CHAPTER IV
RESULTS AND DISCUSSION

4.1 Effect of Hardness on Phase Behavior

For microemulsion formation with motor oil based on our previous work, a mixture of 0.1wt.% Alfoterra 145-3PO, an anionic extended surfactant, and 5wt.% Tergitol 15-S-5, a nonionic surfactant which is a secondary alcohol ethoxylate, was used as a base condition in this study. The phase behavior was illustrated by the solubilization parameters of water and oil (SPw and SPo) as well as optimum salinity (S*) which occurs at the interception of SPw and SPo. At the S* point, the solubilization parameter is known as the optimum solubilization parameter (SP*) which provides the highest oil solubilization capacity of a system. SP is defined as a volume of oil solubilized (SPo) or of water solubilized (SPw) per weight of total surfactants in the microemulsion phase. The details of an determination of SPo and SPw is explained elsewhere (Tongcumpou, 2003; Healy, 1976).

4.1.1 Effect of Hardness on Solubilization Parameter

In order to observe the effect of hardness on solubilization parameter with motor oil, both of Alfoterra 145-3PO and Tergitol 15-S-5 concentrations were fixed at 0.1wt.% and 5wt.%, respectively, and hardness was varied from 0 ppm to 1000 ppm. From Figure 4.1, as the hardness concentration increases, the interception of SPw and SPo or the optimum salinity (S*) appears at a slightly lower salinity. This is because the hardness (divalent cations) in the washing solution can precipitate the anionic surfactant, Alfoterra 145-3PO. Thus, the Alfoterra 145-3PO concentration decreases, affecting the phase diagrams of microemulsions as indicated by the change of the optimum salinity especially at a very high salinity. However, the effect of hardness on microemulsion was not significant.

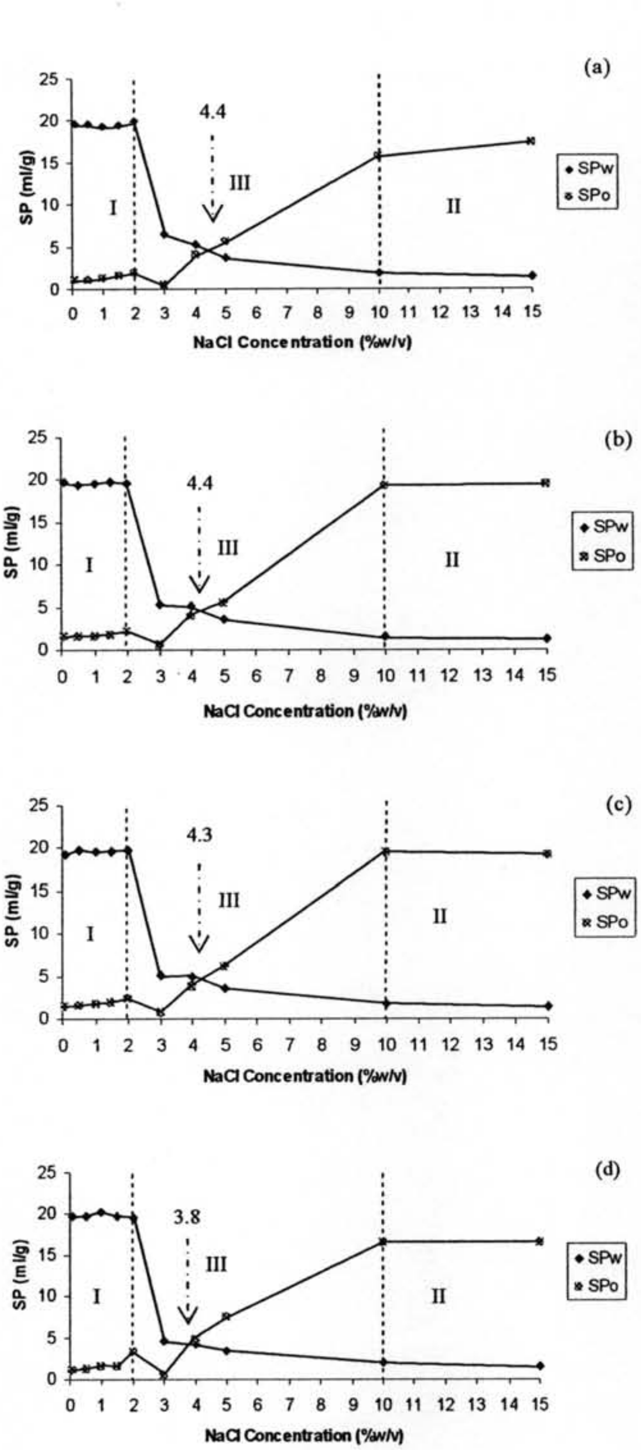

Figure 4.1 Phase diagrams of microemulsions with motor oil by plotting with solubilization parameters as a function of NaCl concentration at different hardness concentrations by using the selected formulation of 0.1wt.% Alfoterra 145-3PO and 5wt.% Tergitol 15-S-5 at an oil-to-water volumetric ratio of 1 to 1, (a) DI water, (b) hardness 100 ppm, (c) hardness 500 ppm, (d) hardness 1000 ppm.

4.1.2 Effect of Hardness on Phase Transformation

For the phase transformation illustrated in Figure 4.2, it shows the effects of NaCl concentrations on phase transformation. As the NaCl concentrations increases, the phase shift from Winsor Type I to Winsor Type III and to Winsor Type II. However, the hardness concentration, which varied from 0 to 1000 ppm, does not effect on phase transformation. Every hardness concentration, The Winsor Type III microemulsion is still appeases at the same range of salinity (3-5%w/v NaCl).

4.1.3 Effect of Hardness on Interfacial Tension

In this phase study, the mixed surfactant to oil ratio was 1:1, the active concentration (%) of the mixed surfactant equaled 5.1% and phase behavior equilibrium times was about one month. But the IFT measured in this thesis work was IFT value between the washing solution and the dyed oil which were determined to simulate more closely the actual situation in the washing bath. This system, the washing solution to dyed oil ratio was much higher than the 1:1 ratio, the active concentration (%) of the mixed surfactant contained only 0.3%w/v and wash cycle was 20 minutes. Besides, the IFT value was measured only at 20-minute. Thus, the IFT value between the washing solution and the dyed oil may be different from the IFT value in phase study (Tongcumpou *et al.*, 2003; Korphol, 2004). As expected, the oil to surfactant ratio may affect IFT which is on of the most influencing parameters in detergency performance (Kissa, 1987; Jacobi, 1987).

The effect of hardness on the IFT value was illustrated in the Figure 4.2 and Figure 4.3. As hardness concentration increases, the IFT value was increased. Due to the divalent cations in hard water can precipitate the anionic surfactant, Alfoterra 145-3PO. Consequently, total mixed surfactants, which adsorb on the interfacial surface between the washing solution and the dyed oil, were decreased. Besides, the lowest IFT values under different hardness concentration were found at the same optimum salinity of 5%w/v NaCl. Hence, at the optimum salinity is expected to give good detergency performance. The relationship between the optimum condition in the middle phase and detergency was demonstrated by several literatures (Azemar, 1996; Raney, 1987; Dillan, 1980; Solan, 1985; Robbins, 1976).

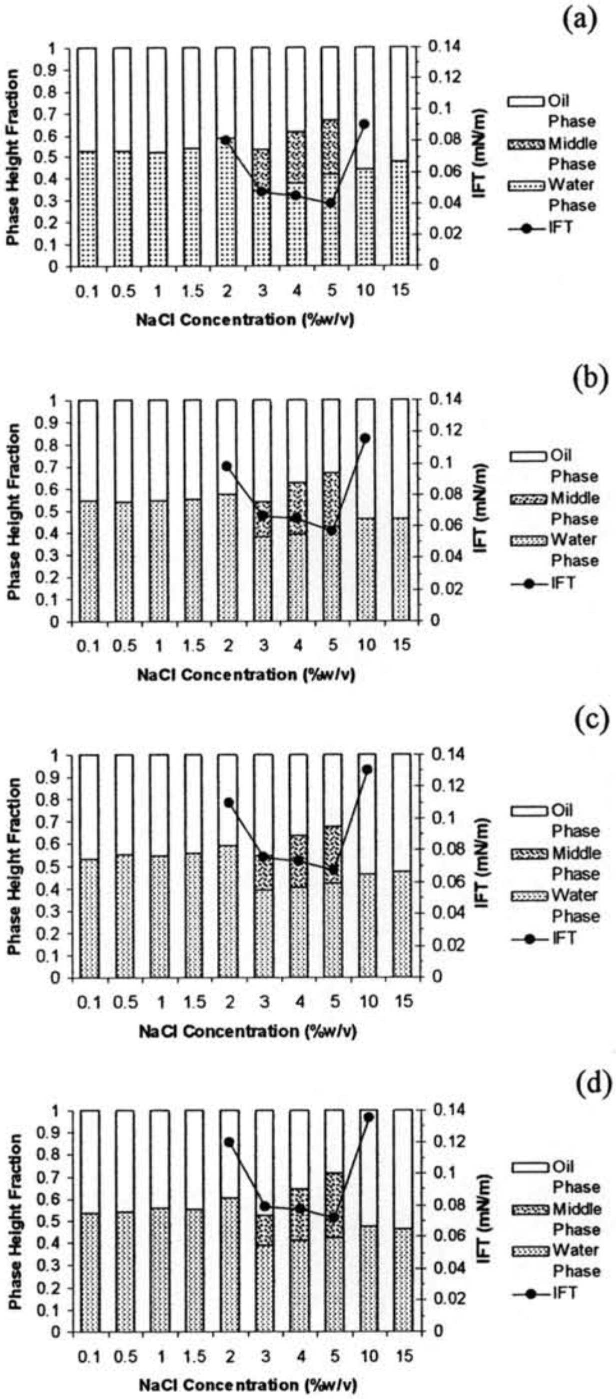

Figure 4.2 Phase Height Fraction and interfacial tension (mN/m) between washing solution (before washing process) and dyed oil at 20-minute as a function of NaCl concentration (%w/v) by using the selected formulation of 0.1wt.% Alfoterra 145-3PO and 5wt.% Tergitol 15-S-5, (a) DI water, (b) hardness 100 ppm, (c) hardness 500 ppm, (d) hardness 1000 ppm.

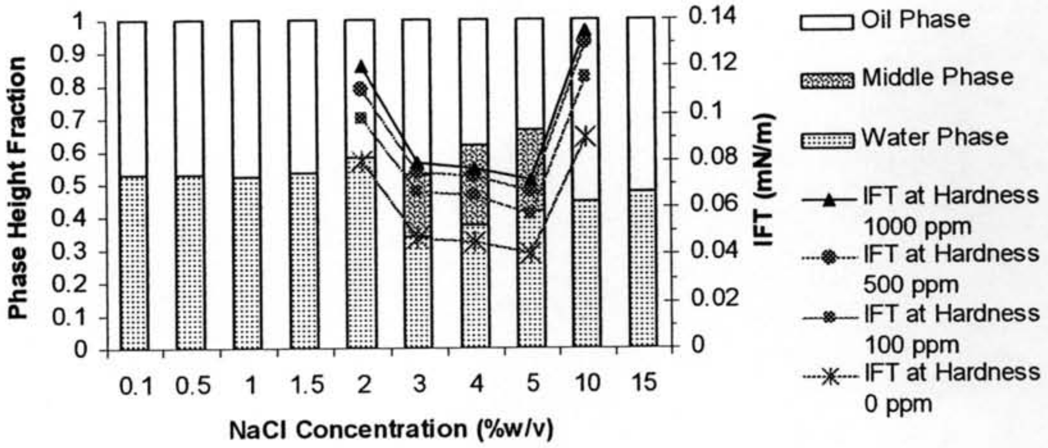

Figure 4.3 Interfacial tension (mN/m) between washing solution (before washing process) and dyed oil at 20-minute at different hardness and NaCl concentrations (%w/v) by using a mixed surfactant of 0.1wt.% Alfoterra 145-3PO and 5wt.% Tergitol 15-S-5 at 0.3%w/v active surfactant concentration.

4.2 Effect of Hardness on the Microemulsion Diagram (Fish Diagram)

In order to observe the transformation of microemulsion formation with different total mixed surfactant concentrations (%) and to indicate the minimum total mixed surfactant concentration (%) that can be used to form the Winsor Type III microemulsion under the presence and absence of hardness, a mixed surfactant of 0.1wt.% Alfoterra 145-3PO and 5wt.% Tergitol 15-S-5 was used as a based condition in this study and total mixed surfactant concentration (%) was varied in the salinity scanning with motor oil by using 1:1 the mixed surfactant to oil ratio. However, at low total mixed surfactant concentration (%), the layer of middle phase was very thin that was difficult to indicate. Thus, the electrical conductivity measurement (Cyberscan, con110) was also used to characterize the type of microemulsion. The electrical conductivity of the microemulsion was measured under gentle magnetic stirring with a platinized Pt cell. Under these conditions, the obtained value remained constant for a long time, and was found to be relatively steady (± 5%). At low salinities or Winsor Type I region, the conductivity increases steadily with salinity. This is because the microemulsion consists of brine droplet dispersed in aqueous solution which is the continuous phase. At high salinities or Winsor Type III region, on the other side, the conductivity is lower than Type I region, and thus essentially zero on the illustrated scale because the brine droplet dispersed in oil phase which is the continuous phase. As far as the Type III region is concerned, the conductivity exhibits in the mid-range (Salager *et al.*, 1983 and 2000; Minana-Perez *et al.*, 1986).

Figure 4.4 illustrates the fish diagram at different hardness concentrations. It indicates that hardness concentration does not effect on microemulsion formation supported with the results of the phase behavior. Thus, the fish diagrams at different hardness concentration have a same trend. And the minimum total mixed surfactant concentration (%), which can be used to form the Winsor Type III microemulsion, is low to 0.5%w/v. However, at lower 0.5%w/v total mixed surfactant concentration, the type of microemulsion can be not indicated because at very low total mixed surfactant concentration (%), there was very high error both from the phase study measurement and from the electrical conductivity measurement.

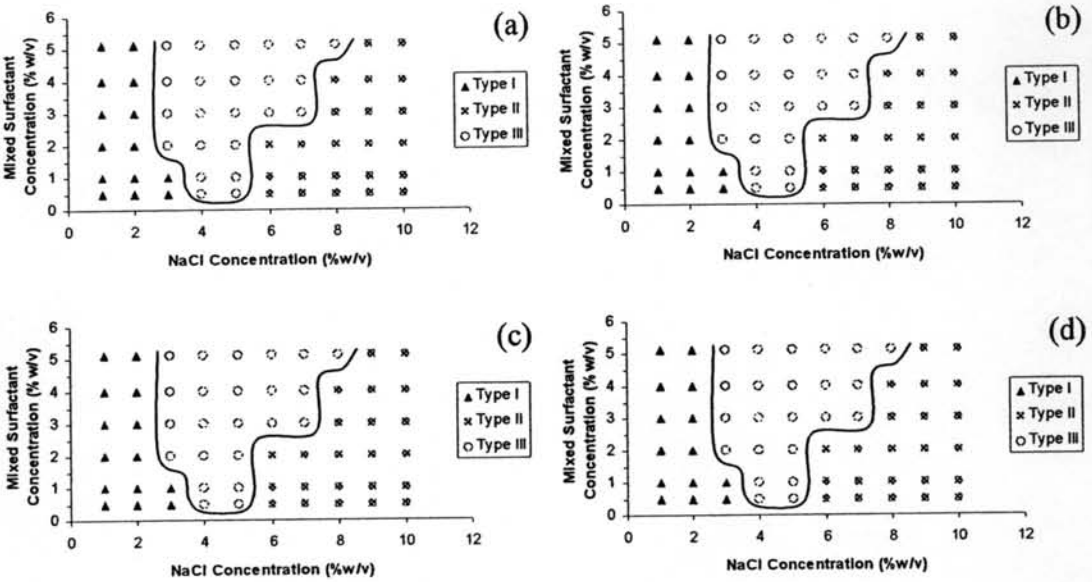

Figure 4.4 The microemulsion diagrams (Fish diagrams), total mixed surfactant concentration (%w/v) as a function of NaCl concentration (%w/v) at different hardness by using a mixed surfactant of 0.1wt.% Alfoterra 145-3PO and 5wt.% Tergitol 15-S-5 with the oil to water volumetric ratio of 1 to 1, (a) DI water, (b) hardness 100 ppm, (c) hardness 500 ppm, (d) hardness 1000 ppm.

4.3 Effect of Hardness on Detergency Performance

For this part, a mixed surfactant system of 0.1wt.% Alfoterra 145-3PO and 5wt.%Tergitol 15S5 with 0.3%w/v active surfactant concentration was selected for detergency experiment for salinity scan, base on previous work. Three types of the standard fabrics (pure cotton, polyester/cotton (65/35) blend fabric, and polyester fabric) were used as a testing fabric. And the hardness concentration added in the wash step and rinse step was varied from 0 to 1000 ppm (0, 100, 500 and 1000 ppm).

4.3.1 Effect of Hardness on Detergency Performance

Figure 4.5 and Figure 4.6 show the total oil removal (%) at different hardness concentration. As the hardness concentration increases, Total oil removal (%) is decreased because divalent cations can precipitate anionic surfactants, Alfoterra 145-3PO. Thus, total mixed surfactants, which adsorb on the interfacial surface between the washing solution and the dyed oil, were decreased. Consequently, the IFT value is increased. And divalent cations can adsorb onto the negatively charged substrate and soil reduces their electrical potentials, thus impeding soil removal and facilitating its redeposition (Scamehorn *et al.*, 1993; Rosen, 2004). Besides, due to spreading effect that can also occur in wash step under the presence of hardness, rinsing by using hard water would slightly dilute the microemulsion film on the fabric surface and IFT value in the first rinse step would not very increase. In the same way, the detachment by emulsification or roll up mechanism of the oil into the first rinse solution can slightly occurs. Consequently, little oil would be removed. Moreover, Figure 4.7 shows that total oil removal (%) on pure cotton was slightly higher than those on the other two types of fabrics and the lowest oil removal was found on the pure polyester. This is because the hydrophobic surface of polyester has a much strong interaction with the oil as compared to the hydrophilic surface of cotton. This result agrees with the results from Korphol *et al.* (2004).

4.3.2 Effect of Salinity on Detergency Performance

The effect of NaCl concentration on detergency performance was carried out by varying NaCl concentration at 0.3%w/v active surfactant concentration of the selected formation, 0.1wt.% Alfoterra 145-3PO and 5wt.%Tergitol 15-S-5. The total oil removal (%) of the studied system at different salinities is shown Figure 4.6 and Figure 4.7. With increasing salinity of the system, significant improvement of the total oil removal (%) was obtained. The higher the NaCl concentration, the lower repulsive force between head groups of anionic surfactant, Alfoterra 145-3PO, is obtained. Consequently, surfactant molecules can adsorb more onto both highly hydrophobic oil droplets and the fabric surface (Korphol *et al.*, 2004). Interestingly, the maximum oil removal not only corresponds to the optimum salinity (5%w/v NaCl) which has the ultra low IFT value but also to the higher salinity (10%w/v NaCl) which has the higher IFT value. The relationship between the IFT value and salinity is shown in the Figure 4.2 and Figure 4.3. This may be because the condition of the IFT value between washing solution (before washing process) and dyed oil, that is measured, is different from real washing process that there are fabrics. And not only the IFT value in the wash step but also the IFT value in the first rinse and second rinse step at various salinity concentrations should be considered to explain the relationship between the total oil removal (%) and the salinity. The hypothesis of the mechanism that correlates the oil removal and the IFT in each step at various salinity concentrations is already discussed by Rattanavoravipa (2006).

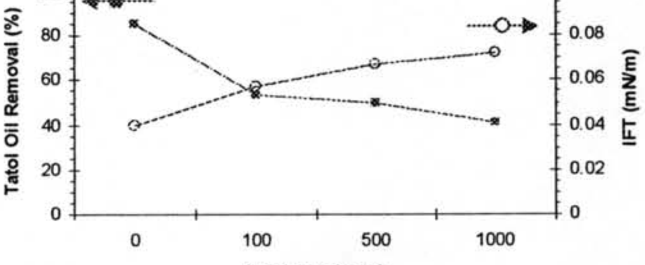

Figure 4.5 Total oil removal (%) of pure cotton fabric and IFT (mN/m) between washing solution (before washing process) and dyed oil at 20-minute as a function of hardness (ppm) by using a mixed surfactant of 0.1wt.% Alfoterra 145-3PO and 5wt.% Tergitol 15-S-5 with 0.3%w/v active surfactant at 5%w/v NaCl.

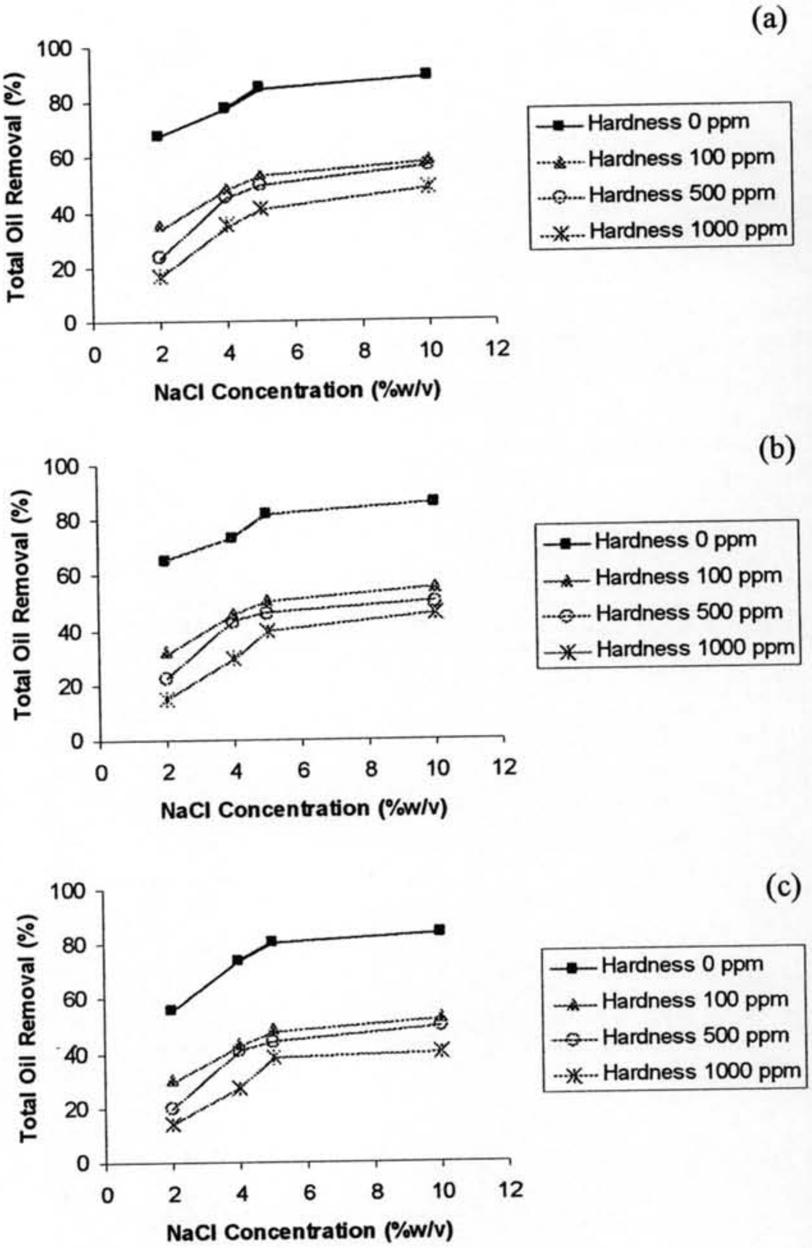

Figure 4.6 Total oil removal (%) at different hardness as a function of NaCl concentration (%w/v) by using a mixed surfactant of 0.1wt.% Alfoterra 145-3PO and 5wt.% Tergitol 15-S-5 with 0.3%w/v active surfactant, (a) pure cotton fabric, (b) polyester/cotton (65/35) blend fabric, (c) pure polyester fabric.

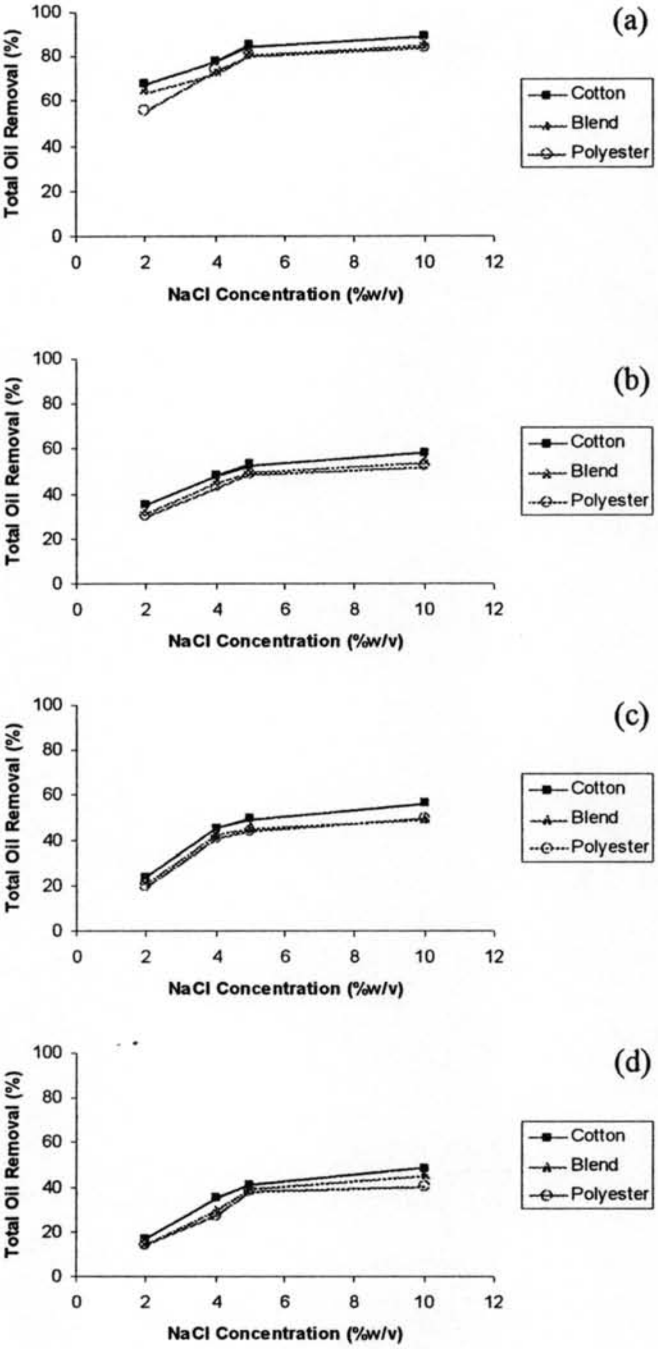

Figure 4.7 Total oil removal (%) on different types of fabrics as a function of NaCl concentration (%w/v) using a mixed surfactant of 0.1wt.% Alfoterra 145-3PO and 5wt.% Tergitol 15-S-5 with 0.3%w/v active surfactant, (a) DI water, (b) hardness 100 ppm, (c) hardness 500 ppm, (d) hardness 1000 ppm.

4.4 Effect of Hardness on Oil Removal in Each Step

For this experiment, the oil removal in the washing and the two-rinsing solution after washing process was extracted by dichloromethane. The volume of washing and rinsing solution to the volume of dichloromethane is 1 to 1. After that the oil that solute in the dichloromethane is measured by UV measurement at wavelength 520 nm.

The oil removal (%) in each step of pure cotton fabric at 5%w/v NaCl by using a mixed surfactant of 0.1wt.% Alfoterra 145-3PO and 5wt.% Tergitol 15-S-5 at 0.3%w/v active surfactant under the present and the absence of hardness is shown in the Figure 4.8. Both the present and the absence of hardness, the oil removal (%) in first rinse step is higher than other step. This result is explained that in the wash step, the spreading effect occurred that leading to a small amount of oil removed in wash step. In the first rinse step, a large amount of oil was removed because the dilution of the microemulsion film. Consequently, spreading oil was removed in this step by roll-up and emulsification mechanisms. In the second rinse step, some surfactant and oil which coat on the fabric surface that can not removed in the first rinse step will be removed by other mechanisms such as surfactant force and/or agitation force (Tongcumpou *et al.*, 2005).

Moreover, Consideration the DI water (hardness 0 ppm) compare with the presence of hardness (hardness100, 500 and 1000 ppm), indicated that the oil removal in wash step will be increased while the oil removal in the first and second rinse step will be decreased as the hardness concentration increase. This because in DI water the spreading effect can more occur than in the hard water due to the presence of hardness results in increasing the IFT value. And there is hardness present in the first and second rinsing solution of hard water, dilution the microemulsion film on the fabric surface is slightly occurred. Besides, divalent cations in the first the second rinse step can adsorb onto the negatively charged substrate and soil reduce their electrical potentials, consequently, impeding soil removal and facilitating its redeposition. Moreover, adding the high amount of hardness concentration results in the higher increasing IFT value, in the higher decreasing the spreading effect, in the higher impeding soil removal and in the higher facilitating redeposition of soil on the fabric surface.

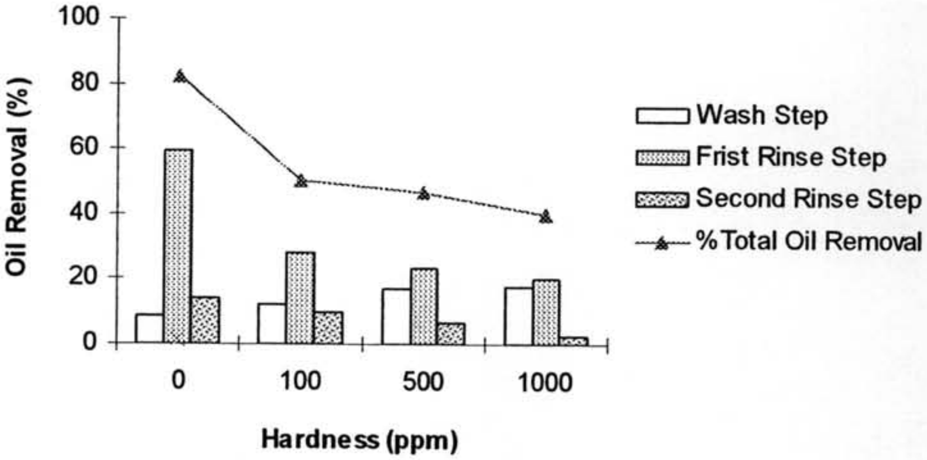

Figure 4.8 Oil removal (%) in each step of pure cotton fabric at 5%w/v NaCl by using a selected formulation as a function of hardness concentration (ppm) by using dichloromethane as solvent to extract the oil from washing and rinsing solution and then measure the solution by UV measurement.

4.5 Titration to Reach Amount of Anionic Surfactant

The amount of anionic surfactant in the washing and the rinsing solution can be measured by titration with the cationic surfactant, following the standard test method for synthetic anionic active ingredient in detergents by cationic titration procedure, ASTM D1681-92. The cationic surfactant which is used for this experiment is 0.005M Hyamine.

4.5.1 Effect of Hardness on Precipitation Alfoterra145-3PO

This part, the washing solution is prepared again by using a mixed surfactant of 0.1wt.% Alfoterra 145-3PO and 5wt.% Tergitol 15-S-5 at 0.3%w/v active surfactant with 5%w/v NaCl. For the study only the effect of hardness on precipitation Alfoterra145-3PO, there are not adding the fabric into the solution in order to eliminate the effect of adsorption of Alfoterra 145-3PO on the fabric surface.

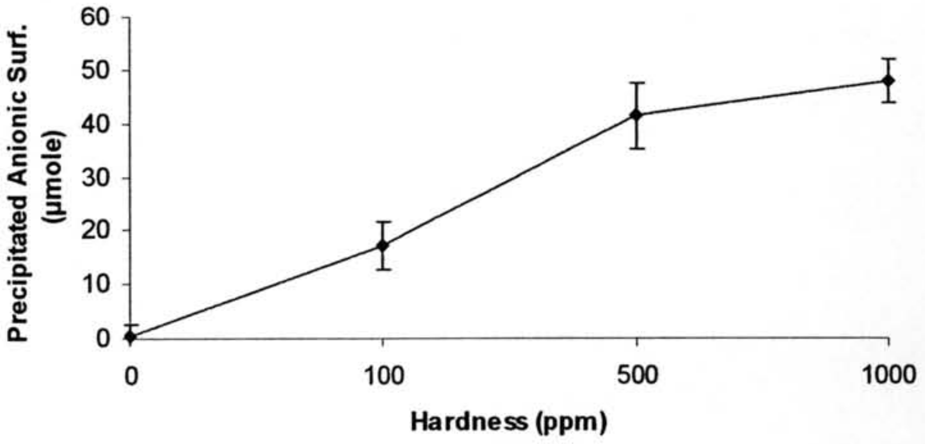

Figure 4.9 The amount of precipitated Alfoterra 145-3PO (µmole) as a function of hardness (ppm) at 0.3%active surfactant with 5%w/v NaCl.

Figure 4.9 shows the amount of precipitated Alfoterra 145-3PO at different hardness concentration. As the hardness concentration increase, the residual anionic surfactant, Alfoterra 145-3PO, is decreased due to divalent cation in the hard water more precipitate the Alfoterra 145-3PO. Thus, the amount of precipitated Alfoterra 145-3PO will be increased as hardness increase (Rosen, 2004).

4.5.2 Effect of Hardness on Amount of Alfoterra 145-3PO in Each Step

For this experiment, the washing and the two-rinsing solution after washing process of pure cotton fabric at 5%w/v NaCl with a selected formulation of mixed surfactant (Initial amount of Alfoterra 145-3PO is 121.74 µmole) were titrated by cationic surfactant, 0.005M Hyamine, to reach the amount of anionic surfactant, Alfoterra 145-3PO in each step. The titration method followed ASTM standard guide D1681-92.

Figure 4.10, Figure 4.11 and Figure 4.12 show distribution of Alfoterra 145-3PO after wash step, the amount of Alfoterra 145-3PO in each step, and the amount of Alfoterra 145-3PO is changed along washing process at different hardness concentration, respectively. In the wash step, the amount of Alfoterra 145-3PO increase as the hardness concentration increase, although the precipitated Alfoterra 145-3PO is increased. This because, as the hardness concentration increases, the adsorption of Alfoterra 145-3PO is much more decreased than increasing of precipitated Alfoterra 145-3PO. In the first and second rinse step, the residual Alfoterra 145-3PO decreases, as the hardness concentration increase, because the increasing of hardness results in the lower dilution of spreading effect (Tongcumpou, 2005). According to a theory, if spreading effect occurs, the high amount of oil removal will appear at first rinse step (Tongcumpou, 2005; Korphol, 2004). Consequently, the residual Alfoterra 145-3PO in the first rinse step must be higher than other steps, due to the spreading oil is removed from the fabric by solubilization in the core of micelle (Tongcumpou, 2005; Rattanavoravipa, 2006). But from the results are shown in Figure 4.11 and Figure 4.12, the amount of Alfoterra 145-3PO in wash step is higher than that in the first rinse step. This result indicates that 0.3%w/v active surfactant concentration of a mixed surfactant used in this detergency experiment is excess. These excess surfactants do not help removing the oily soil from the fabric surface but make the high investment fund. However, at 0.3%w/v active surfactant concentration may be useful and necessary in removing an amount of oil which is much higher than that in this detergency experiment. An amount of oil loading used in this study was shown in Table 4.1. Moreover, Figure 4.12 also shows the residual surfactant on the fabric surface after washing process supported by the result of Ratchatawetchakul (2005). This residual surfactant is resulted by spreading effect. At the minimum IFT, the middle phase microemulsion was trapped in the fiber bundles of fabric proposed by Thompson (1994). All surfactants trapped in the fiber bundles are difficult to remove, although the IFT value in the rinse step will increase. Thus, some surfactants still are in the fiber bundles. The more spreading effect results in the more residual surfactant. The excess surfactant that is used in the wash step and the residual surfactant that occurs in the washing process of soiled cotton fabric agree with the result of washing process of unsoiled cotton that is shown in the Figure 4.13 and 4.14.

Table 4.1 An amount of oil loading on different types of fabrics

Type of Fabrics	Weight of Oil Avg. / 1000 ml Washing Solution (g/1000ml)
Cotton	1.153
Polyester/Cotton Blend	0.972
Polyester	0.770

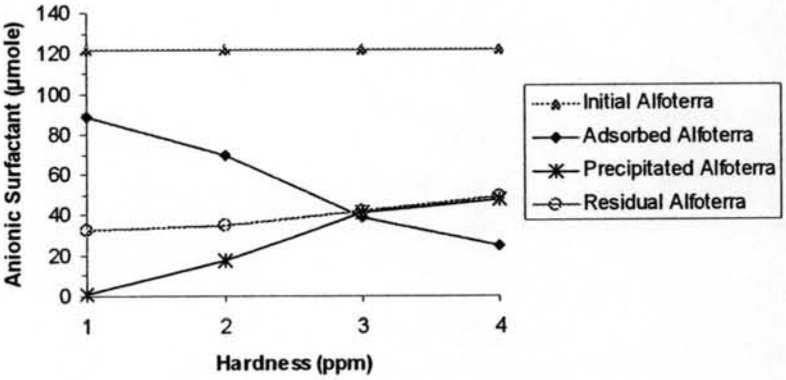

Figure 4.10 Distribution of Alfoterra 145-3PO (µmole) after the wash step as a function of hardness.

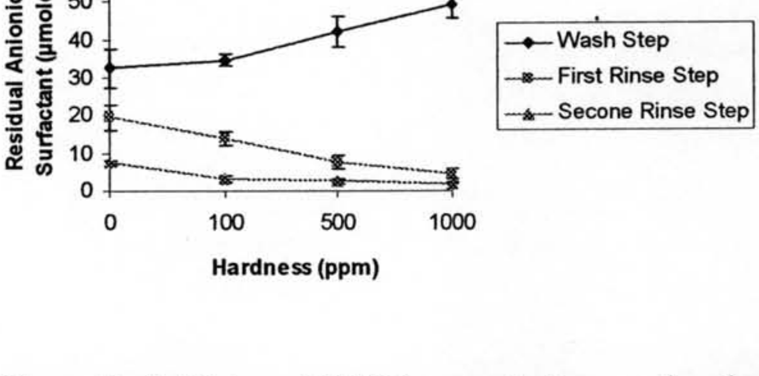

Figure 4.11 The residual Alfoterra 145-3PO concentration as a function of hardness in each step of washing process of soiled cotton fabric at 0.3%active surfactant and 5%w/v NaCl.

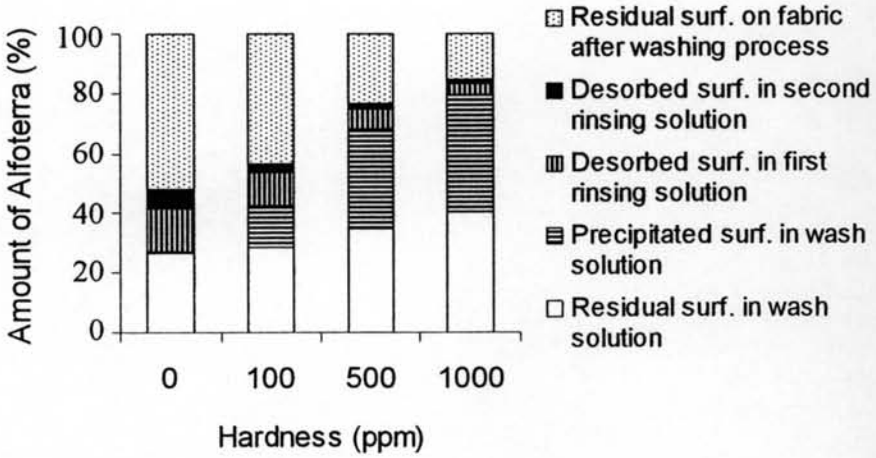

Figure 4.12 Distribution of Alfoterra 145-3PO during washing process of soiled cotton fabric at 0.3%active surfactant and 5%w/v NaCl as a function of hardness.

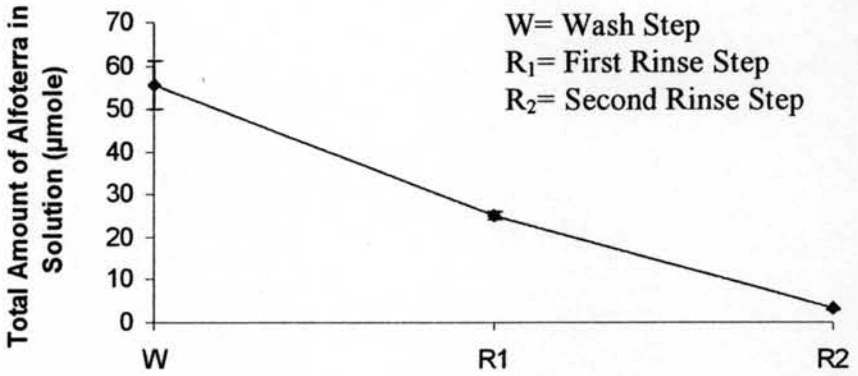

Figure 4.13 The amount of Alfoterra 145-3PO (µmole) in each step of washing process of unsoiled cotton fabric by using a mixed surfactant of 0.1wt.% Alfoterra 145-3PO and 5wt.% Tergitol 15-S-5 at 0.3%active surfactant concentration with 5%w/v NaCl under the absence of hardness (DI water).

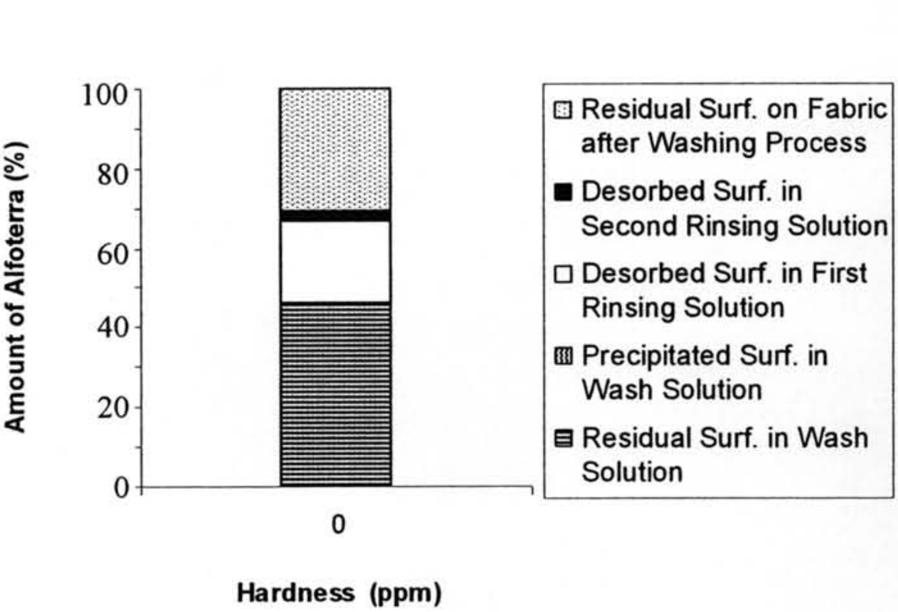

Figure 4.14 Distribution of Alfoterra 145-3PO during washing process of unsoiled cotton fabric by using a mixed surfactant of 0.1wt.% Alfoterra 145-3PO and 5wt.% Tergitol 15-S-5 at 0.3%active surfactant concentration with 5%w/v NaCl under the absence of hardness (DI water).

4.6 Effect of Builder on Detergency Performance

For this experiment, the hypothesis that adding builder can improve the detergency is expected (Rosen, 2004). A mixed surfactant system of 0.1wt.% Alfoterra 145-3PO and 5wt.%Tergitol 15-S-5 at 0.3%w/v active surfactant concentration was selected for this study under DI water and fixed hardness 500 ppm. Three types of the standard fabrics (pure cotton, polyester/cotton (65/35) blend fabric, and polyester fabric) were used as a testing fabric. And the concentrations of two types of builders (STPP and EDTA) were varied to be several times hardness. The builder is added in only the wash step, while the 500 ppm of hardness is added in both wash step and rinse step.

Figure 4.15 and Figure 4.16 show the total oil removal (%) on three types of fabrics at different builder concentration under hardness 500 ppm and under DI water, respectively. In the DI water that absent hardness, adding builder can not help improving the detergency performance. For the hardness 500 ppm, adding builder can help improving the detergency performance only at a certain level. However the total oil removal (%) that is improved by adding builder is still lower than that under the absence of hardness. This because the builder reduces the effect of hardness by reaction with divalent cations, only in the wash step but in the first and the second rinse step is still affected of hardness, thus, divalent cations in the first and second rinse step can adsorb onto the negatively charged substrate and soil reduces their electrical potentials, consequently, impeding soil removal and facilitating its redeposition. Besides, in the first and the second rinse step which are still affected of hardness, the microemulsion film on the fabric surface is slightly diluted. Moreover, the builder may be also react with monovalent cations (Na^+) both of NaCl and of Alfoterra 145-3PO in the washing solution. The structures of Alfoterra145-3PO and Tergitol 15-S-5 are shown in the Table 3.1.

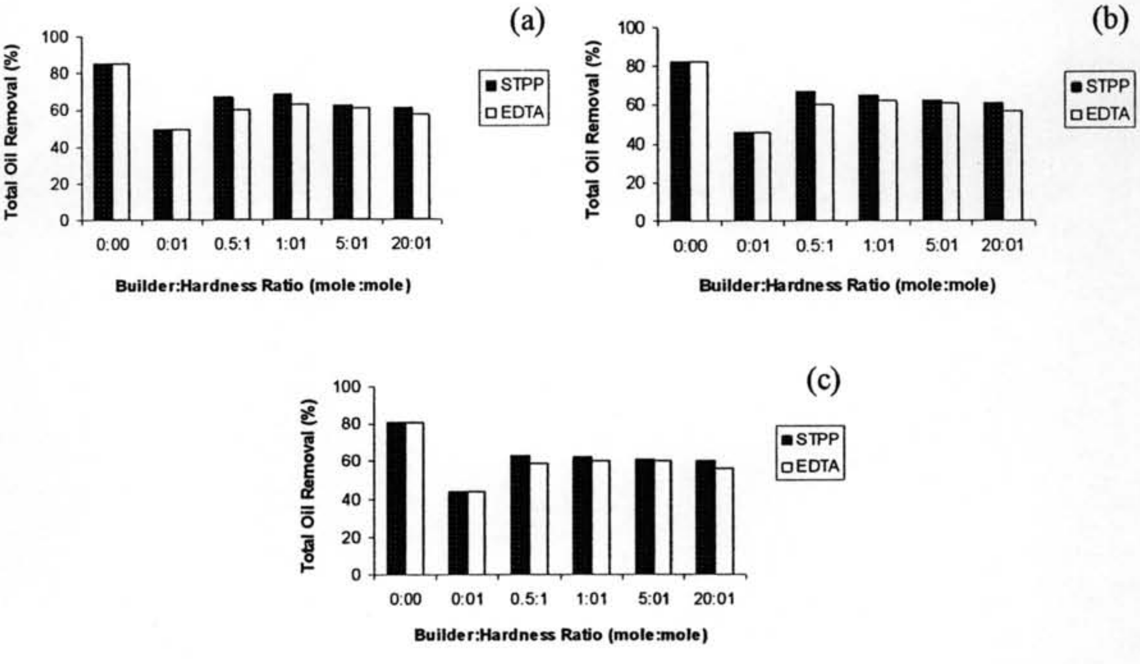

Figure 4.15 Total oil removal (%) as a function of Builder : Hardness ratio (mole: mole) under hardness 500 ppm with a mixed surfactant of 0.1wt.% Alfoterra 145-3PO and 5wt.% Tergitol 15-S-5 at 0.3%active surfactant and with two types of builders (STPP and EDTA), (a) pure cotton fabric, (b) polyester/cotton (65/35) blend fabric, (c) pure polyester fabric.

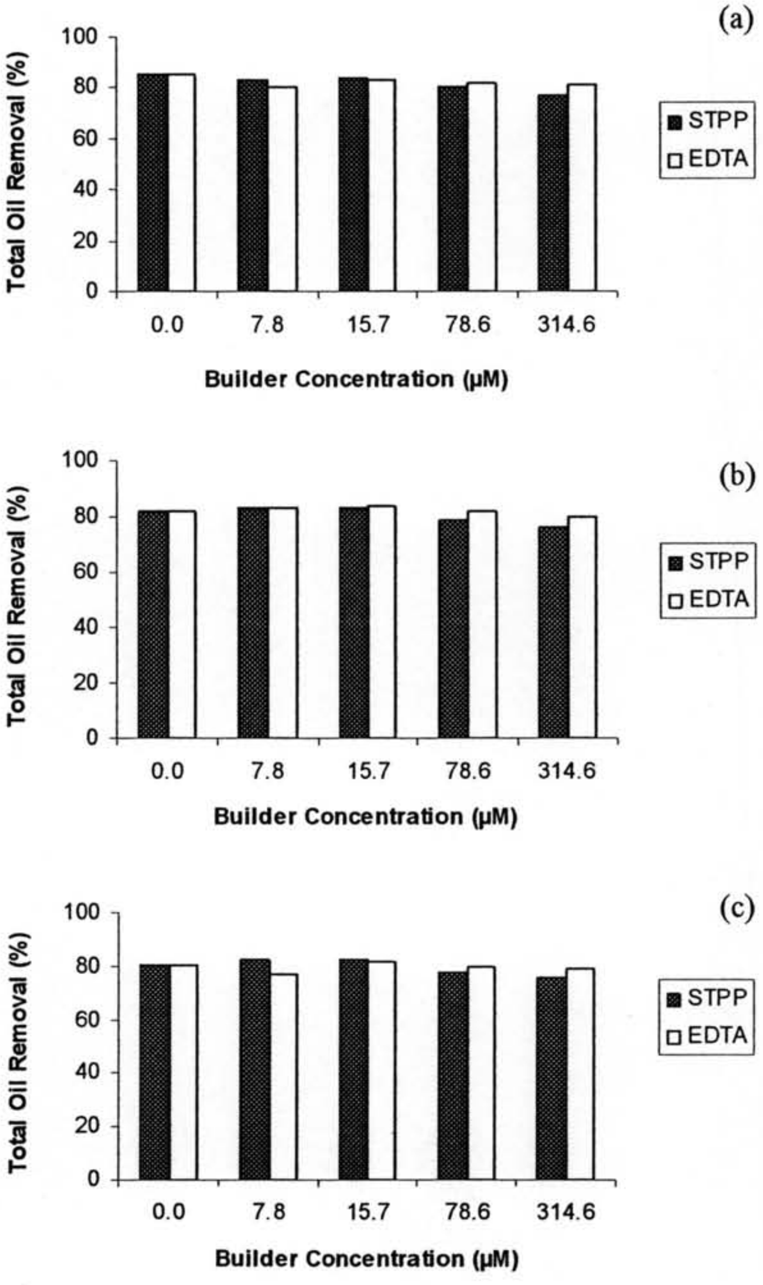

Figure 4.16 Total oil removal (%) as a function of builder concentration (µM) under DI water with a mixed surfactant of 0.1wt.% Alfoterra 145-3PO and 5wt.% Tergitol 15-S-5 at 0.3%active surfactant and with two types of builders (STPP and EDTA), (a) pure cotton fabric, (b) polyester/cotton (65/35) blend fabric, (c) pure polyester fabric.