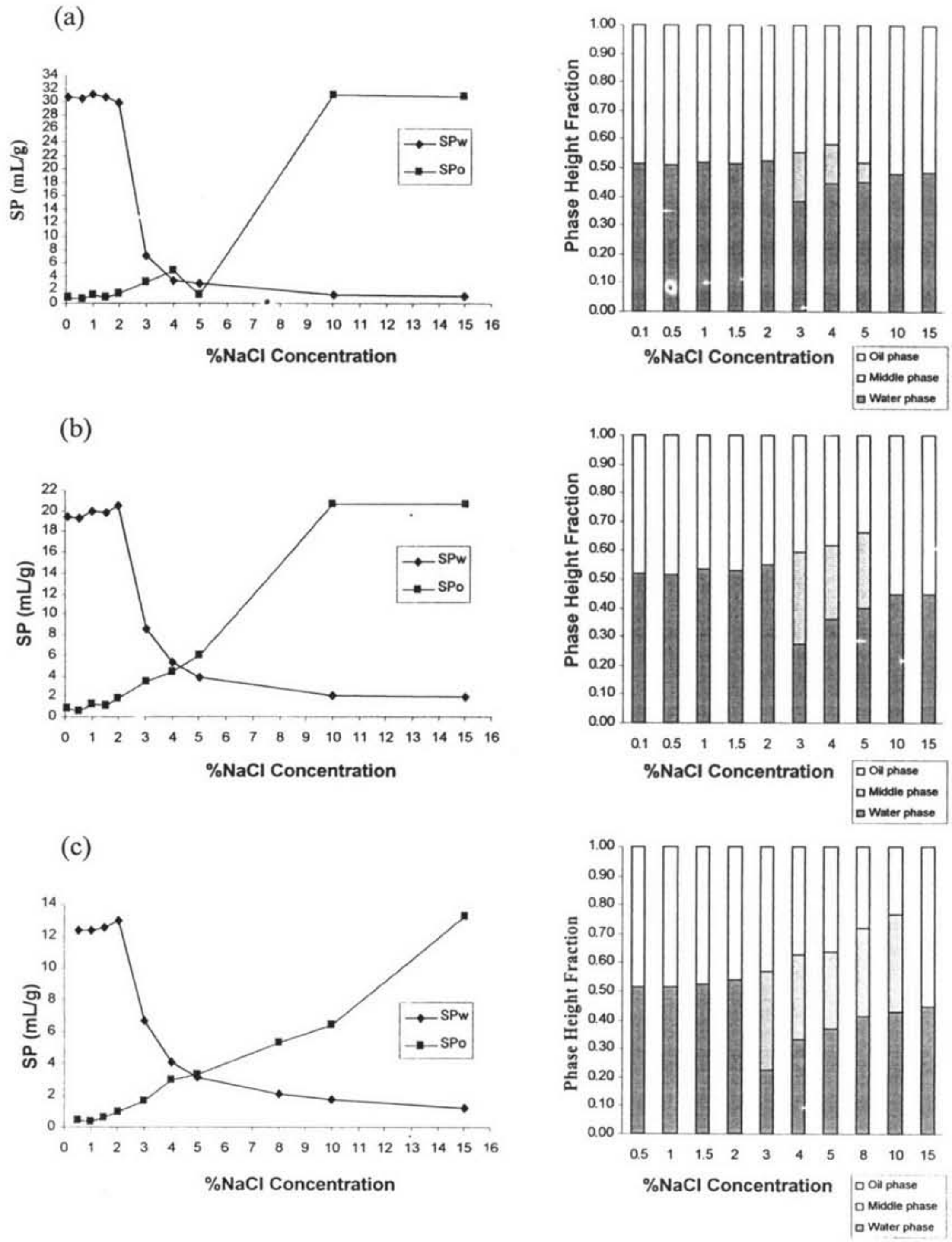


**Figure 4.3** Solubilization parameter as a function of NaCl concentration at different surfactant formulations at the oil to water volumetric ratio of 1 to 1 and Phase transformation , (a) 0.1 wt% Alfotera, 3 wt% Tergitol 15S5, (b) 0.1 wt% Alfotera, 5 wt% Tergitol 15S5, (c) 0.1 wt% Alfotera, 8 wt% Tergitol 15S5.

## 4.2 The Detergency Performance Study

The correlation of phase behavior of microemulsion systems and detergency performance has been studied comprehensively for decades (Chantra, 2005)

### 4.2.1 Effect of Composition of Mixed Surfactant

From the phase behavior study, the three systems of different concentrations of Tergitol at 3%, 5% and 8% were selected for laundry experiments. The experiments were carried out at different concentrations of salt in washing solutions. However, for all three cases, the detergency performance results were insignificant different as shown in the Figure 4.4. Therefore, the system with 5% Tergitol was selected further study.

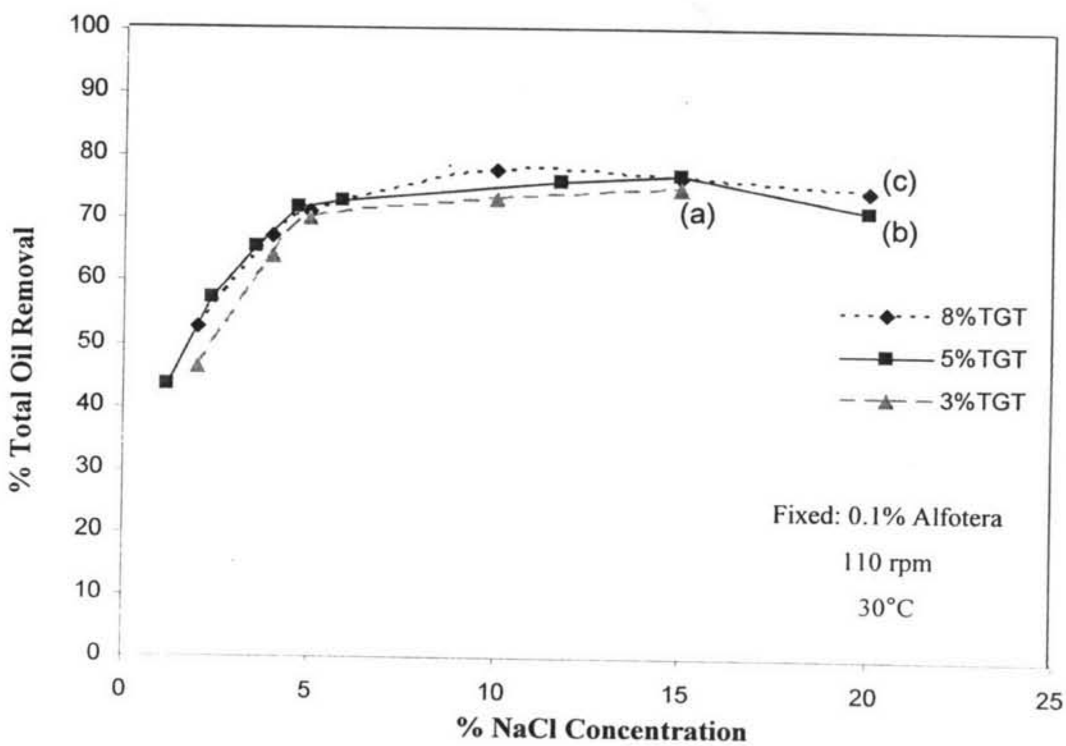


**Figure 4.4** Total oil removal at the different Tergitol concentration as a function of salinity, ( a) 0.1% wt Alfotera and 3% wt Tergitol, (b) 0.1% wt Alfotera and 5% wt Tergitol, (c) 0.1% wt Alfotera and 8% wt Tergitol.

4.2.2 Effect of Salinity Concentration

The effect of NaCl concentration on detergency performance was carried out by varying salinity concentration of the formulation; 0.1 wt% Alfotera, 5wt% Tergitol. As shown in Figure 4.5, significant improvement of the detergency performance was obtained when the salinity was increased. This is may be because a lower repulsive force between the head groups of the anionic surfactant is obtained. And lower IFT at the higher salinity. Although at 15% concentration of the salinity presented the maximum of oil removal, the higher salinity concentration greatly damages the washing machine. The mixture of 0.1% concentration of Alfotera and 5% concentration of Tergitol at 5% concentration of salinity, which can shown 82.04% oil removal, was selected as the most interesting for real applications and environmental concerns.

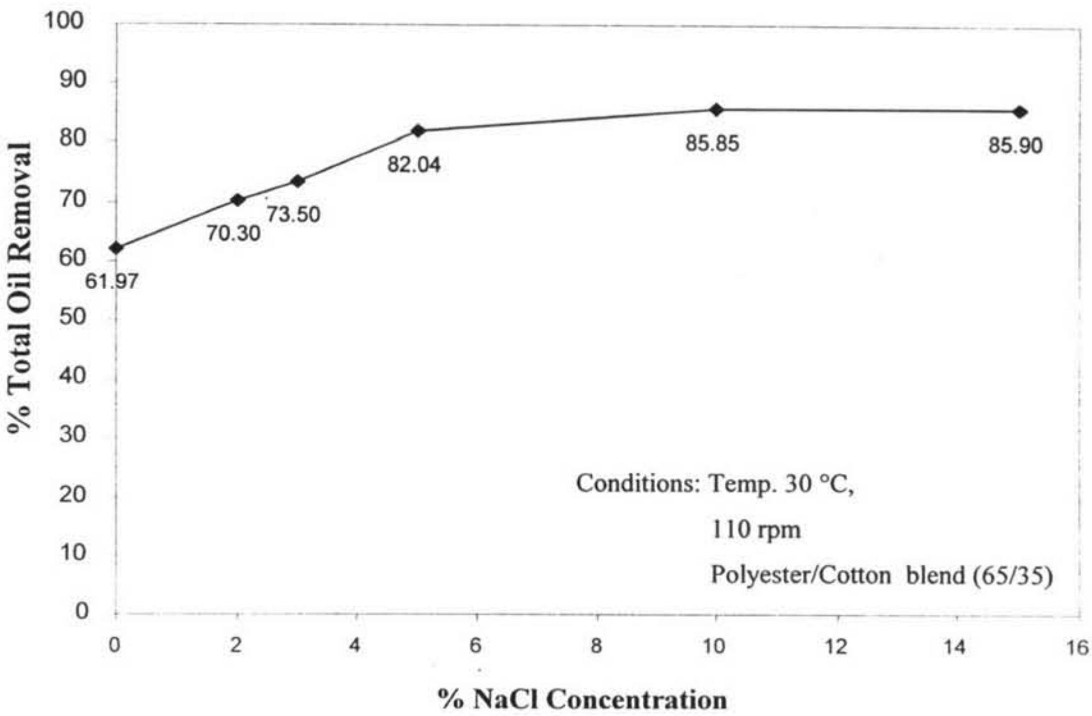


**Figure 4.5** Total oil removal as a function of salinity using the selected formulation, 0.1% wt Alfotera and 5% wt Tergitol, at 0.3% active surfactant.

4.2.3 Effect of Salinity Concentration on Interfacial Tension

In this study, the selected formulation was measured the interfacial tension as varying salinity. There are reported that the maximum detergency corresponding to the minimum IFT (Azemar, 1997 and Gole, 2000). As expected the minimum interfacial tension was found at the optimum salinity. The interfacial of the selected formulation showed the value about 0.033 mN/cm when the oil meet the solution about 10 minute. The washing time was increased; the lower interfacial tension was obtained which resulted in detergency performance to the maximum levels. However, about 20 minute used in washing step in the experiment, the selected formulation exactly reach the ultra low interfacial tension.

By the way, the IFT of the commercial liquid detergent at the same active concentration was measured. This IFT is not reach ultra low value.

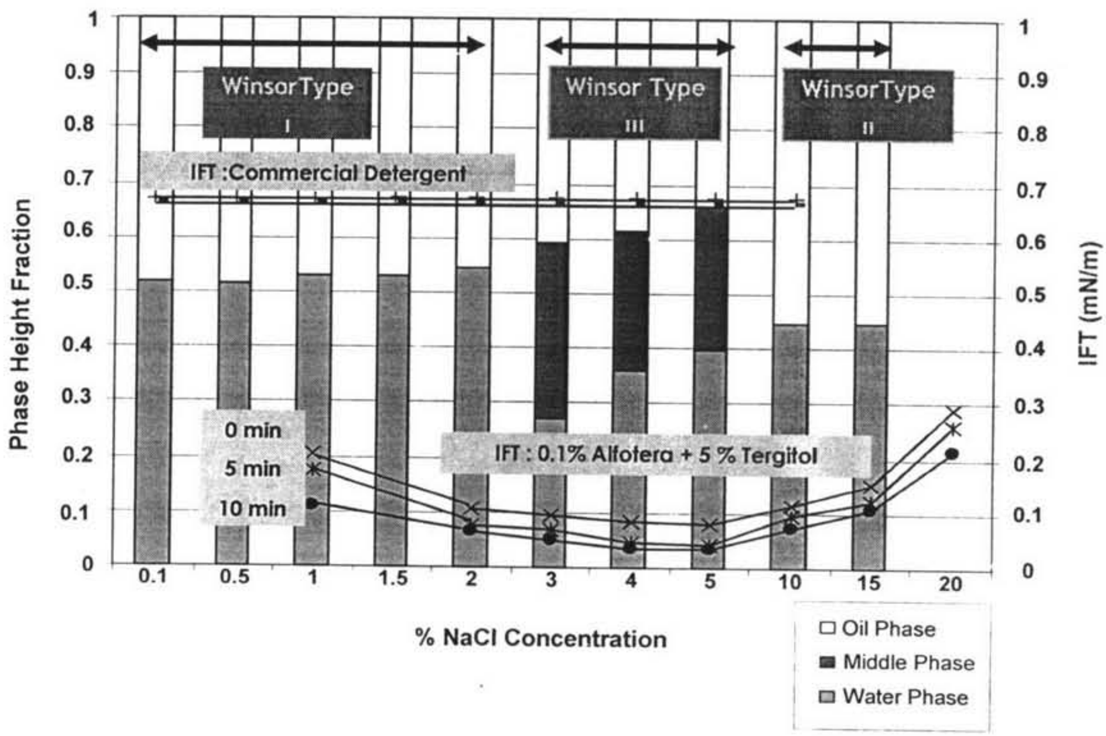


**Figure 4.6** The interfacial tension at anytime between the water phase the oil phase as a function of salinity using the selected formulation, 0.1% wt Alfotera and 5% wt Tergitol, at 0.3% active surfactant.

## 4.3 Effect of Surfactant Concentration on Detergency Performance

In order to minimize the surfactant used for laundry, the study for optimum active concentration of the selected surfactant solutions was determined. Solans, C., and Azemar, N. (1992) reported that 80% detergency was achieved for a pure nonionic surfactant, $C_{12}EO_4$, with the same polyester/cotton fabric. However, the active concentration used in their study was 1%, which is four times higher than that used in the present study. In this study, varying of active concentrations for the system at 0.1% Alfotera 5% Tergitol and 5% salinity was conducted for detergency experiments and also compared with the commercial liquid detergent.

The results as shown in Figure 4.7, the graph for our surfactant solution was found to be plateau from 0.1% active concentration and getting to be constant at around 0.3% active concentration. As a result, we consider at 0.3% which showed the detergency performance at about 83% of the studied formulation as an optimum concentration for household applications which is the lowest active concentration recommended in the range of 0.3%-0.8% active concentration of commercial detergents (Jakobi G., 1987).

In addition, we found that our formulation shows better detergency performance than the commercial grade liquid detergent at all cases. The result from this study can be confirm the correlation of improving detergency with decreasing IFT, consistent with several previous studies (Raney, 1991 Azemar, 1996, Gole, 2000). Surprisingly, our formulation, the mixture of 0.1% Alfotera and 5% Tergitol, showed the extremely high oil removal at the same active concentration when compared with the commercial grade detergent.

Moreover, the visualization detergency performance was observed. The detergency performance by visualization showed in Figure 4.8. The detergency performance sometime will mention by visual check The swatch after washing by selected formulation show rather satisfied detergency performance.

The detergency performance for removing the motor oil at this research had compared to the previous research; Chantra T. (2003), Parichat K. (2004), and Pantipa R. (2005) as show in Table 4.1.

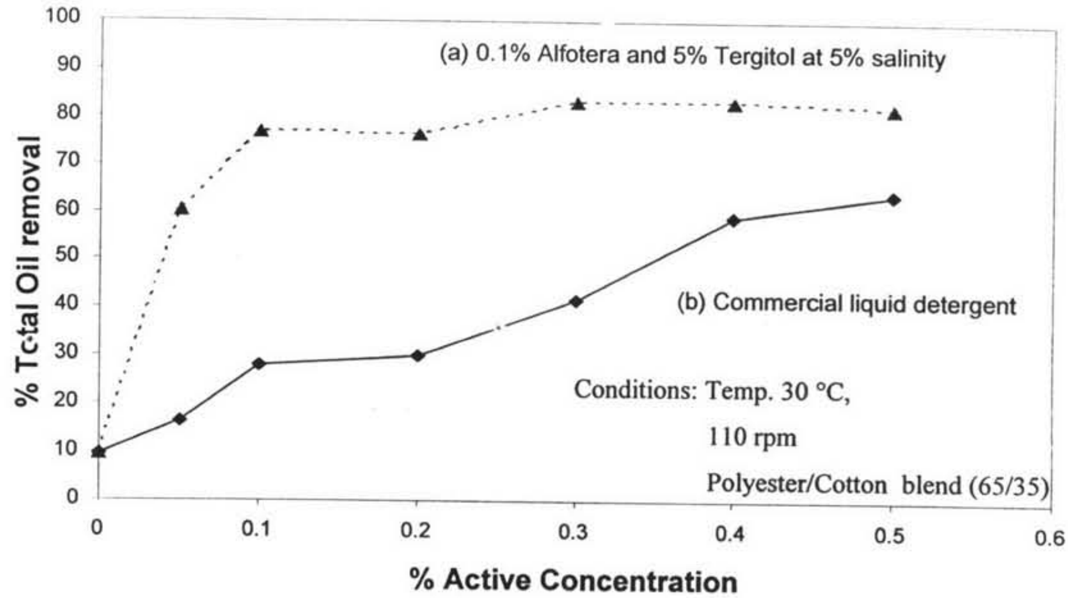


**Figure 4.7** Total oil removal as a function of active concentration the selected formulation , (a) 0.1% Alfotera and 5% Tergitol, at 5% salinity and (b) Commercial liquid detergent.

(a) Unsoiled Fabric (b) Soiled Fabric (c) Fabric after washing

**Figure 4.8** The detergency performance by visualization, (a) Unsoiled Fabric, (b) Soiled Fabric with motor oil and (c) Fabric after washing with 0.1% Alfotera and 5% Tergitol, at 5% salinity at 0.3% active concentration.

| Comparison | Chantra T., 2003 | Parichat K., 2004 | Pantipa R., 2005 | Thitima R., 2006 |
|---|---|---|---|---|
| Selected Formulation | 2% ADPODS<br>3% AOT<br>2% SPAN 80 | 1.5% ADPODS<br>5% AOT<br>5% SPAN 80 | 0.5% ADPODS<br>5% AOT<br>3% SPAN 80 | 0.1% Alfotera 145-3PO<br>5% Tergitol 15S5 |
| % Total Surfactant Concentration | 7 | 11.5 | 8.5 | 5.1 |
| % Active Concentration | 0.112 | 0.1 | 0.119 | 0.3 |
| % Salinity | 12 *, 16 | 2.83 | 3 | 5 |
| % Temperature | 30°C | 30°C | 30°C | 30°C |
| % Maximum Detergency<br>(At selected formulation) | 75 *, 78 | 80 | 80 | 82.04 |
| Detergents Regulation | ADPODS can be used in I&I **applications until Oct 2007 | | | Passed |

* In the solubilization region

** Industrial and institutional (I&I) detergents/cleaners.

**Table 4.1** The detergency performance for removing the motor oil comparison table, Chantra T. (2003), Parichat K. (2004), Pantipa R. (2005), and Thitima R. (2006)

## 4.4 Effect of Temperature on Detergency Performance

For a non-ionic surfactant, an increase in temperature generally results in an increase in the extent of solubilization for both polar and nonpolar oil. Figure 4.9, shows the relationship between detergency performance and temperature, the detergency performance at the mixture of 0.1% Alfotera and 5% Tergitol is obviously increased by temperature. Nevertheless detergency performance slightly decreases when the temperature is increased over 50°C.

There are several works have been done to confirm the optimum detergency correlated with PIT (phase inversion temperature) for nonionic-anionic mixtures due to the lower IFT of the systems at higher temperature. This is attributed to an ultralow oil/water interfacial tension encountered with these surfactants near their PIT, with increase necking and emulsification of oily soil leading to enhance detergency (Thompson, 1994). However, an anionic system may be considered as insensitive temperature for IFT changes, temperature plays another role on reducing viscosity of oil and may results to mobilization of oil from fabric surface (Powe, W.C., 1963 and Kissa E., 1971). This may be an explanation for our result.

Tergitol 15S5 is a surfactant that is dispersible but insoluble in water, it does not have an exact cloud point temperature and can degrade if the temperature is increased over 50°C. There was a report about the temperature of optimum detergency efficiency of alcohol exthoxylate, $C_{12}(OE)_5$, nonionic surfactant/hexadecane system as a function of electrolyte concentration. The optimum temperature is 52 °C (Azemar N., Carrera I., Solans C., 1993). As a result, our recommendation for detergency by the mixture of 0.1% Alfotera and 5% Tergitol 15S5 should be in the range of 30°C-50°C since the performance slightly decreases above 50°C.

In order to achieve a greater understanding of the effect of temperature on detergency performance, the detergency experiments at the same temperatures with only water was carried out. The result of the solely water washing shows the same trend that the higher temperature, the high oil removal. Nonetheless, the higher temperature with solely water washing was found less effect on oil removal as compared to the washing with the surfactant solution. This may be explained by the fact that mobilization of oil from fabric surface by heating can occur at some extent, however, to associate with the surfactant solution that provides low IFT can enhance degree of oil removal.

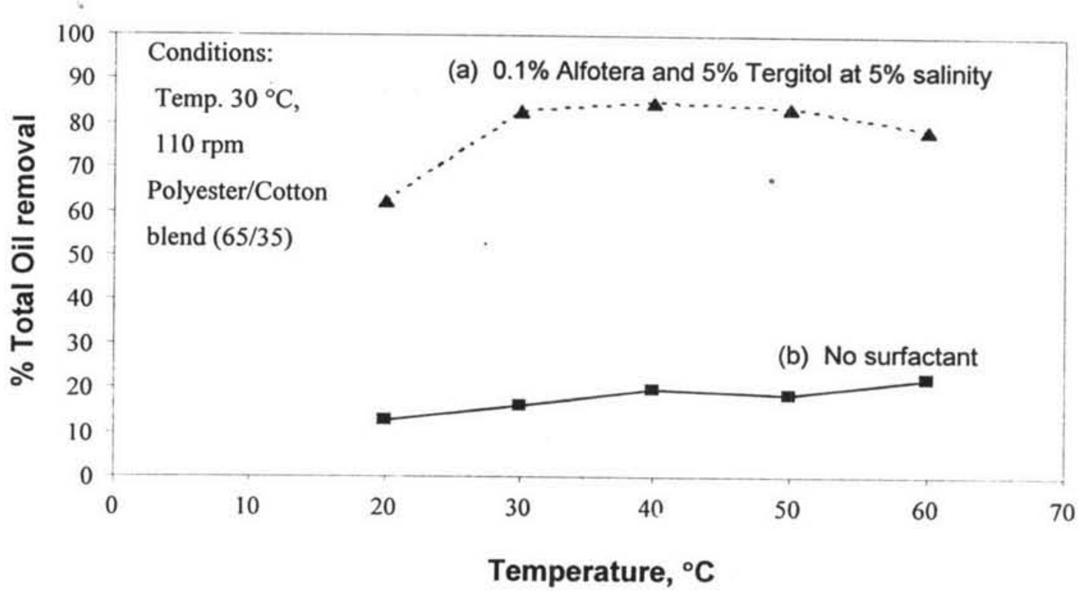


**Figure 4.9** Total oil removal as a function of active concentration the selected formulation, (a) 0.1% wt Alfotera and 5% wt Tergitol, at 5% salinity, (b) no surfactant.

### 4.5 Effect of Re-wash and Pretreatment on Detergency Performance

In order to achieve the higher percentage of total oil removal, the re-wash has been study in this work. It is said that the re-wash is the increasing of total oil removal, from the Figure 4.10. However, the improvement was only advantaged in the second wash. The third wash is no insignificance. According to the first wash, the large amount of oil was removed (82.04% Total oil removal). The second wash can play easily detach the left oil on the fabric (88.61% total oil removal).

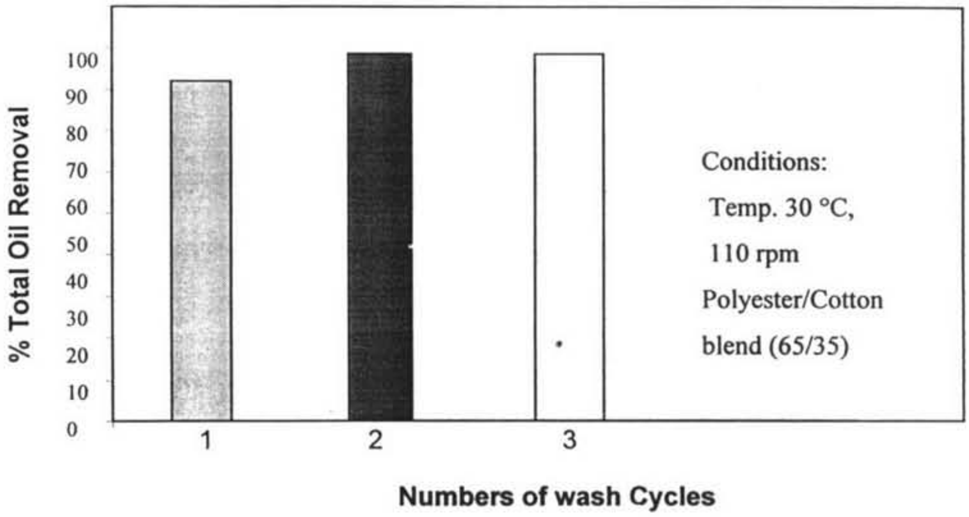


**Figure 4.10** Total oil removal as a function of numbers of wash cycles of selected formulation, 0.1% Alfotera + 5% Tergitol + 5% NaCl at 0.3% active concentration.

The efficiency of total oil removal of the pretreatment was illustrated in Figure 4.11. The pretreatment solution is the same surfactant concentration and equal of amount of surfactant as the selected formulation, 0.1%Alfotera and 5%Tergitol at 0.3% active concentration. It was said that the pretreatment totally improved the total oil removal according to the high concentration of surfactants and higher adsorption time. The total oil removal of pretreatment were extremely increased both pure water and commercial liquid detergent which are wash solution after pretreatment. However, the total oil removal was slightly increased on the selected formulation.

In order to study the effect of the pretreatment, the commercial liquid detergent had been used as the pretreatment solution. The oil removal when soak the commercial liquid detergent as a pretreatment solution is not quite high as compare to our selected formulation. Tergitol 15S5 is the excellent chemical used in prewash spotter or pretreatment solution due to the low foam property. In addition, 5% salinity was added into the pretreatment solution in order to enhance the efficiency of pretreatment. Unfortunately, the addition of salinity had no effect the pretreatment efficiency. However; the lower amount of salinity concentration, the lower damage the cloth and the washing machine beside the environmental problem.

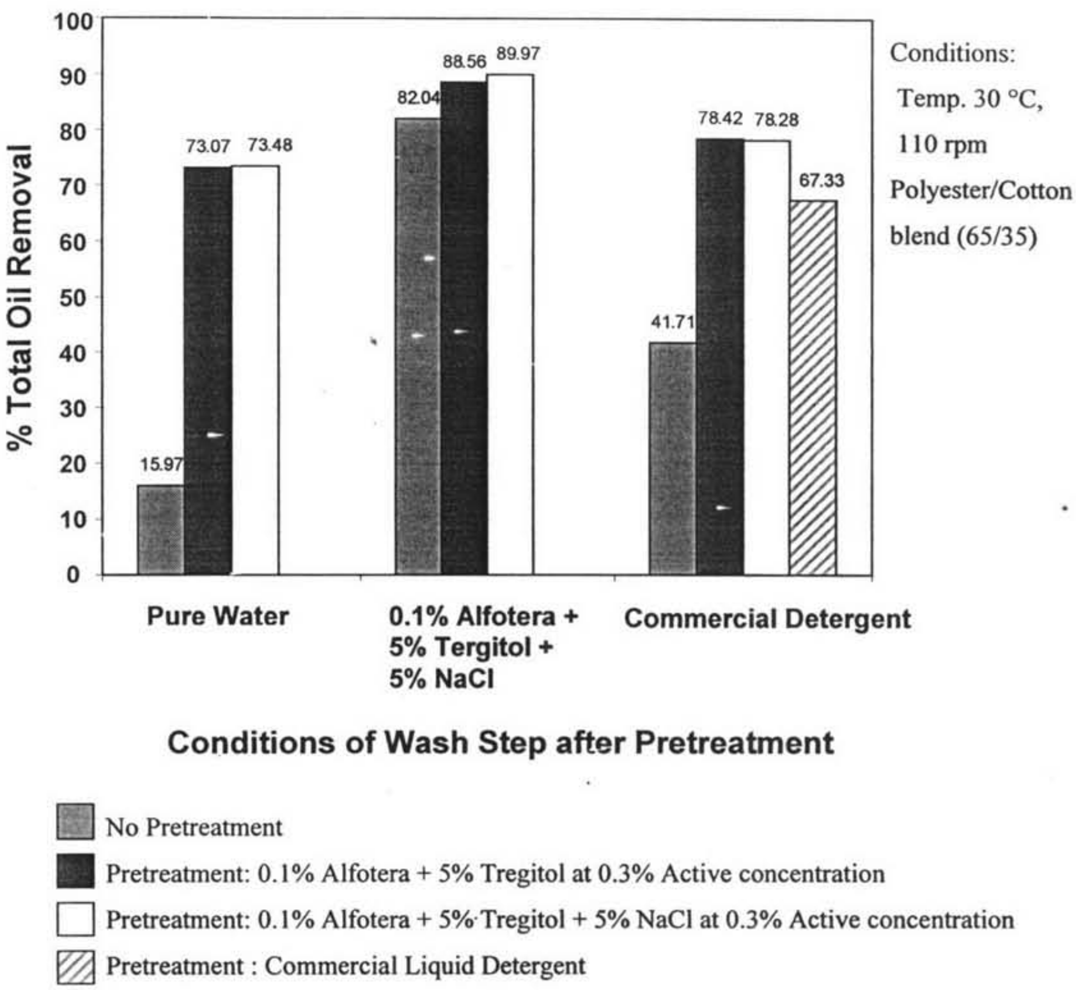


**Figure 4.11** Total oil removal comparison at different wash step after pretreatment condition.

Moreover, the pretreatment was studied to compare the efficiency with the re-wash cycles. From the Figure 4.12, the total oil removal of pretreatment without salt showed 88.56 % total oil removal which is not significant difference from the total oil removal of the second wash cycles (88.61%). By the way, the lowest times of wash cycles needs to be considered. The use of lower numbers of wash cycles could result in a substantial reduction in the amount of energy and water used in laundering. The pretreatment before normal washing is an advantage to improve the efficiency of detergency.

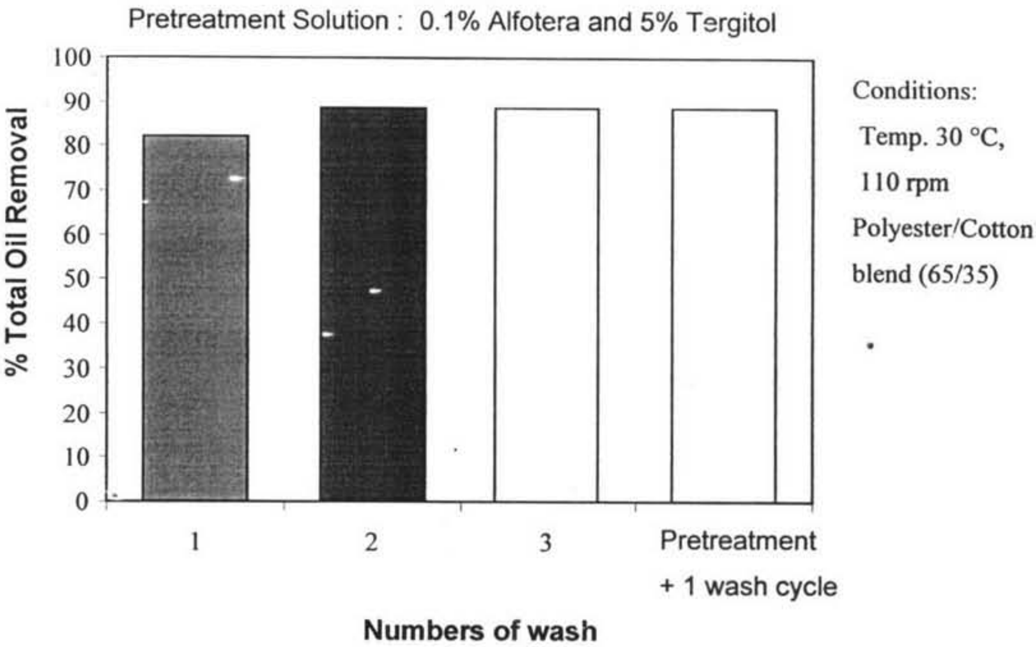


**Figure 4.12** Total oil removal as a function of numbers of wash and pretreatment.

The pretreatment had studied as varying the amount of pretreatment solution as show in the Figure 4.13. The pretreatment at 0.3% active concentration of the selected formulation, 0.1%Alfotera and 5% Tergitol , was used at the equal amount as washing solution (1 time). The result show that the total oil removal is not significance improved when the amount of pretreatment solution increased to 2 or 3 times and wash with the selected formulation as a normal wash. The 0.25 time amount of the mixture of 0.1% Alfotera and 5% Tergitol at 0.3% active surfactant concentration used as the pretreatment solution show the excellent detergency performance due to the less of amount used. However, the total oil removal is slightly increased with high amount of pretreatment solution and wash with distillated water. It is due to no salinity in the system. The increasing of the total oil removal is obtained by increasing the amount of pretreatment solution or surfactant.

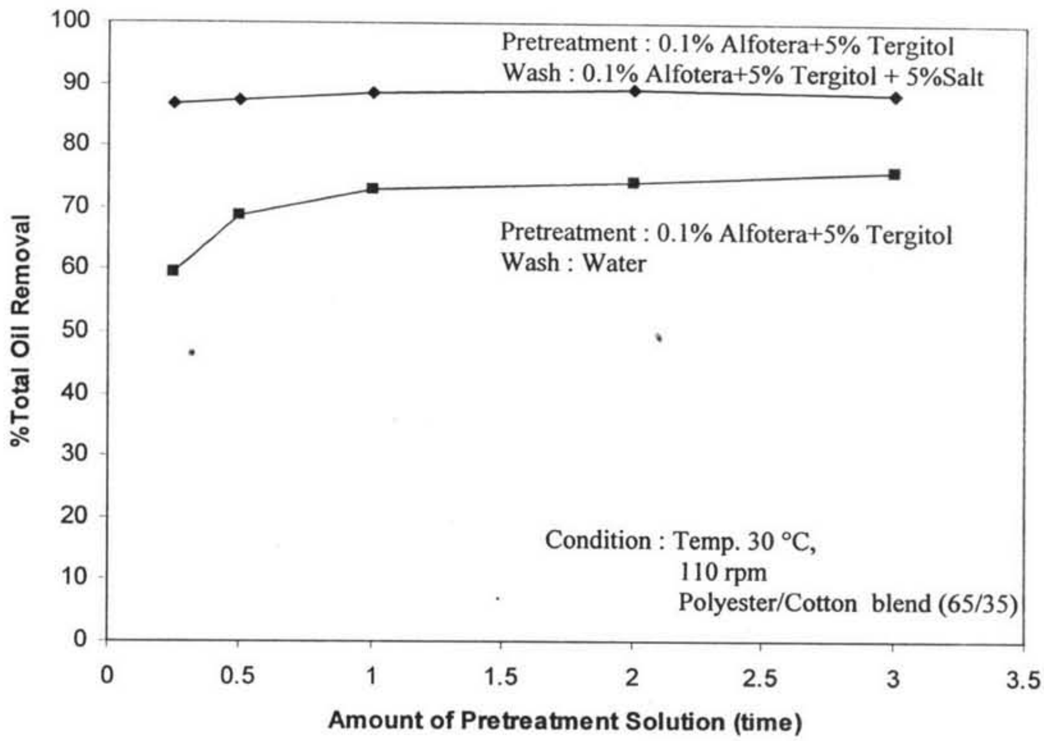


**Figure 4.13** Total oil removal comparison as a function of amount of pretreatment solution at 0.3% active surfactant concentration of the mixure of 0.1% Alfotera and 5% Tergitol.

### 4.6 Correlation of Oil Removal and Interfacial Tension

In this study, the washing experiment was done with the selected formulation (0.1 wt% Alfotera, 5wt% Tergitol) and 0.3% active concentration as varying the salinity. The comparison of oil removal of each step in detergency process is illustrated in the Figure 4.14. Interestingly, there was significance different in the step of oil removal between salt presented and no salt presented. The result shows clearly that the amount of salt affect the oil removal step.

In the Figure 4.15, about 46% oil was removed in wash step by our selected formulation without the salinity presented. In the rinse steps, the oil removals were less than 10%. As the present of salinity, the large amount of oil was removed in the first rinse. The increasing in the salinity results the increasing in the oil removal in second rinse. However, the oil removal in was step was decrease when the salinity was increased.

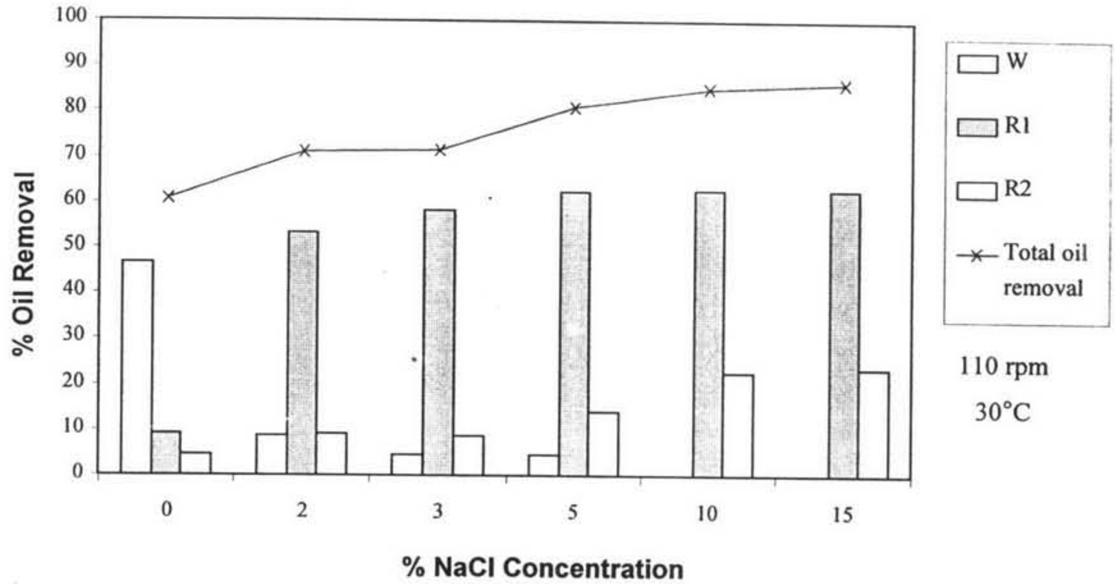


**Figure 4.14** The oil removal of each step and the total oil removal with different NaCl concentration using the selected formulation, 0.1% Alfotera and 5% Tergitol at 0.3% active surfactant concentration.

Figure 4.15, 4.16 and 4.17 show oil removal and IFT at wash, the first rinse and the second rinse, respectively. In Figure 4.14, when the salinity presented, the IFT was sharply decreased and a small amount of oil was removed. By the present of salt, the IFT values are very low leading to spreading effect of the oil on the fabric. As a result, it is more difficult for the oil to be removed in wash systems. This is why the oil removed of the washing step in this study due to a small amount of the oil removed. This result is good agreement with previous results (Tongcumpua, 2003 and Korphol, 2004)

This phenomenon can be understood using the concepts of cohesion and adhesion work ($W_C$ and $W_A$) (Thomson, 1994)

$$W_C = 2\Upsilon_{o/w} \quad (4.1)$$

$$W_A = \Upsilon_{o/w}(\cos\theta + 1) \quad (4.2)$$

where $\Upsilon_{o/w}$ (IFT) is the IFT between oil and the surfactant solution. Hence, the reduction of IFT reduces the cohesion work that leading to easily snap off of the oil deposited on the fabric surface.

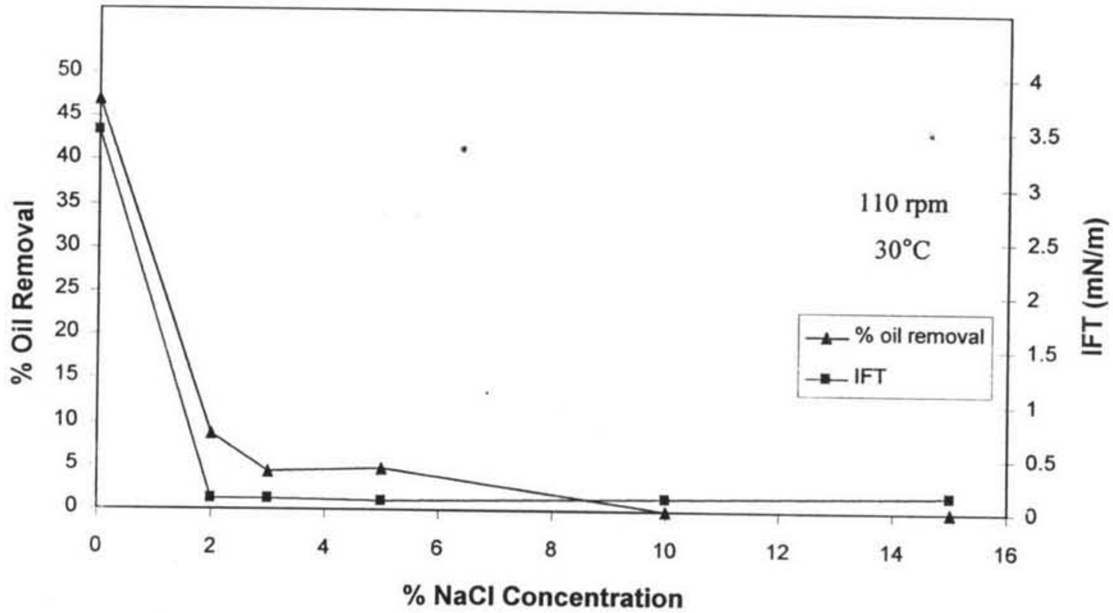


**Figure 4.15** The Oil removal and the IFT between oil and wash solution at various salt concentration using the selected formulation, 0.1wt% Alfotera 5 wt% Tergitol.

The interfacial tension at no salt present show the highest oil removal although the IFT values shows is high. It is not reach ultra low interfacial tension. The oil removed might be remove form other forces, not microemulsion, such as aggregation force. Thompson, 1994 argued that maximum detergency did not always correspond to the minimum interfacial tension of the system and proposed another mechanism by which the maximum detergency might correlate with an increase in oil/substrate contact angle.

In Figure 4.16 illustrate the % oil removal and the IFT between oil and the first rinse solution at various salt concentrations. The IFT in the first rinse were found to be much higher than that of the wash step that bring the reducing in the spreading effect. According to the lost of surfactant in rinse solution, the IFT has been increased. In addition, the rinse solution no salt is added to the solution, then

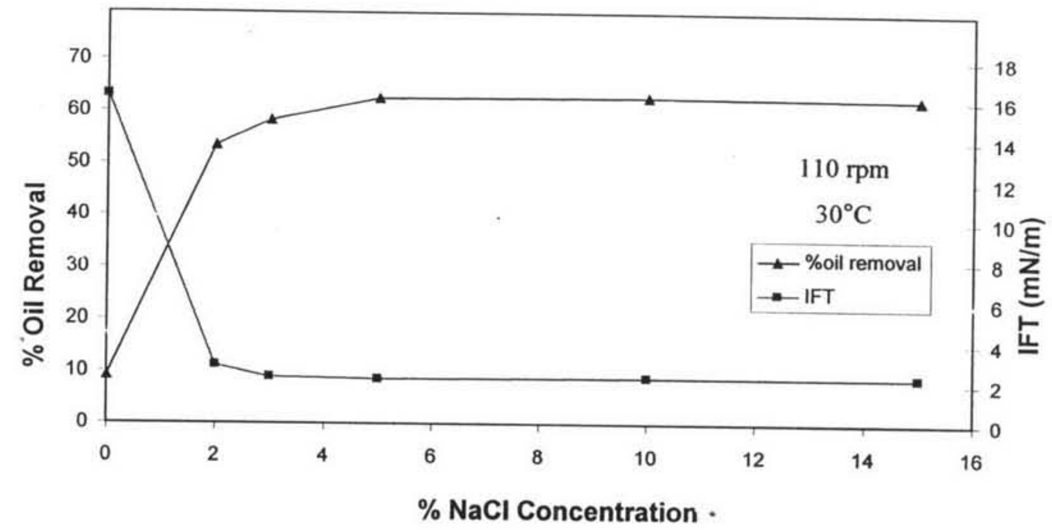


**Figure 4.16** The Oil removal and the IFT between oil and the first rinse solution at various salt concentrations using the selected formulation, 0.1wt% Alfotera 5 wt% Tergitol.

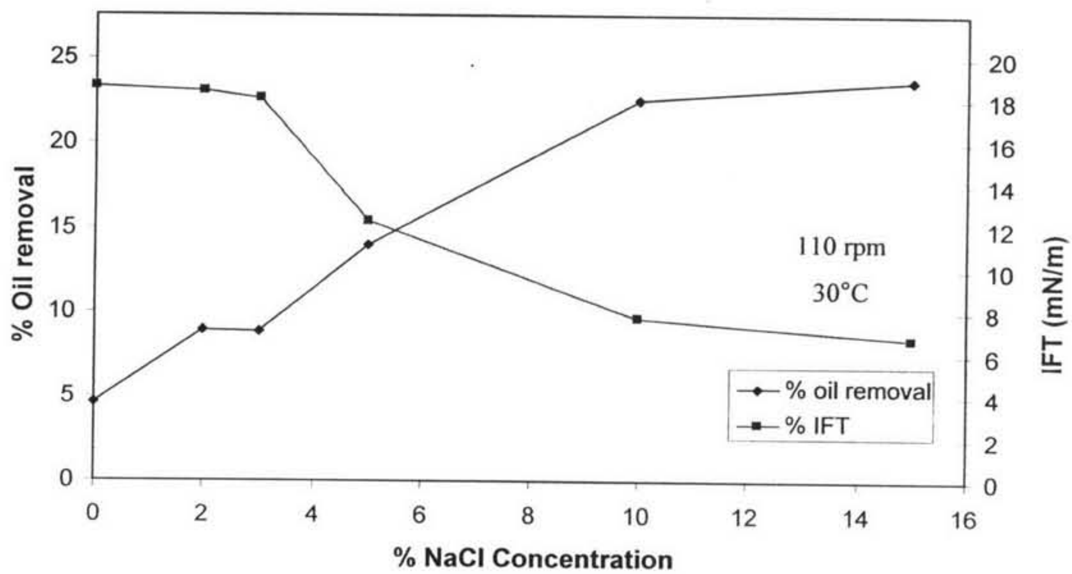


**Figure 4.17** The Oil removal and the IFT between oil and the second rinse solution at various salt concentrations using the selected formulation, 0.1wt% Alfotera 5 wt% Tergitol.

the system should be at salt concentrations that correspond to the Winsor Type I which far away from the optimum condition leading to discontinuity and the detachment by emulsification or roll up mechanism of the oil into the rinse solution (Rosen, 1988).

In the second rinse, the percentage of oil removal and the IFT between oil and rinse solution at various salt concentrations was shown in the Figure 4.17. It showed a very high IFT when compared with the first rinse. The oil removed in the second rinse was increased as the salinity increase.

The hypothesis of the mechanism that correlate the oil removal and the IFT in each step need to be shown. In the wash step, the spreading effect was occurred that leading to a small amount of oil removed in wash step. Anyhow, the salinity in the wash step was increased; it might be caused the more spreading and more stable deposit on the fabric surface that show the no removal of the oil at high salinity concentrations in the wash step (Figure 4.14). In the first rinse step, a large amount of oil was removed which is approximately 60% maximum (Figure 4.15). Hence, the spreading oil was not completely removed in this step by roll-up and emulsification mechanisms when the high salinity in the wash step was presented. In the second rinse step, the oil removed was increased as the salinity increase in the wash step (Figure 4.16). It might be confirmed that in the first rinse can not removed some surfactant and oil which coat on the fabric surface at the high concentration of salinity. The IFT in the second rinse were therefore decreased as increase the salinity in the wash step. The decreasing of the IFT shows that there was the surfactant in the second rinse. Hence the oil can be removed in the second rinse by another mechanisms, surfactant force and/or agitation force.

However, the relative order oil removal at the high concentration of the salinity is not relevant to actual application since the salinity is the major caused to damage the washing machine. The hypothesis that a microemulsion film formed at the high concentration of the salinity difficultly removes needs to be explored more fully; further studies should attempt to identify and characterize such film.